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THERMAL BEHAVIOUR OF SOLID COMPLEXES OF PHENOXYALKANOIC ACIDS AND DIVALENT METALS

III. Study on cobalt(II) and nickel(II) phenoxyacetates

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Solid Co(II) and Ni(II) phenoxyacetates were studied by DSC and TG techniques. The results showed that they were dihydrate and tetrahydrate respectively in the solid state. No evidence of the location of water molecules in different coordination shells was obtained. Both compounds decomposed with the formation of oxide as final product; the corresponding activation energies suggested a stronger metal-carboxylate bond in the nickel salt.

Keywords: complexes

Introduction

The formation of complexes in solution between pesticides and metals has been largely investigated because of the interest in connection with environmental problems [1]. Several papers have been published on the aqueous solutions of complexes between phenoxyalkanoic acids and divalent metals important for some vital functions of plants [2–5], but few papers have been published on the behaviour of these salts in the solid state [6–10].

In previous papers we reported our studies on the thermal behaviour of solid zinc and copper(II) phenoxyacetates [11, 12], and we observed differences in respect to some literature data.

In this work we investigated the thermal behaviour of other two compounds of the same series, the cobalt(II) and nickel(II) phenoxyacetates.

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Experimental

Materials

Cobalt(II) and nickel(II) phenoxyacetates were prepared by mixing aqueous solutions of phenoxyacetic acid (Fluka), KOH (C. Erba RP) and cobalt(II) sulphate (C. Erba RP) or nickel(II) sulphate (C. Erba RP) in stoichiometric ratios. The solid products obtained (the cobalt salt is dark red and green is the nickel one) were crystallized from water and successively filtered and dried by pump at room temperature.

DSC measurements

The DSC measurements were performed with a Mettler DSC 20 equipment, in a dynamic nitrogen atmosphere ($5\ l\cdot h^{-1}$).

The DSC curves were recorded putting a weighed quantity of the investigated compound in a sealed aluminium pan, another empty sealed aluminium pan was used as reference. The ΔH values associated with the thermal processes were evaluated using $\Delta_{fuss}H$ of indium ($28.46\ J\cdot g^{-1}$) as calibration standard.

TG and DTG measurements

The TG and DTG measurements were performed by a Mettler TA 3000 thermoanalyser, in alumina open crucibles, in a dynamic nitrogen atmosphere ($3.6\ l\cdot h^{-1}$), the sample weight was 15–30 mg. The activation energies were evaluated from the TG and DTG curves by a literature method [12] and by a built-in algorithm of the used equipment, but no difference was observed between the results obtained.

Results and discussion

The DSC curves of the two compounds studied were recorded at $4\ deg\cdot min^{-1}$ heating rate and compared with that of phenoxyacetic acid previously reported [11]. A single endothermic peak, followed by an irregular exothermic one at higher temperature, was observed for both compounds (Figs 1 and 2). We attributed the endothermic effect to dehydration process and the exothermic one to the decomposition of the dehydrated solid compounds.

The measurements were then repeated at $0.2\ deg\cdot min^{-1}$ to investigate if the dehydration processes occurred in one or more steps. Also at this very low heat-

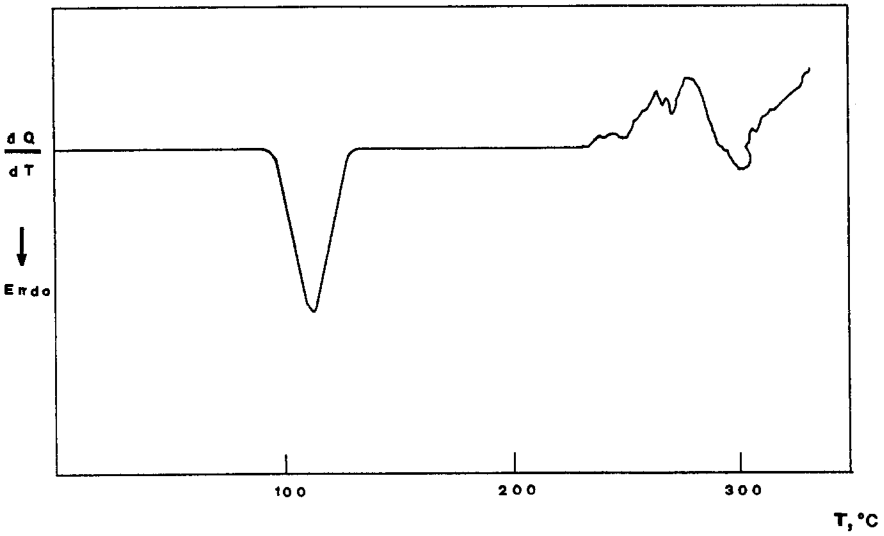

Fig. 1 The DSC curve of Co(II) phenoxyacetate dihydrate

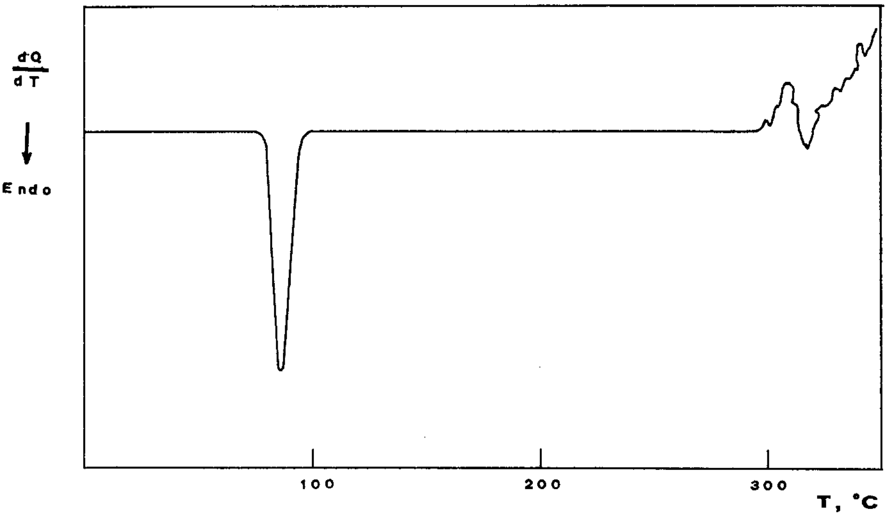

Fig. 2 The DSC curve of Ni(II) phenoxyacetate tetrahydrate

ing rate a single endothermic peak was observed, so we drew the conclusion that the dehydration took place in one single step.

TG and DTG measurements were then performed to obtain further information about the thermal processes observed by DSC technique (Figs 3 and 4). They showed, for both compounds, a first single step at lower temperature due to dehydration. The weight losses were evaluated and indicated that Co(II) salt was dihydrate and Ni(II) salt was tetrahydrate in the solid state. At higher temperatures both dehydrated compounds decomposed in two consecutive steps; the corresponding weight losses indicated that CoO and NiO were the final products, but did not give information about the intermediate products formed. The temperatures, the enthalpic values and the activation energies of the thermal processes were reported in Table 1.

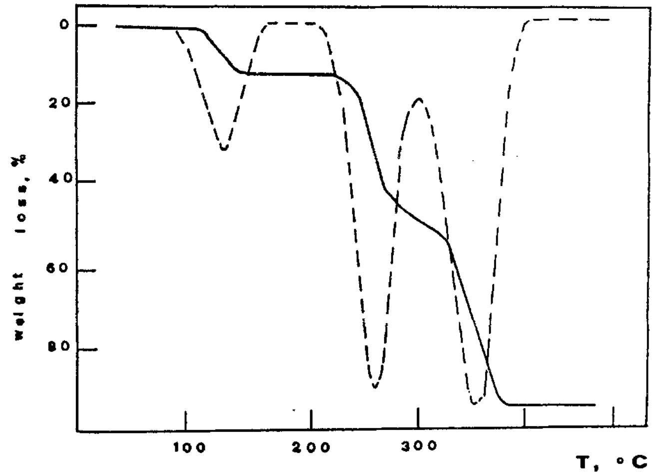

Fig. 3 The TG and DTG curves of Co(II) phenoxyacetate dihydrate

The DSC, TG and DTG results agreed with each other, apart from little differences in the temperatures of the processes due to different experimental conditions.

The thermal processes occurred according to the following scheme:

a) $(C_6H_5\text{-}O\text{-}CH_2\text{-}COO)_2M \cdot nH_2O_{(s)} \xrightarrow[\text{1 step}]{\text{lower temp.}} (C_6H_5\text{-}O\text{-}CH_2\text{-}COO)_2M_{(s)} + nH_2O_{(v)}$

b) $(C_6H_5\text{-}O\text{-}CH_2\text{-}COO)_2M_{(s)} \xrightarrow[\text{2 step}]{\text{higher temp.}} MO_{(s)}$ + gaseous products

in which M = Co(II), Ni(II) and $n = 2, 4$.

Differently from the analogous Zn and Cu(II) complexes previously studied, for which two dehydration steps were observed at very low heating rate [11, 12], no evidence was obtained of the location of water molecules in different coordination shells. It disagreed with literature data for Co(II) complexes [10].

The total activation energy associated with the comprehensive decomposition process b) of the Ni(II) salt was higher than that of Co(II) salt. It suggested a stronger Ni(II)-carboxylate bond. These values and the corresponding ones as-

Table 1 T, ΔH, weight losses and activation energies of the thermal processes

Complexes	DSC measurements			TG measurements			E_a / kJ·mol^{-1}
	T /°C	ΔH /kJ·mol^{-1}	Process	T /°C	weight loss / %	Process	
$(C_6H_5–O–CH_2–COO)_2Co·2H_2O$	91.9 – 134.1	325.9	Dehydration	87.9 – 153.0	9.35	Dehydration	106.4
	225.0	n.e.	Decomposition	217.9 – 297.8	30.61	1st step of decomp.	503.8
				297.8 – 399.9	39.90	2nd step of decomp.	88.0
$(C_6H_5–O–CH_2–COO)_2Ni·4H_2O$	74.5 – 100.3	495.1	Dehydration	63.8 – 110.2	16.42	Dehydration	101.7
	295.0	n.e.	Decomposition	289.9 – 330.1	14.74	1st step of decomp.	170.3
				330.1 – 374.3	48.64	2nd step of decomp.	586.9

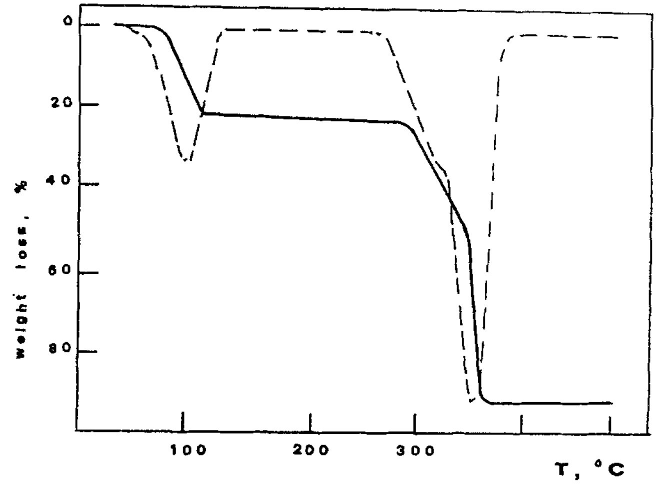

Fig. 4 The TG and DTG curves of Ni(II)phenoxyacetate tetrahydrate

sociated with the decomposition of Cu(II) and Zn phenoxyacetates [11, 12] indicated that the *M*(II)-carboxylate bond strength of phenoxyacetates decreases according to this order:

Ni(II) > Cu(II) > Zn > Co(II)

It agrees with the thermodynamic formation constants (^{T}K) in aqueous solution [5] apart from the Ni(II) phenoxyacetate, for which the smaller ^{T}K value was found. It could be explained with the presence, in this salt, of four hydration water molecules, which stabilize this compound in the solid state.

* * *

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Zusammenfassung — Mittels DSC und TG wurden Co(II)- und Ni(II)-phenoxyacetat als Feststoffe untersucht. Die Ergebnisse zeigten, daß es sich dabei im festen Zustand um das Di- bzw. Tetrahydrat handelt. Für die Lokalisation der Wassermoleküle in den verschiedenen Koordinationssphären konnten keine Beweise erbracht werden. Beide Verbindungen zersetzen sich unter der Bildung des Oxides als Endprodukt; die entsprechenden Aktivierungsenergien scheinen auf eine stärkere Metall-Carboxylat-Bindung im Nickelsalz schließen zu lassen.