

THERMAL STUDIES ON 2,3-XYLYLIMINODIACETATO COMPOUNDS

J.M. SALAS-PEREGRIN *

Department of Inorganic Chemistry, Faculty of Sciences, University of Granada, 18071 Granada (Spain)

M. ROMÁN-CEBA, J.C. AVILA-ROSON and J. SUÁREZ-VARELA

Department of General Chemistry, University of Granada, 18071 Granada (Spain)

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ABSTRACT

2,3-Xylyliminodiacetato compounds of Al(III), Cr(III), Fe(II), Co(II), Ni(II), Zn(II), Cd(II), Ba(II) and Pb(II) have been prepared and studied by IR spectroscopy and thermal analysis. The thermal behaviour of these compounds has been studied using TG, DTG and DSC techniques. Dehydration energies have been calculated.

INTRODUCTION

The iminodiacetic acids $RN(CH_2-COOH)_2$ are excellent complexing agents for most di- and trivalent cations [1–8]. These compounds are weak acids with “zwitterion” or dual-type ion formation causing considerable differences in the dissociation of the acid group [9]. When partially neutralized, these acids readily form chelate compounds with most cations; in these compounds, chelate formation occurs through the nitrogen and acid groups [10].

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, González-Vilchez and co-workers [12,13] 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 2,3-xylyliminodiacetato com-

* To whom all correspondence should be addressed.

pounds of Al(III), Cr(III), Fe(II), Co(II), Ni(II), Zn(II), Cd(II), Ba(II) and Pb(II) are reported.

EXPERIMENTAL

Materials

2,3-Xylyliminodiacetic acid (2,3-H₂XIDA) was synthesized following the method described by Salinas et al. [14]. The isolated acid, once filtered and dried at 60°C, was recrystallized in ethyl ether or ethyl ether-petroleum ether mixtures. Elemental analysis for this acid was: found (%): C, 60.69; H, 6.82; N, 5.87; calcd. for C₁₂H₁₃NO₄ (%): C, 60.75; H, 6.37; N, 5.90. In the preparation of this acid and the compounds described below only reagent grade chemicals were used.

All the 2,3-xylyliminodiacetato compounds were synthesized in a similar way: 4 mmol of 2,3-xylyliminodiacetic acid were suspended in 20 ml of distilled water; to this suspension was added 2 M NaOH until all the acid was dissolved; then, an aqueous solution containing 4 mmol of the corresponding metal nitrate (for Fe(II), sulphate was used) 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

TABLE 1

Elemental analysis data for the isolated compounds

		C	H	N
Al(C ₁₂ H ₁₃ NO ₄)(C ₁₂ H ₁₄ NO ₄)·3H ₂ O	Found	51.92	5.84	5.06
	Calc.	52.17	6.02	5.07
Cr(C ₁₂ H ₁₃ NO ₄)(C ₁₂ H ₁₄ NO ₄)·2H ₂ O	Found	52.07	5.59	5.19
	Calc.	51.52	5.58	5.01
Fe(C ₁₂ H ₁₃ NO ₄)·H ₂ O	Found	46.31	4.99	4.50
	Calc.	46.63	4.89	4.53
Co(C ₁₂ H ₁₃ NO ₄)·H ₂ O	Found	46.24	4.85	4.56
	Calc.	46.17	4.84	4.48
Ni(C ₁₂ H ₁₃ NO ₄)·H ₂ O	Found	46.57	4.94	4.46
	Calc.	46.20	4.85	4.49
Zn(C ₁₂ H ₁₃ NO ₄)·2H ₂ O	Found	43.06	5.29	4.36
	Calc.	42.81	5.09	4.16
Cd(C ₁₂ H ₁₃ NO ₄)·H ₂ O	Found	40.10	4.04	3.88
	Calc.	39.42	4.14	3.83
Ba(C ₁₂ H ₁₃ NO ₄)	Found	38.80	3.52	3.87
	Calc.	38.68	3.52	3.76
Pb(C ₁₂ H ₁₃ NO ₄)	Found	33.03	3.04	2.93
	Calc.	32.58	2.96	3.16

have been realized in the microanalytical laboratories of the Department of Bioorganic Chemistry, Barcelona. The data obtained are shown in Table 1.

Apparatus

Infrared spectra in the region 4000–200 cm^{-1} of samples in KBr pellets were recorded using a Beckman 4250 spectrophotometer.

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 $10^\circ\text{C min}^{-1}$ in a dynamic atmosphere (100 ml min^{-1} of pure air), using samples varying in weight from 4.130 (Al(III) compound) to 18.350 mg (Ni(II) compound). In all cases, the 40–700°C temperature range was studied. DSC curves were taken at a heating rate of 5°C min^{-1} in a static air atmosphere in the 35–550°C temperature range. In these cases, the sample weights employed varied between 2.06 (Al(III) compound) and 2.57 mg (Cd(II) compound).

RESULTS AND DISCUSSION

The IR spectrum of 2,3- H_2XIDA shows two bands at 2660 and 2550 cm^{-1} corresponding to $\nu(\text{OH})$, which suggests a dimeric structure for this acid [15]; that is, intermolecular hydrogen bonds exist between the COOH groups of two molecules of 2,3- H_2XIDA . This fact is also confirmed by the position of the bands corresponding to $\nu(\text{C}-\text{O})$ and $\nu(\text{O}-\text{H})$ (1410 and 1250 cm^{-1} , respectively). Likewise, the IR spectrum of 2,3- H_2XIDA shows a strong band at 1705 cm^{-1} due to the carboxyl absorption characteristic of unionized carboxylic acids.

The IR spectra of the isolated divalent 2,3-xylyliminodiacetato compounds are very similar, showing a band due to the asymmetric stretching vibration of carboxylate groups linked to metal ions. This band appears in the different 2,3-xylyliminodiacetato compounds at 1640 (Fe(II), Co(II) and Ni(II)), 1590 (Zn(II)), 1580 (Pb(II)), and 1570 cm^{-1} (Cd(II) and Ba(II)). Likewise, all the IR spectra show a weak band around 1400 cm^{-1} due to the symmetric stretching vibration of the carboxylate group.

The difference in the frequency between the asymmetric and the symmetric vibration bands of the carboxylate groups can be interpreted in terms of the degree of covalent metal–oxygen bonding [15]. This difference increases as the bonding becomes more covalent, and, in our case, is maximum for 2,3-xylyliminodiacetates of barium(II) and lead(II) and minimum for Fe(II), Co(II) and Ni(II) 2,3-xylyliminodiacetato compounds.

On the other hand, hydrated 2,3-xylyliminodiacetato compounds show, in the 3600–3500 cm^{-1} range, bands corresponding to $\nu(\text{O}-\text{H})$ of water. These

bands did not appear in the IR spectra of 2,3-xylyliminodiacetates of barium(II) and lead(II).

The IR spectra of hydrated aluminium(III) and chromium(III) 2,3-xylyliminodiacetates show characteristic bands corresponding to the stretching vibrations of a carbonyl group (1730 and 1725 cm^{-1} , respectively) and a coordinated carboxylate group (1610 and 1580 cm^{-1}) [4]. These results, along with the elemental analysis data, permit to propose for both compounds structures analogous to those found for 2,6-xylyliminodiacetato compounds of aluminium(III) [14] and chromium(III) [16].

The TG and DSC diagrams for 2,3- H_2XIDA are given in Fig. 1. The TG curve for 2,3- H_2XIDA shows that this acid is thermally stable in the $35\text{--}170^\circ\text{C}$ range. Its pyrolytic decomposition starts at 175°C , and finishes at 500°C with the total elimination of the sample. The DSC curve of 2,3- H_2XIDA displays an endothermic effect at 142°C corresponding to fusion. The value of the fusion enthalpy calculated from the area of this effect was 34.5 kJ mol^{-1} . Liquid 2,3- H_2XIDA decomposed immediately (exothermic effects at 260 and 310°C). Endothermic effects due to decarboxylation processes were not observed in the DSC curve of 2,3- H_2XIDA , since the release of the carboxylic groups is simultaneous with the pyrolysis of an important part of the 2,3- H_2XIDA .

TG and DSC diagrams for the prepared 2,3-xylyliminodiacetato compounds are shown in Figs. 2 and 3, respectively. Under the experimental conditions used in the present work, it was only in the Al(III), Cr(III), Zn(II) and Cd(II) compounds that the dehydration process did not overlap with the

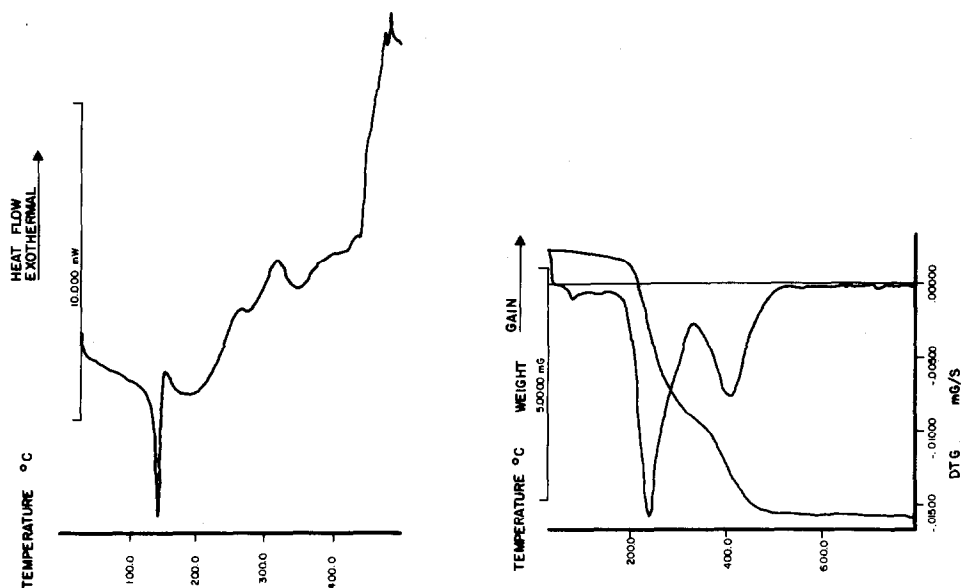


Fig. 1. TG and DSC curves of 2,3- H_2XIDA .

pyrolytic process of the 2,3-xylyliminodiacetato anion. These dehydration processes occur in the 50–170°C temperature range in which the observed weight losses: 9.20% (Al(III)); 6.81% (Cr(III)); 11.79% (Zn(II)) and 5.62% Cd(II) are in good agreement with theoretical values (9.78, 6.43, 10.70 and 4.93%, respectively). The expected endothermic behaviour of the dehydration processes associated with these compounds has been observed from their DSC curves. The dehydration energies calculated from the corresponding areas of the endothermic effects were: 26.0, 34.1, 37.3 and 33.9 kJ mol⁻¹ H₂O, respectively.

The anhydrous compounds are stable in a small temperature range, and show a strong decomposition in two or more steps, which finishes at ~ 450°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 2.

In all cases, the nature of the residues of pyrolytic decomposition of 2,3-xylyliminodiacetato compounds was established from X-ray diffraction methods.

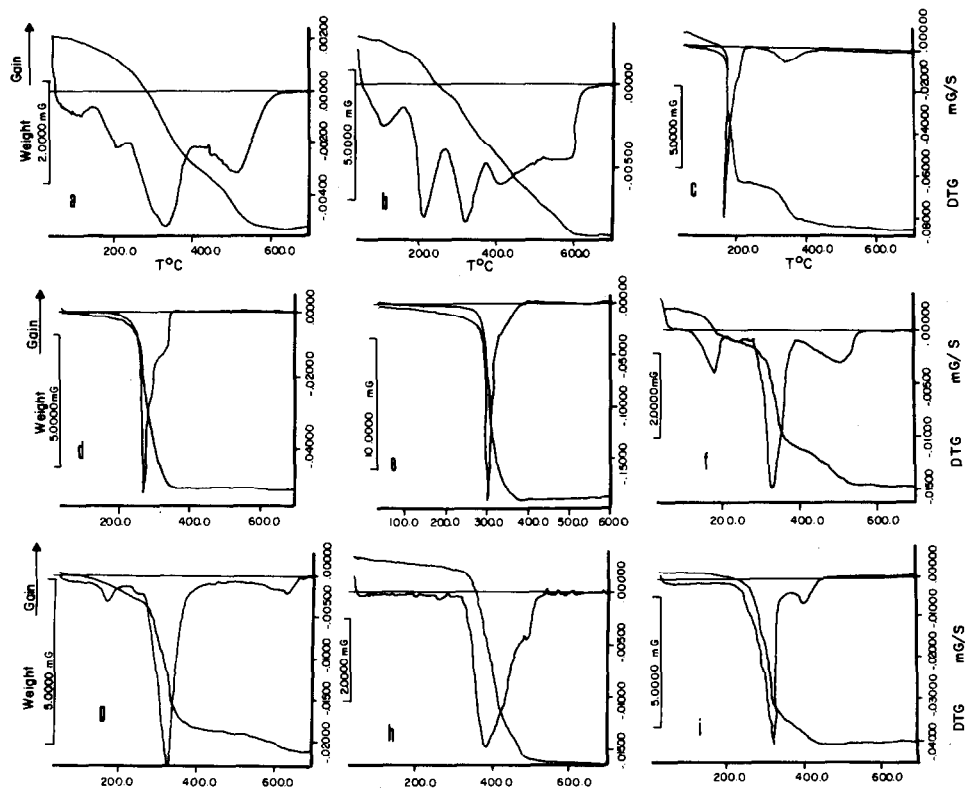


Fig. 2. TG curves of 2,3-xylyliminodiacetato compounds of: Al(III) (a); Cr(III) (b); Fe(II) (c); Co(II) (d); Ni(II) (e); Zn(II) (f); Cd(II) (g); Ba(II) (h); and Pb(II) (i).

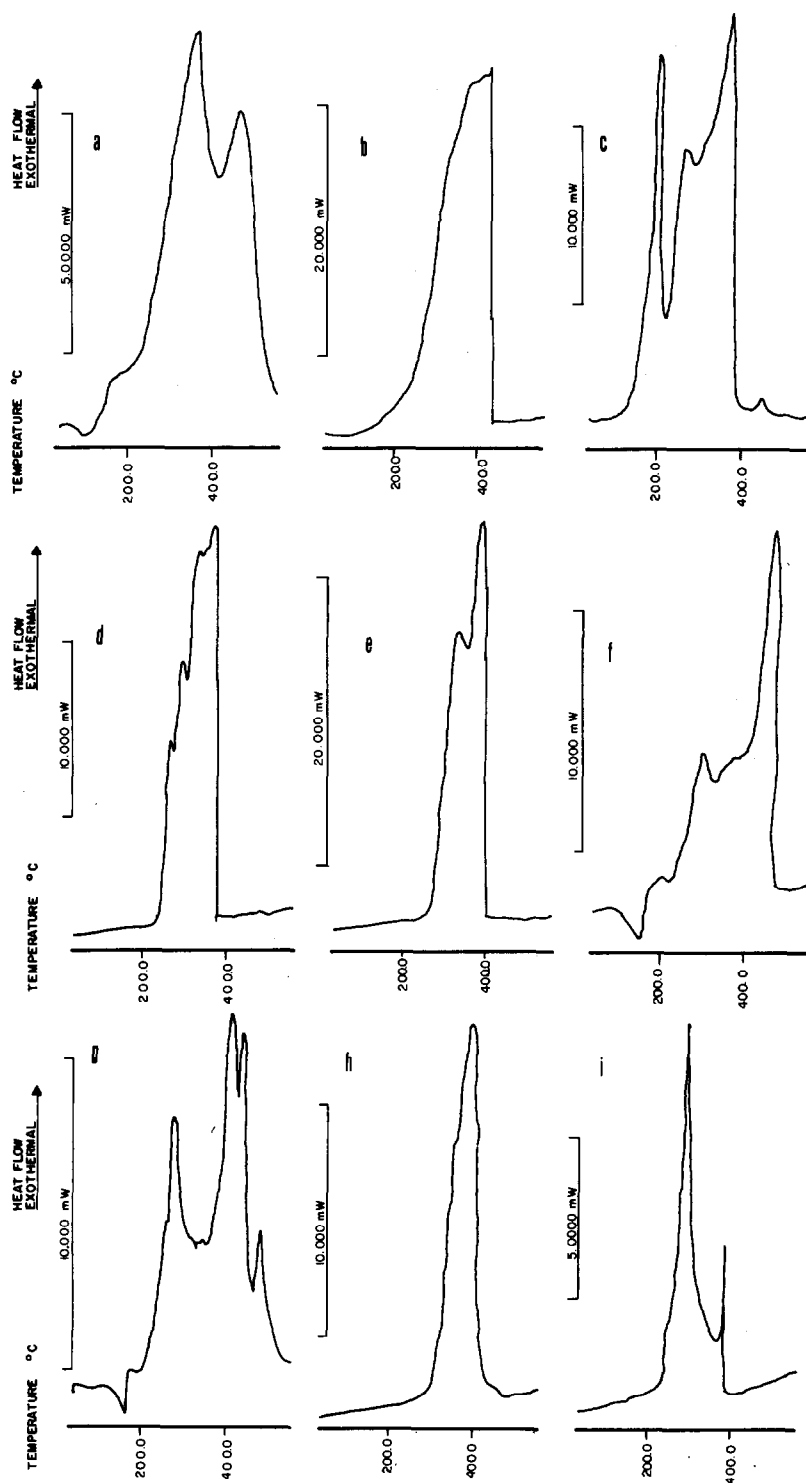


Fig. 3. DSC curves of 2,3-xylyliminodiacetato compounds of: Al(III) (a); Cr(III) (b); Fe(II) (c); Co(II) (d); Ni(II) (e); Zn(II) (f); Cd(II) (g); Ba(II) (h) and Pb(II) (i).

TABLE 2

TG and DSC data for the pyrolytic processes

Process	DSC peaks (°C) and thermal nature of the transformation ^a	Residue weight loss (%)	
		Calc.	Found
2,3-H ₂ XIDA → pyrolysis products	260, 310, 460	—	—
Al(2,3-XIDA)(2,3-HXIDA) → Al ₂ O ₃	365, 470	9.23	10.36
Cr(2,3-XIDA)(2,3-HXIDA) → Cr ₂ O ₃	400	13.58	12.88
Fe(2,3-XIDA) → Fe ₂ O ₃	190, 250, 360	25.83	25.51
Co(2,3-XIDA) → Co ₃ O ₄	260, 280, 360	25.71	24.71
Ni(2,3-XIDA) → NiO	315, 370	23.95	22.21
Zn(2,3-XIDA) → ZnO	285, 455	24.17	23.75
Cd(2,3-XIDA) → CdO	275, 415, 440	35.14	33.51
Ba(2,3-XIDA) → BaCO ₃	360	52.95	52.32
Pb(2,3-XIDA) → PbO	285, 375	50.44	49.12

^a All the effects are exothermic.

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