

THERMAL STUDIES ON ACETYLENEDICARBOXYLIC ACID COMPOUNDS OF IRON(II), COBALT(II), NICKEL(II), COPPER(II) AND ZINC(II)

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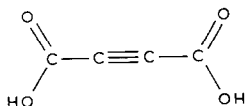
ABSTRACT

Some new compounds of acetylenedicarboxylic acid with iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) have been prepared in aqueous solution. The thermal behaviour of these compounds has been studied by thermogravimetry (TG) and differential scanning calorimetry (DSC) techniques. The compounds of cobalt, nickel and zinc are hydrated. Thermal decomposition studies show that these compounds lose water of crystallisation followed by organic ligand to give the metal oxide. The iron and copper compounds are anhydrous. Thermal decomposition studies show that these compounds lose organic ligand to form the metal oxide.

INTRODUCTION

A great deal of interest has been shown in the acetylenic compounds, particularly the potential industrial importance of the polyacetylenes and polydiacetylenes [1,2]. Many polymers currently being investigated for electrical conduction properties have molecular backbones containing conjugated multiple bonds.

Acetylenedicarboxylic acid is a strong acid [3] which was first reported in the literature in 1920 [4].



Acetylenedicarboxylic acid (C₄O₄H₂)

This acid has two different types of donor sites: the oxygen atoms of the carboxylic acid groups and the electron rich acetylenic bond. This paper reports the thermal analysis studies of acetylenedicarboxylic acid together

with the complexes formed by the acid and the transition metals, iron(II), cobalt(II), nickel(II), copper(II) and zinc(II).

The complexes are all new compounds. Spectral and magnetic studies have been used to characterise each complex and to interpret the type of coordination which takes place to the metal ion. Depending on how the transition metal ions coordinate to the acid the possibility exists of producing polymer systems containing triple bonds. A study of the thermal stability of acetylenedicarboxylic acid complexes has been carried out. No thermal decomposition data have been reported for any of these compounds in the literature.

EXPERIMENTAL

Preparation of complexes

Method A

Acetylenedicarboxylic acid (10 mmol) was dissolved in hot water and the metal carbonate was added in small amounts, with stirring until effervescence ceased. The solution was filtered and the filtrate evaporated until the volume had decreased and the complex precipitated. The precipitate was filtered, washed with water and dried.

Method B

Hydrated iron(II) chloride (3 mmol) was dissolved in enough hot water to form a saturated solution. Acetylenedicarboxylic acid (6 mmol) was dissolved in the minimum amount of hot water. The two solutions were mixed and left aside for 48 h. The iron complex which was precipitated was filtered, washed with water and dried.

Apparatus

The infrared spectra were obtained using KBr discs, 4000–600 cm^{-1} , and polyethylene discs, 600–200 cm^{-1} on a Perkin-Elmer infrared spectrophotometer Model 598.

The electronic spectra were obtained on a Beckmann ACTA M-IV spectrophotometer as solid diffuse reflectance spectra.

Magnetic measurements were carried out by the Gouy method using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as calibrant.

The thermal analysis studies were carried out on a Stanton Redcroft Model STA 781 thermobalance and a Mettler differential scanning calorimeter (model DSC TA 3000). Thermogravimetry curves were obtained at a heating rate of 6 $^{\circ}\text{C min}^{-1}$ in static air. In all cases the 20–500 $^{\circ}\text{C}$ temperature range was studied. DSC curves were obtained at a heating rate of 10 $^{\circ}\text{C min}^{-1}$ in a static atmosphere of air in the 30–500 $^{\circ}\text{C}$ temperature range.

The concentration of the metal ion was obtained by a Perkin-Elmer 373 atomic absorption spectrophotometer, the carbon and hydrogen analyses using a Carlo Erba elemental analyser.

RESULTS AND DISCUSSION

The compounds prepared are listed in Table 1. The iron complex was prepared using method B since no compound of suitable stoichiometry could be isolated from method A. The copper compound was isolated as a copper(I) complex.

In Table 2 the main bands in the infrared spectra are listed. The bands in the 3600–3300 cm^{-1} region are assigned to the $\nu(\text{O-H})$ of water [5]. The bands in the 2120–2090 cm^{-1} region have been assigned to the $\nu(\text{C}\equiv\text{C})$ vibration [6]. The $\nu(\text{C}\equiv\text{C})$ vibration is little altered from the values of the free ligand showing that no bonding is taking place with the metal ions. The slight lowering of the frequency of this signal in the spectra of the complexes is attributed to the effect of $d_{\pi}-p_{\pi}$ overlap.

The complex, $\text{Fe}(\text{C}_4\text{O}_4\text{H})_2$ shows characteristic bands corresponding to the stretching vibrations of the carboxyl group at 1685 cm^{-1} and a coordinated carboxylate group at 1590 cm^{-1} [7,8]. The other complexes clearly show that the $\nu(\text{C-O})$ vibration has been lowered to $\sim 1375 \text{ cm}^{-1}$ due to the stretching vibration of the carboxylate groups linked to the metal ions [9,10]. The $\nu(\text{M-O})$ vibrations have been identified and are listed in Table 2. No infrared spectrum was obtained for the black copper complex.

The electronic spectra (Table 3) and the magnetic measurements (Table 1) would suggest that for the iron, cobalt and nickel complexes the metal ion is

TABLE 1
Elemental analysis data and magnetic moments for isolated compounds

Compound		C	H	M	μ (B.M.)
$\text{Fe}(\text{C}_4\text{O}_4\text{H})_2$	Found	32.89	0.91	19.18	5.80
	Calc.	34.04	0.71	19.86	
$\text{Co}(\text{C}_4\text{O}_4)3\text{H}_2\text{O}$	Found	22.76	2.45	25.33	5.26
	Calc.	21.33	2.66	26.22	
$\text{Ni}(\text{C}_4\text{O}_4)4\text{H}_2\text{O}$	Found	20.30	2.85	23.44	3.31
	Calc.	19.78	3.29	24.1	
$\text{Cu}(\text{C}_4\text{O}_4\text{H})$	Found	25.08	0.48	34.68	Dia ^a
	Calc.	27.19	0.56	35.98	
$\text{Zn}(\text{C}_4\text{O}_4)3\text{H}_2\text{O}$	Found	21.90	1.82	27.79	
	Calc.	20.78	2.59	28.14	

^a Dia = diamagnetic.

TABLE 2

Infrared spectra (4000–200 cm^{-1}) for isolated compounds

Compound	$\nu_{\text{O-H}}(\text{H}_2\text{O})$	$\nu_{\text{C}\equiv\text{C}}$	ν_{COOH}	ν_{COO^-}	$\nu_{\text{C-O}}$	$\nu_{\text{M-O}}$
$\text{C}_4\text{O}_4\text{H}_2$		2120	1690		1455	
$\text{Fe}(\text{C}_4\text{O}_4\text{H})_2$		2090	1685	1590		240, 300
$\text{Co}(\text{C}_4\text{O}_4)3\text{H}_2\text{O}$	3700–3100(b)	2100		1580	1375	255
$\text{Ni}(\text{C}_4\text{O}_4)4\text{H}_2\text{O}$	3700–3100(b)	2100		1580	1380	258
$\text{Zn}(\text{C}_4\text{O}_4)3\text{H}_2\text{O}$	3700–3100(b)	2100		1585	1370	252

in an octahedral environment [5]. The copper complex is diamagnetic so that a d^{10} configuration is present and no $d-d$ bands are observed in the electronic absorption spectrum.

The insolubility of the complexes in both polar and non-polar solvents would suggest the presence of polymeric structures for these compounds [5].

In the compounds of cobalt, nickel and zinc it is suggested that a planar metal oxygen chain is formed between two molecules of the acetylene dicarboxylate and a metal ion. Each metal ion is thus bonded to four oxygen atoms in the plane and to oxygen atoms in adjacent planes to give a layer structure and a coordination number of six for the metal ion. A similar structure is suggested for the copper complex except that the bonding to the copper atom is from carboxylate and carboxylic acid groups. In the iron complex it is suggested that each iron atom is bonded to two anions of the type $\text{C}_4\text{O}_4\text{H}^-$ by means of the carboxylate group to give a planar arrangement. Oxygen atoms from a similar planar arrangement above and below this plane bond to the iron to give a coordination number of six and a layer type polymeric structure.

The TG and DSC traces for acetylenedicarboxylic acid and the complexes with iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) are given in Figs. 1 and 2.

TABLE 3

Electronic spectra for some of the isolated compounds

Compound	Band position (cm^{-1})	$d-d$ transition
$\text{Fe}(\text{C}_4\text{O}_4\text{H})_2$	8620	
	10090	${}^5T_{2g} \rightarrow {}^5E_g$
$\text{Co}(\text{C}_4\text{O}_4)3\text{H}_2\text{O}$	8064	${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F})$
	19230	${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{1g}(\text{P})$
$\text{Ni}(\text{C}_4\text{O}_4)4\text{H}_2\text{O}$	8620	${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{2g}(\text{F})$
	14970	${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{F})$
	25630	${}^3A_{2g}(\text{F}) \rightarrow {}^3T_{1g}(\text{P})$

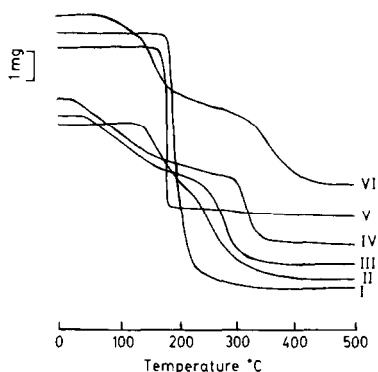


Fig. 1. Thermogravimetric curves of (I) acetylene dicarboxylic acid, sample weight 9.1 mg; (II) $\text{Fe}(\text{C}_4\text{O}_4\text{H})_2$, sample weight 8.78 mg; (III) $\text{Co}(\text{C}_4\text{O}_4)_3\text{H}_2\text{O}$, sample weight 8.28 mg; (IV) $\text{Ni}(\text{C}_4\text{O}_4)_4\text{H}_2\text{O}$, sample weight 8.05 mg; (V) $\text{Cu}(\text{C}_4\text{O}_4\text{H})$, sample weight 8.23 mg; (VI) $\text{Zn}(\text{C}_4\text{O}_4)_3\text{H}_2\text{O}$, sample weight 9.08 mg.

The TG curve for acetylenedicarboxylic acid shows that the acid is thermally stable in the temperature range 20–190 °C. Its pyrolytic decomposition begins at 190 °C and finishes at 380 °C with total elimination of the sample. The DSC curve of acetylenedicarboxylic acid shows an endothermic peak at 191.8 °C due to melting. The acid then decomposes immediately producing an exothermic peak and shoulder at 192.5 and 197.5 °C, respectively.

The TG and DSC curves for the complexes formed between acetylenedicarboxylic acid and iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) are given in Figs. 1 and 2. The TG and DSC curves for the cobalt, nickel and zinc complexes are similar. The dehydration of the complexes starts below 100 °C suggesting that the water is present as water of crystallisation [11]. The dehydration of the complexes takes place in one step. The observed weight losses for these processes compare favourably with the theoretical values (Table 4). The expected endothermic peak for the dehydration processes associated with these compounds has been observed in their DSC curves. The dehydration enthalpies have been calculated and are given in Table 4. The decomposition of the anhydrous complexes follows im-

TABLE 4

Dehydration processes for the cobalt, nickel and zinc compounds

Process	Temp. (°C)	Thermal nature of transformation	Weight loss (%)		Enthalpy (kJ mol ⁻¹)
			Calc.	Found	
$\text{Co}(\text{C}_4\text{O}_4)_3\text{H}_2\text{O} \rightarrow \text{Co}(\text{C}_4\text{O}_4)_3$	50	Endo	24.00	23.86	46
$\text{Ni}(\text{C}_4\text{O}_4)_4\text{H}_2\text{O} \rightarrow \text{Ni}(\text{C}_4\text{O}_4)_4$	75	Endo	29.69	28.57	104
$\text{Zn}(\text{C}_4\text{O}_4)_3\text{H}_2\text{O} \rightarrow \text{Zn}(\text{C}_4\text{O}_4)_3$	40	Endo	26.31	25.51	4

mediately after the dehydration processes and the residual weights are in good agreement with the values required for metallic oxides. In the DSC curves, the decomposition processes correspond to exothermic and endothermic effects for the cobalt and nickel complexes and exothermic effects for the zinc complex as shown in Table 5. The TG and DSC traces for the iron complex show that it undergoes an endothermic reaction at 157 °C followed by exothermic reactions at 205, 245 and 304 °C with loss of the organic ligand to form the oxide. The TG and DSC traces for the copper compound show that it undergoes an extremely rapid exothermic reaction at 170 °C with loss of organic ligand and the formation of the oxide. The speed with

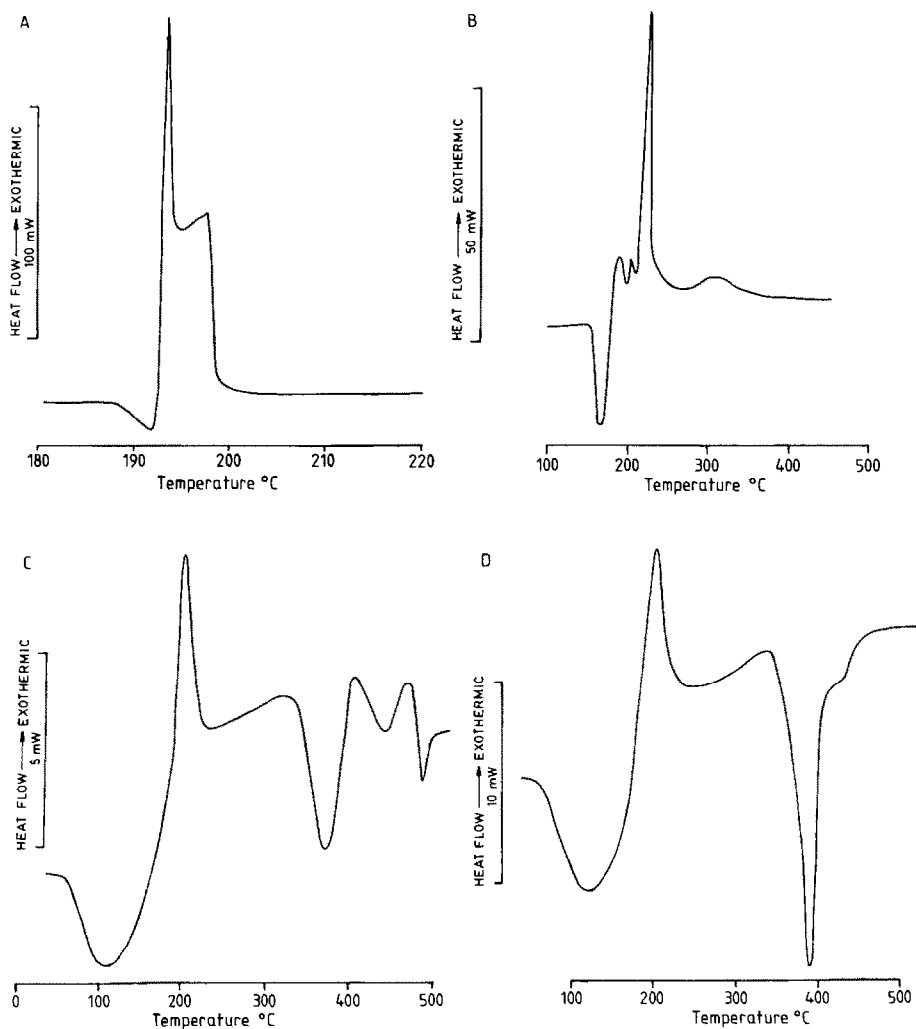


Fig. 2. DSC curves of (A) acetylenedicarboxylic acid; (B) $\text{Fe}(\text{C}_4\text{O}_4\text{H})_2$; (C) $\text{Co}(\text{C}_4\text{O}_4)_3\text{H}_2\text{O}$; (D) $\text{Ni}(\text{C}_4\text{O}_4)_3\text{H}_2\text{O}$; (E) $\text{Cu}(\text{C}_4\text{O}_4\text{H})$; (F) $\text{Zn}(\text{C}_4\text{O}_4)_3\text{H}_2\text{O}$.

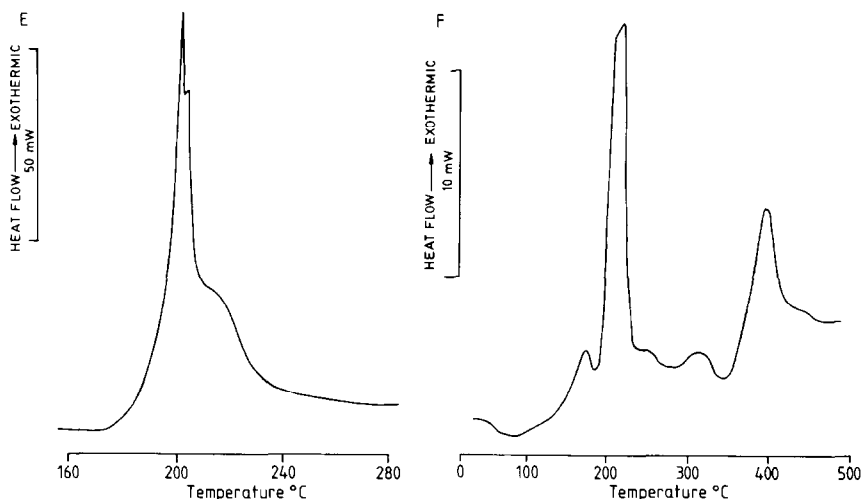


Fig. 2 (continued).

TABLE 5

Decomposition processes of the acetylenedicarboxylic acid and the metal complexes

Process	Temp. range (°C)	Thermal nature of transformation	Residue weight loss (%)	
			Calc.	Found
$C_4O_4H_2 \rightarrow$ pyrolytic process	190–380	Exo	–	–
$Fe(C_4O_4H)_2 \rightarrow Fe_2O_3$	140–440	Endo/Exo	28.36	29.84
$Co(C_4O_4) \rightarrow Co_3O_4$	185–475	Exo/Endo	35.55	36.00
$Ni(C_4O_4) \rightarrow NiO$	190–480	Exo/Endo	30.77	29.81
$Cu(C_4O_4H) \rightarrow Cu_2O$	170–330	Exo	40.22	32.62
$Zn(C_4O_4) \rightarrow ZnO$	190–480	Exo	34.27	36.73

which the organic ligand is removed in this compound could account for the discrepancy between the expected and observed weight losses in Table 5.

This research work continues with other similar acetylenic ligands.

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