Thermochimica Acta, 56 (1982) 15–23
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

STUDIES ON THE THERMAL DECOMPOSITION OF SOME METAL COMPLEXES OF 5,5′-METHYLENDISALICYLHYDROXAMIC ACID

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(Received 19 November 1981)

ABSTRACT

The thermal behaviour of the chelates of 5,5′-methylendisalicylhydroxamic acid with Pb(II), Zn(II), Ni(II), Cd(II), Fe(III), Cr(III), Al(III), Ti(IV), V(V), Mo(VI) and Cu(II) has been studied by thermogravimetry (TG), differential thermal analysis (DTA), IR spectroscopy and X-ray diffraction.

The compounds decompose through three major steps, dehydration, transformation of the anhydrous hydroxamates to intermediate *N*-hydroxylactams, which decompose to yield metal oxides as the final products.

INTRODUCTION

Most of the common hydroxamic acids have been investigated as precipitating agents for metal ions [1], but practically no work has been reported on the thermal decomposition of these compounds and their metal complexes [2].

Our recent paper [3] presents the synthesis and physico-chemical properties of 5,5′-methylendisalicylhydroxamic acid (MEDSHA) as well as its coordination ability to numerous metal ions in aqueous solution.

In this paper, we present a study of the thermal stability of metal complexes of MEDSHA with Pb(II), Zn(II), Ni(II), Cd(II), Fe(III), Cr(III), Al(III), Ti(IV), V(V), Mo(VI) and Cu(II).

EXPERIMENTAL

Preparation of reagent and chelates

All chemicals used in this work were reagent grade. The 5,5′-methylendisalicylhydroxamic acid was prepared by the method reported earlier [3].

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TABLE 1

Analytical data

Complex *	Colour	Metal (%)		Carbon (%)		Hydrogen (%)		Nitrogen (%)	
		Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
RH_2Pb	White	38.47	39.59	33.94	34.40	2.33	2.29	5.14	5.35
$(RH_2)Zn \cdot 2\,H_2O$	White	15.90	15.66	42.77	43.12	3.84	3.83	6.58	6.70
$(RH_2)Ni \cdot 2\,H_2O$	Blue–violet	14.21	14.29	43.08	43.82	4.00	3.89	6.71	6.81
$(RH_2)Cd \cdot 2.5\,H_2O$	Dirty-white	23.43	23.74	38.50	38.02	3.29	3.59	5.75	5.91
$(RH_2)_3Fe_2 \cdot 6\,H_2O$	Dark-red	9.32	9.56	46.17	46.24	3.88	4.11	6.71	7.19
$(RH_2)Cr(OH) \cdot 2\,H_2O$	Green	12.13	12.35	42.38	42.75	3.83	4.03	6.55	6.65
$(RH_2)Al(OH) \cdot 2\,H_2O$	Pink	7.02	6.81	45.21	45.45	4.03	4.29	6.78	7.07
$(RH_2)_3Ti_2(OH)_2 \cdot 4\,H_2O$	Yellow	8.30	8.33	46.48	46.96	3.93	4.00	7.19	7.31
$(RH_3)VO_2 \cdot 2\,H_2O$	Violet–black	11.34	11.68	41.42	41.67	3.80	3.93	6.32	6.48
$(RH_2)(MoO_2) \cdot 3\,H_2O$	Light-yellow	19.23	19.26	36.29	36.15	3.24	3.61	5.71	5.62
$(RH)_2(RH_2)Cu_4 \cdot 6\,H_2O$	Green	19.36	19.44	41.15	41.31	3.30	3.44	6.25	6.42

* $RH_4 = C_{15}H_{14}N_2O_6$

The metal chelates were prepared by interaction of reagent and the corresponding metal solutions in hot water [4]. Table 1 contains elemental analysis data. The water content in the substances, was obtained from the TG curves, and the metal content gravimetrically as oxides.

Apparatus

The simultaneous TG and DTA were performed with a Setaram GDTD-10 thermoanalyzer fitted with a B-70 electrobalance with thermocouples of Pt/Pt–Rh in an alumina base. The measurements were made in static air atmosphere, at a heating rate of 2°C min^{-1}. Approximately 10 mg samples were taken in an alumina crucible using calcinated α-alumina as reference material.

Infrared spectra were recorded with a Beckman 4240 IR spectrophotometer in the 4000–250 cm^{-1} range, using the KBr pellet technique. X-Ray analyses of the residues were carried out on a Philips PW 1060.

RESULTS AND DISCUSSION

Thermogravimetric analysis curves for the metal chelates of MEDSHA are present in Fig. 1 and differential thermal analysis curves are given in Fig. 2.

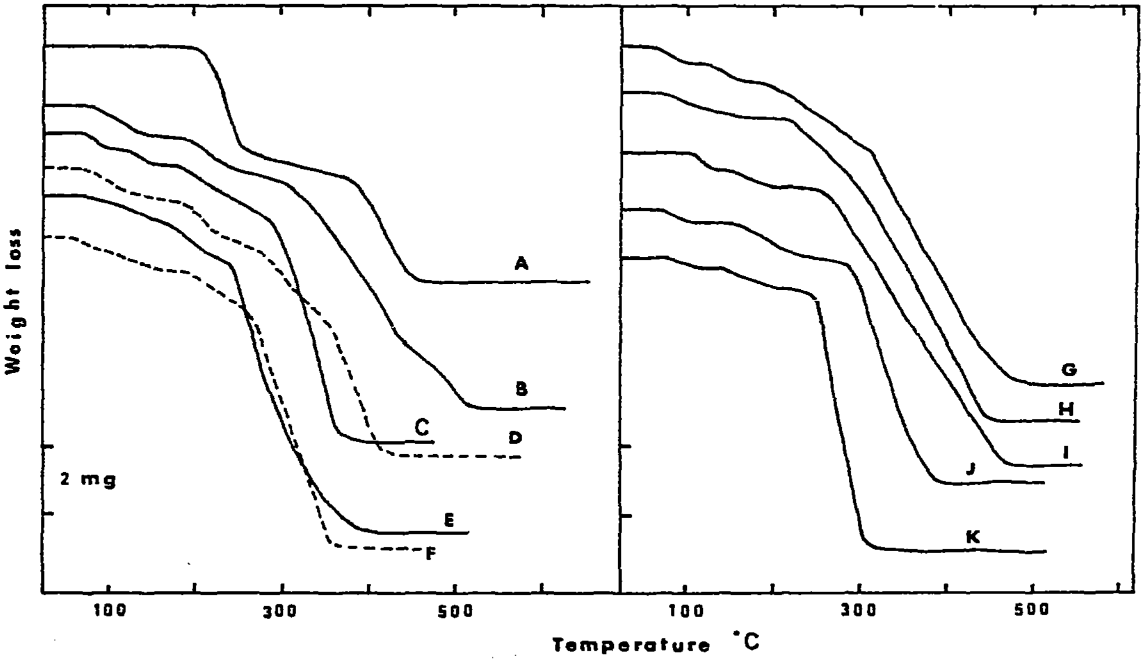


Fig. 1. Thermogravimetric analysis curves of the metal chelates of 5,5′-methylendisalicylhydroxamic acid. A, RH_2Pb; B, $(RH_2)Zn \cdot 2\,H_2O$; C, $(RH_2)Ni \cdot 2\,H_2O$; D, $(RH_2)Cd \cdot 2.5\,H_2O$; E, $(RH_2)_3Fe_2 \cdot 6\,H_2O$; F, $(RH_2)Cr(OH) \cdot 2\,H_2O$; G, $(RH_2)Al(OH) \cdot 2\,H_2O$; H, $(RH_2)_3Ti_2(OH)_2 \cdot 4\,H_2O$; I, $(RH_3)VO_2 \cdot 2\,H_2O$; J, $(RH_2)MoO_2 \cdot 3\,H_2O$; K, $(RH)_2(RH_2)Cu_4 \cdot 6\,H_2O$.

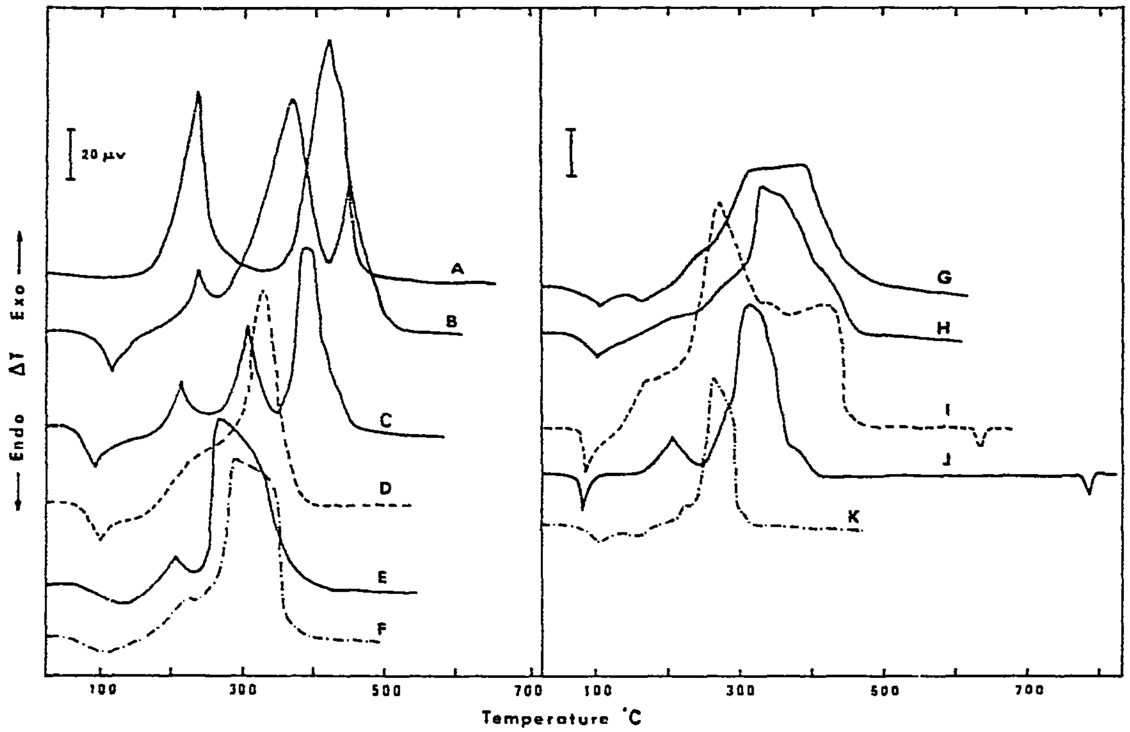


Fig. 2. Differential thermal analysis curves for the metal chelates of 5,5′-methylendisalicylhydroxamic acid. A, RH_2Pb; B, $(RH_2)Zn \cdot 2\,H_2O$; C, $(RH_2)Cd \cdot 2.5\,H_2O$; D, $(RH_2)Ni \cdot 2\,H_2O$; E, $(RH_2)_3Fe_2 \cdot 6\,H_2O$; F, $(RH_2)Cr(OH) \cdot 2\,H_2O$; G, $(RH_2)Al(OH) \cdot 2\,H_2O$; H, $(RH_2)_3Ti_2(OH)_2 \cdot 4\,H_2O$; I, $(RH_3)VO_2 \cdot 2\,H_2O$; J, $(RH_2)MoO_2 \cdot 3\,H_2O$: K, $(RH)_2(RH_2)Cu_4 \cdot 6\,H_2O$.

The temperatures and the characteristics of the peaks occurring on the DTA curves for all investigated 5,5′-methylendisalicylhydroxamates are shown in Table 2.

In order to obtain some direct evidence concerning the thermal decompositions, the infrared spectra of sinters were studied (see Table 5). The sinters were obtained under conditions similar to those used in thermal analysis.

Dehydration

At the first stage of the thermal decomposition of hydrated complexes, water is eliminated with a corresponding mass loss on the TG curves occurring between 50 and 200°C. The data for calculated and observed weight losses and the corresponding temperature ranges, for the dehydration processes, are given in Table 3.

The dehydration reactions start at a relatively low temperature, 50–60°C, except for the vanadium complex (105°C).

The DTA curves of these compounds exhibit an endothermic effect in one

TABLE 2

DTA peak temperatures of 5,5′-methylendisalicylhydroxamates

Compound *	Temperatures (°C) and characters of DTA peaks			
RH_2Pb		238 exo intensive	418 exo intensive	
$RH_2Zn \cdot 2\ H_2O$	114 endo	236 exo	370 exo intensive, 450 exo	
$RH_2Ni \cdot 2\ H_2O$	100 endo, 150 endo (shoulder)	225 exo	325 exo intensive	
$RH_2Cd \cdot 2.5\ H_2O$	91 endo	213 exo	310 exo, 381-exo intensive	
$(RH_2)_3Fe_2 \cdot 6\ H_2O$	135 endo	208 exo	270 exo intensive	
$(RH_2)Cr(OH) \cdot 2\ H_2O$	101 endo	225 exo	289 exo intensive	
$(RH_2)Al(OH) \cdot 2\ H_2O$	105 endo, 170 endo	240 exo	311 exo intensive, 391 exo intensive	
$(RH_2)_3Ti_2(OH)_2 \cdot 4\ H_2O$	100 endo	222 exo	270 exo, 333 exo intensive	
$(RH_3)VO_2 \cdot 2\ H_2O$	112 endo	194 exo	296 exo intensive, 455 exo	660 endo
$(RH_2)(MoO_2) \cdot 3\ H_2O$	80 endo	208 exo	390 exo intensive	785 endo
$(RH)_2(RH_2)Cu_4 \cdot 6\ H_2O$	107 endo, 160 endo	225 exo	265 exo intensive	

* $RH_4 = C_{15}H_{14}N_2O_6$

step for the Zn(II), Cd(II), Fe(III), Cr(III) and Ti(IV) complexes, in the temperature range 50–190°C, which can be ascribed to the loss of 2, 2.5, 6, 2 and 4 molecules of water, respectively. For the Ni(II), Al(III), V(V) Mo(VI) and Cu(II) complexes, two dehydration steps are observed according to the schemes shown in Table 3.

In the Mo complex, the second step of dehydration is accompanied by partial decomposition of the hydroxamate, as indicated by a substantial

TABLE 3

Temperature ranges and weight losses for the dehydration processes

Reaction	Calculated wt. loss (%)	Observed wt. loss in TG (%)	Temperature range (°C)
$(RH_2)Zn \cdot 2\,H_2O \rightarrow (RH_2)Zn + 2\,H_2O$	8.62	8.3	68–165
$(RH_2)Ni \cdot 2\,H_2O \rightarrow (RH_2)Ni \cdot H_2O + H_2O$	4.38	4.1	70– 95
$(RH_2)Ni \cdot H_2O \rightarrow (RH_2)Ni + H_2O$	4.38	4.2	117–180
$(RH_2)Cd \cdot 2.5\,H_2O \rightarrow (RH_2)Cd + 2.5\,H_2O$	9.51	8.6	66–187
$(RH_2)_3Fe_2 \cdot 6\,H_2O \rightarrow (RH_2)_3Fe_2 + 6\,H_2O$	9.25	8.8	63–180
$(RH_2)Cr(OH) \cdot 2\,H_2O \rightarrow (RH_2)Cr(OH) + 2\,H_2O$	8.55	8.6	50–165
$(RH_2)Al(OH) \cdot 2\,H_2O \rightarrow (RH_2)Al(OH) \cdot H_2O + H_2O$	4.55	4.5	60–105
$(RH_2)Al(OH) \cdot H_2O \rightarrow (RH_2)Al(OH) + H_2O$	4.55	4.5	118–160
$(RH_2)_3Ti_2(OH)_2 \cdot 4\,H_2O \rightarrow (RH_2)_3Ti_2(OH)_2 + 4\,H_2O$	6.26	6.1	60–155
$(RH_3)VO_2 \cdot 2\,H_2O \rightarrow (RH_3)VO_2 \cdot H_2O + H_2O$	4.13	4.2	105–150
$(RH_3)VO_2 \cdot H_2O \rightarrow (RH_3)VO_2 + H_2O$	4.13	4.0	150–203
$(RH_2)(MoO_2) \cdot 3\,H_2O \rightarrow (RH_2)(MoO_2) \cdot 2\,H_2O + H_2O$	3.61	3.7	65–103
$(RH_2)(MoO_2) \cdot 2\,H_2O \rightarrow (RH_2)(MoO_2) + 2\,H_2O$ + dissociation product	7.22		150–?
$(RH)_2(RH_2)Cu_4 \cdot 6\,H_2O \rightarrow (RH)_2(RH_2)Cu_4 \cdot 4\,H_2O + 2\,H_2O$	2.7	2.7	65–115
$(RH)_2(RH_2)Cu_4 \cdot 4\,H_2O \rightarrow (RH)_2(RH_2)Cu_4 + 4\,H_2O$	5.5	5.4	134–208

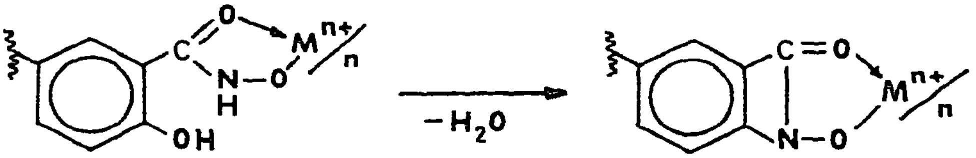
modification on the IR spectrum of a sample obtained isothermally at 190°C.

Common features of the spectra of the hydrated compounds are the broad νOH band above 3200 cm^{-1} and the δHOH band near 1630 cm^{-1} [5]. All synthesized compounds, except the Pb complex, have a shoulder band (see Table 5) between 3400 and 3700 cm^{-1} which disappears on heating, hence it is suitable for assignment to the νOH (H_2O) vibration. In the case of the Zn, Ni, Fe and Ti complexes, the absorption in the region 1600–1665 cm^{-1} is removed by heating and may be thus related to the δHOH (H_2O) band.

Decomposition of anhydrous complexes

Thermal decomposition of the anhydrous chelates is a multi-step process as indicated by the thermoanalytical TG and DTA curves. The procedural decomposition temperatures, for the first step, obtained from these curves are given in Table 4.

It can be seen in the DTA curves (Fig. 2) that all of the chelates exhibited an exothermic peak or shoulder between 190 and 250°C, involving mass loss. The IR spectra of the heated compounds (Table 5) contain a strong absorption centered around 1750 cm^{-1}. This frequency is characteristic of a stretching of a C=O which belongs to a four membered ring [6]. Furthermore, the δOH phenolic band (at 1360 cm^{-1} approx.) is decreased in intensity on heating. These effects must be attributed to the *N*-hydroxylactam formation according to the reaction.



It was observed that the transformation degree depends on the heating time of the samples. The same thermal behaviour was observed with the

TABLE 4

TG procedural decomposition temperatures (°C) for 5,5'-methylendisalicylhydroxamic acid chelates

Chelate	*T* (°C)	Chelate	*T* (°C)
Pb(II)	180	Al(III)	180
Zn(II)	185	Ti(IV)	184
Ni(II)	180	V(V)	250
Cd(II)	187	Mo(VI)	?
Fe(III)	180	Cu(II)	220
Cr(III)	182		

TABLE 5

Fundamental frequency assignment

Compound	Frequencies of vibration (cm^{-1})			
	ν(C=O) hydroxamic	ν(C=O) *N*-hydroxylactam	ν(OH) (H_2O)	δ(HOH) (H_2O)
Pd	1590 s			
200°C sinter	1590 s	1750 m		
Zn	1590 s		3400–3700 sh	1630 sh
200°C sinter	1590 s	1745 m		
Ni	1600 s		3400–3680 sh	1615 sh
200°C sinter	1600 s	1740 m		
Cd	1618 s		3400–3660 sh	
200°C sinter	1618 s	1750 s		
Fe	1610 s		3400–3680 sh	1665 sh
200°C sinter	1610 s	1750 m		
Cr	1600 s		3400–3680 sh	
200°C sinter	1600 s	1755 m		
Al	1610 s		3400–3700 sh	
200°C sinter	1610 s	1750 s		
Ti	1595 s		3400–3660 sh	1630 sh
200°C sinter	1600 s	1760 s		
V	1600 s		3400–3660 sh	
200°C sinter	1600 s	1760 m		
Mo	1615 s		3400–3680 sh	
200°C sinter	1615 s	1760 s		
Cu	1605 s		3500–3700 sh	
225°C sinter	1605 s	1750 s		

reagent [3] which loses two molecules of water between 150 and 202°C.

The decreasing order of thermal stability for decomposition of the Cu, Zn and Ni chelates is Cu > Zn > Ni, which is in accord with the Irving–Williams [7] order for divalent metal ions of the 3*d* series. The order Zn > Ni has been observed earlier [8], where the relatively low value of Ni was attributed to steric hindrance preventing the formation of a square planar structure.

Finally, the intermediate *N*-hydroxylactams decompose in the temperature range 250–500°C, exhibiting one or two pronounced exothermic peaks. These must be attributed to the combustion of the organic matter. The final products (residues) were oxides, as revealed by X-ray pattern.

Apart from these thermal effects, small endothermic effects can be observed in the DTA curves of the V and Mo compounds at 660 and 785°C, respectively, corresponding to the fusion of the oxides. These temperatures agree with published data [9].

In order to find complementary information about these compounds, we are investigating at present the evaluation of the kinetic parameters of the pyrolytic decomposition of metal complexes of 5,5′-methylendisalicylhydroxamic acid.

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