Thermochimica Acta, 80 (1984) 115–122
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMAL STUDIES ON 2,6-XYLYLIMINODIACETATO COMPOUNDS OF SOME TRANSITION METAL IONS

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(Received 23 April 1984)

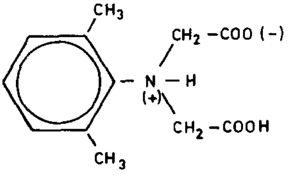
ABSTRACT

Some new 2,6-xylyliminodiacetato compounds of Mn(II), Fe(III), Ni(III), Zn(II) and Cd(II) have been prepared in aqueous media. The thermal behaviour of these compounds has been studied by TG, DTG, and DSC techniques. Heats of dehydration have been calculated from the DSC curves.

INTRODUCTION

The iminodiacetic acids $RN(CH_2–COOH)_2$ are excellent complexing agents for most di- and trivalent cations [1–6]. These compounds are weak acids with "zwitterion" or dual type ion formation causing considerable differences in the dissociation of the acid groups [7]. When partially neutralized, these acids readily form chelate compounds with most cations; in these compounds chelate formation occurs through the nitrogen and acid groups [8].

An aryl derivative of iminodiacetic acid, the 2,6-xylyliminodiacetic acid, 2,6-H_2 XIDA (Scheme 1), was synthesized by Skubin et al. [9] who determined its first dissociation constant (p$K = 2.92$). Recently, Salinas et al.



Scheme 1

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[10] reported the solid compounds formed between this acid and Cu(II), Ba(II) and Al(III) ions; they found that 2,6-xylyliminodiacetic acid gives complexes of stoichiometry 1 : 1 and 1 : 2 with Cu(II) and Al(III) ions, respectively.

Several studies on the thermal stability of iminodiacetic acid and some metal iminodiacetato complexes have been described in the literature; thus, Khramov et al. [11] studied the thermal decomposition of iminodiacetic acid. Recently, Gonzalez-Vilchez and co-workers [12–14] have synthesized and characterized several iminodiacetato complexes of the platinum group metals by thermal analysis.

In this paper the preparation and characterization (mainly by IR spectral data) and thermal behaviour of some new 2,6-xylyliminodiacetato compounds of Mn(II), Fe(III), Ni(II), Zn(II) and Cd(II) are reported.

EXPERIMENTAL

Materials

2,6-Xylyliminodiacetic acid (2,6-H_2 XIDA) was synthesized by a modification of Skubin's method [9], using 6 N HCl for direct precipitation. The isolated acid was recrystallized in boiling water. Elemental analysis for this acid was: found (%): C, 60.76; H, 6.60; N, 6.03; calcd. for $C_{12}H_{15}NO_4$ (%): C, 60.74; H, 6.37; N, 5.90. In the preparation of this acid and the compounds described below only reagent grade chemicals were used.

2,6-Xylyliminodiacetato compounds of Mn(II), Fe(III), Ni(II), Zn(II) and Cd(II) were synthesized in a similar way: 5 mmol of 2,6-xylyliminodiacetic acid were suspended in 25 ml of distilled water; to this suspension were added several drops of 2 M NaOH solution until all the acid was dissolved. A solution containing 5 mmol of the corresponding metal nitrate was slowly added. At this point a precipitate appears. The precipitates were separated from the mother liquor, washed with cold water, and then dried in air at room temperature. The elemental analyses of C, H and N for these compounds have been recorded in the microanalytical laboratories of the Department of Bioorganic Chemistry, Barcelona. The data obtained are shown in Table 1.

Apparatus

All IR spectra were taken on a Beckman 4250 spectrophotometer using potassium bromide pellets; in all cases, the 4000–200 cm^{-1} wavenumber range was studied.

Magnetic measurements were carried out on a conventional Gouy balance, using a 1.5-in. electroiman Newport SM-12 and current intensities of 0.8, 1.1 and 1.5 A. $[Ni(en)_3]S_2O_3$ was used for calibrating.

Thermal studies were carried out on a Mettler TA 3000 system provided with a Mettler TG 50 thermobalance and a Mettler differential scanning calorimeter (model DSC 20). Thermogravimetric curves were obtained at a heating rate of 10 °C min^{-1} in a dynamic atmosphere (100 ml min^{-1} of pure air), using samples varying in weight from 8.890 (Zn(II) compound) to 4.842 mg (free acid). In all cases, the 40–600 °C temperature range was studied. DSC curves were taken at a heating rate of 5 °C min^{-1} in a static atmosphere of air in the 35–550 °C temperature range. In these cases, the sample weights employed varied between 2.330 (Fe(III) compound) and 5.750 mg (Zn(II) compound).

RESULTS AND DISCUSSION

In Table 2 the spectral data for the isolated compounds are given. The assignments have been realized according to the literature for these compounds [8,15–18]. The bands in the 3600–3400 cm^{-1} region can be assigned to ν(O–H) of water. From IR data two types of coordination can be established. Thus, the IR spectrum of Fe(2,6-H XIDA)(2,6-XIDA) shows characteristic bands corresponding to the stretching vibrations of a carbonyl group (1720 cm^{-1}) and a coordinated carboxylate group (1605 cm^{-1}) [6,16]. From the elemental analysis and IR data for this compound, and according to Vieles and Israily [6], the structure indicated in Scheme 2 is proposed.

The IR spectra of the remaining 2,6-xylyliminodiacetate compounds are very similar; showing one or two absorption bands around 1600 cm^{-1} due to the stretching vibration of carboxylate groups linked to metal ions. The position of these bands are in accordance with those of the oxygen–metal

TABLE 1

Elemental analysis data for the isolated compounds

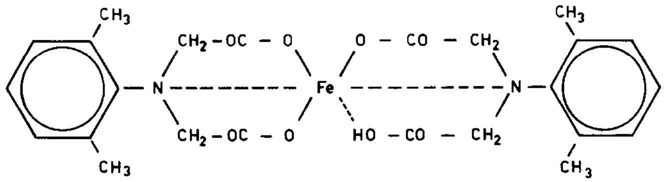
		C	H	N	M
$Mn(C_{12}H_{13}NO_4)\cdot H_2O$	Found	46.91	4.84	4.56	18.23
	Calc.	46.77	4.91	4.54	17.81
$Fe(C_{12}H_{14}NO_4)(C_{12}H_{13}NO_4)$	Found	54.42	5.74	5.38	10.34
	Calc.	54.66	5.16	5.34	10.59
$Ni(C_{12}H_{13}NO_4)\cdot 2\ H_2O$	Found	43.74	5.36	4.47	20.35
	Calc.	43.68	5.19	4.25	17.79
$Zn(C_{12}H_{13}NO_4)\cdot 2\ H_2O$	Found	42.67	5.20	4.16	18.34
	Calc.	42.81	5.09	4.16	19.42
$Cd(C_{12}H_{13}NO_4)\cdot H_2O$	Found	39.79	4.06	3.85	28.79
	Calc.	39.42	4.13	3.83	30.74

TABLE 2

IR absorption bands of complexes containing 2,6-xylyliminodiacetato anions [a]

$2,6\text{-}H_2XIDA$	$Mn(2,6\text{-}XIDA)\cdot H_2O$	Fe(2,6-HXIDA)(2,6-XIDA)	$Ni(2,6\text{-}XIDA)\cdot 2\ H_2O$	$Zn(2,6\text{-}XIDA)\cdot 2\ H_2O$	$Cd(2,6\text{-}XIDA)\cdot H_2O$	Assign.
–	3430	–	3500 b	3560 m	3540 m	ν(O–H)
2950 w		2950 w	2950 w	2950 w	2930 w	ν(C–H)
2910 w	2920 w	2910 w	2910 w	2910 w		
2700–2400 b	–	2700–2400 b	–	–	–	ν(O–H)
1735 w						
1715 w	–	1720 s	–	–	–	ν(COOH)
1655 s						
–	1590 s 1555 s	1605 s	1580 s	1600 s	1590 s 1560 s	$\nu(COO^-)$
1400 s	1390 m	1395 s	1400 s	1395 s	1390 s	ν(C–O)

[a] s, strong; m, medium; w, weak; b, broad.



Scheme 2

bonds, which, in these compounds, must be essentially electrostatic, since, if a carboxyl group is linked to a metal ion, the carboxylate resonance will increase as the ionic character to the oxygen–metal link increases. Likewise, an increase in carboxylate resonance imparts enhanced single-bond character to the carbonyl group, and also causes a lowering of the frequency of the C=O stretching vibration [17].

The values found for the magnetic moments of the metal ions in these compounds also show that the metal–2,6-xylyliminodiacetate bonds are typically electrostatic [5.86 B.M. Mn(II) and 3.55 B.M. Ni(II)].

The TG and DSC diagrams for 2,6-H_2 XIDA and their Mn(II), Fe(III), Ni(II), Zn(II) and Cd(II) compounds are given in Figs. 1 and 2.

The TG curve for 2,6-H_2 XIDA (Fig. 1A) shows that this acid is thermally stable in the 40–170 °C range. Its pyrolitic decomposition starts at 170 °C and finishes around 500 °C with the total elimination of the sample. The DSC curve of 2,6-H_2 XIDA (Fig. 2A) displays an endothermic effect at 168.9 °C corresponding to fusion. The value of the fusion enthalpy calculated from the area of this effect was 29.9 kJ mol^{-1}. Liquid 2,6-H_2XIDA decomposed immediately (exothermic effects at 290, 370 and 465 °C).

The TG and DSC curves for divalent 2,6-xylyliminodiacetato compounds

TABLE 3

Thermal stability of some 2,6-xylyliminodiacetato compounds (dehydration processes)

Process	Temp. (°C)	Thermal nature of the transformation	Weight loss (%)		Enthalpy (kJ mol^{-1})
			Calcd.	Found	
2,6-H_2XIDA$_{(s)}$ → 2,6-H_2XIDA$_{(l)}$	168.9	endo	–	–	29.9
Mn(2,6-XIDA)·H_2O → Mn(2,6-XIDA)	182.9	endo	6.4	5.84	41.9
Ni(2,6-XIDA)·2 H_2O → Ni(2,6-XIDA)	89.6	endo	10.8	10.92	31.9
Zn(2,6-XIDA)·2 H_2O → Zn(2,6-XIDA)	82.4	endo	11.8	10.70	66.4
Cd(2,6-XIDA)·H_2O → Cd(2,6-XIDA)	144.6	endo	5.4	4.93	47.2

are very similar. The dehydration processes can be observed in the 80–183 °C range. Under the experimental conditions used in the present work, the dehydration of these compounds takes place in one step. The observed weight losses for these processes are in good agreement with theoretical

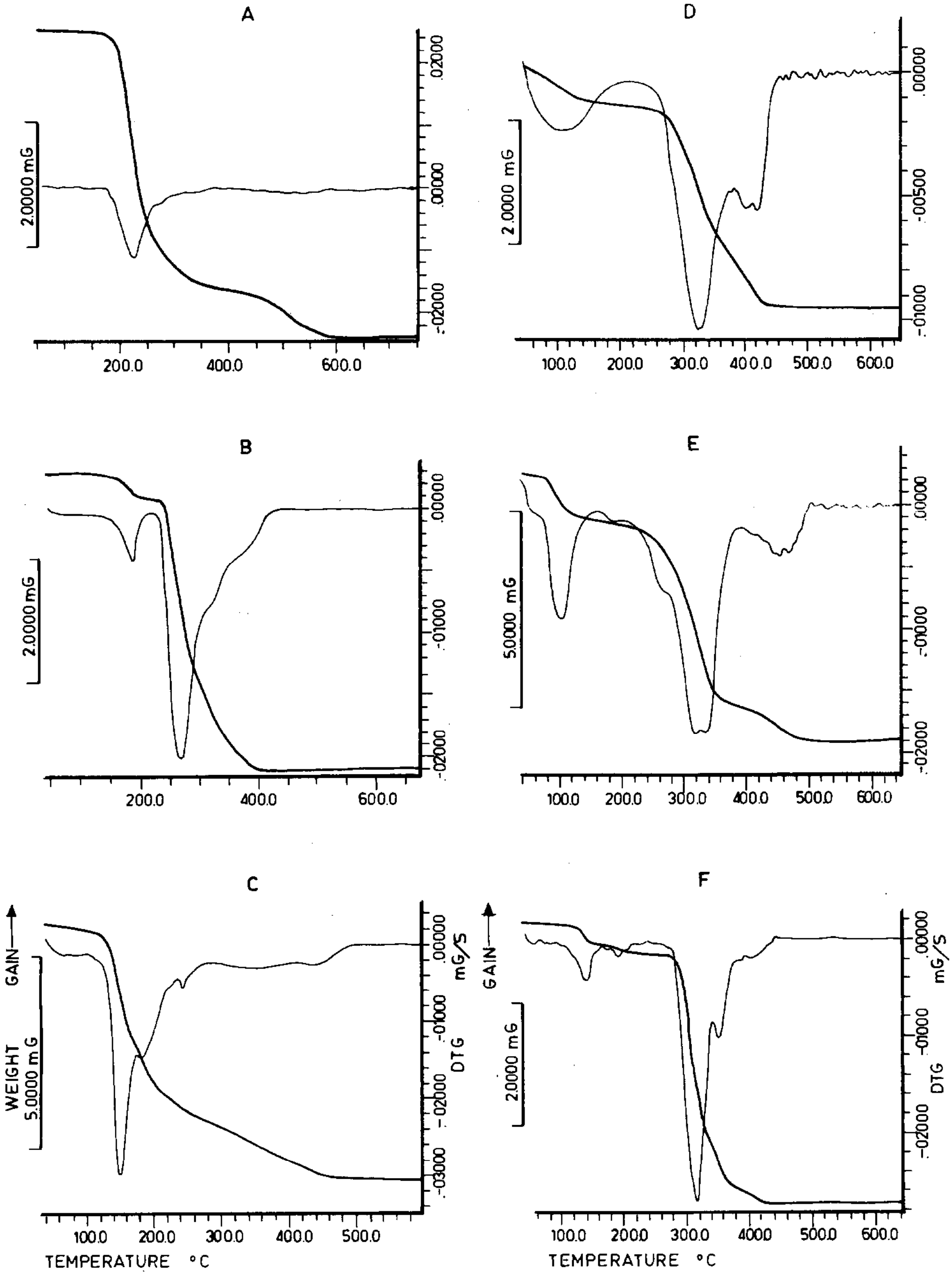


Fig. 1. Thermogravimetric curves of 2,6-xylyliminodiacetic acid (A) and its Mn(II) (B); Fe(III) (C); Ni(II) (D); Zn(II) (E); and Cd(II) (F) compounds.

values (Table 3). The expected endothermic behaviour for the dehydration processes associated with these compounds have been observed from their DSC curves. The dehydration enthalpies calculated are also given in Table 3.

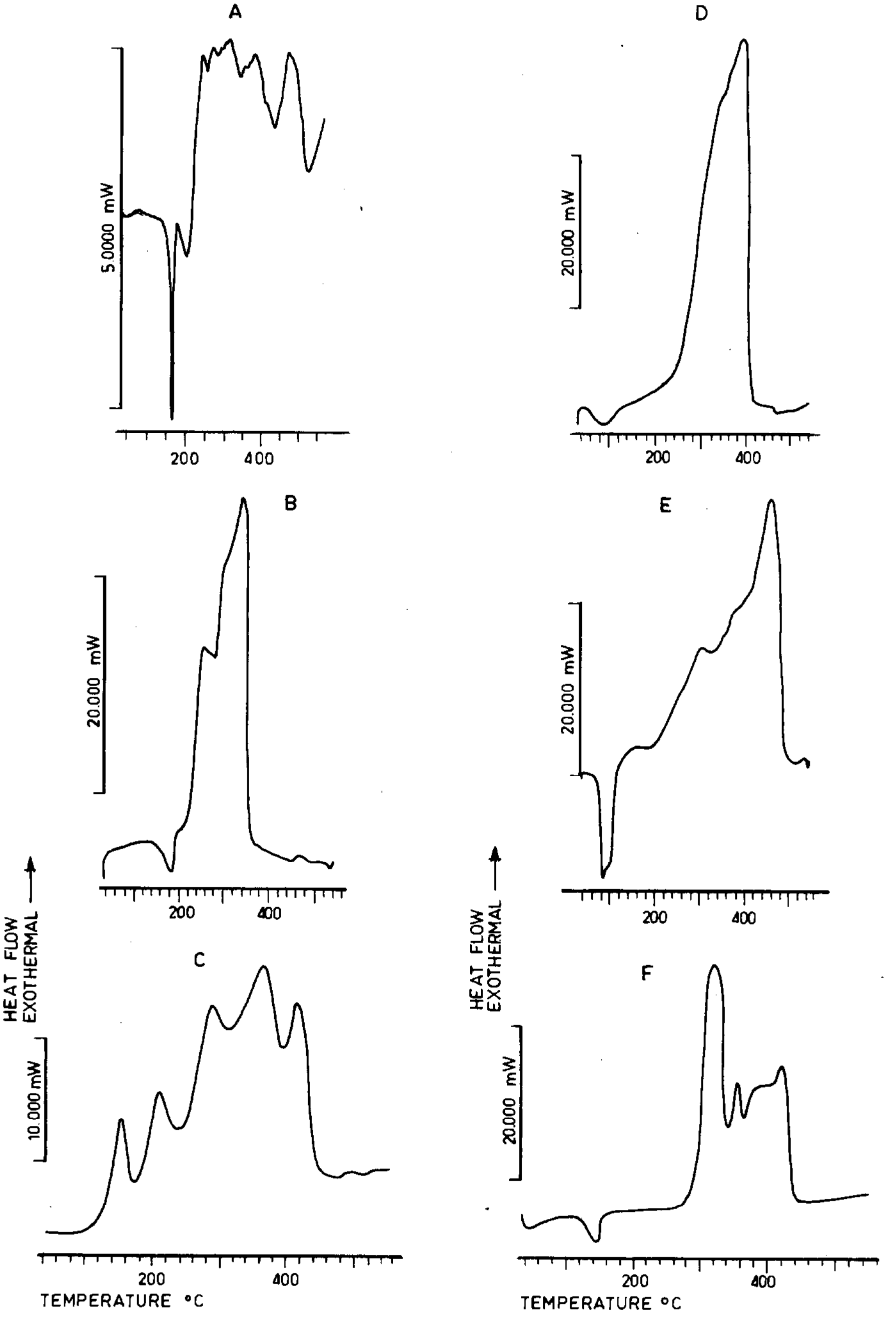


Fig. 2. DSC curves of 2,6-xylyliminodiacetic acid (A) and its Mn(II) (B); Fe(III) (C); Ni(II) (D); Zn(II) (E); and Cd(II) (F) compounds.

TABLE 4

Thermal stability of some 2,6-xylyliminodiacetato compounds (decomposition processes)

Process	Temp. range (°C)	Thermal nature of the transformation	Residue weight loss (%)	
			Calc.	Found
2,6-H_2XIDA → pyrolitic process	170–600	exo	–	–
Mn(2,6-XIDA) → Mn_2O_3	220–425	exo	25.58	23.04
Ni(2,6-XIDA) → NiO	220–430	exo	22.64	23.41
Zn(2,6-XIDA) → ZnO	160–510	exo	24.17	22.83
Cd(2,6-XIDA) → CdO	245–445	exo	33.54	35.12
Fe(2,6-XIDA)(2,6-HXIDA) → Fe + Fe_2O_3	100–500	exo	15.18 (Fe_2O_3) 10.62 (Fe)	12.8

The anhydrous compounds are stable in a short temperature range, and show a strong decomposition in two steps, which finishes at ~ 470 °C. At this point, the residual weights are in good agreement with the required values for metallic oxides. In the DSC curves, the decomposition processes correspond to exothermic effects which have been indicated in Table 4.

The nature of the residues of pyrolitic decomposition of 2,6-xylyliminodiacetato compounds was established from their corresponding X-ray diffraction patterns [19]. In the case of the residue of Fe-(2,6-XIDA)(2,6-HXIDA), the discrepancy between experimental and theoretical values of weight loss for the residue is due to partial reduction of Fe_2O_3 to Fe(0).

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