

THERMAL STUDIES ON ITACONIC ACID COMPOUNDS OF SOME TRANSITION METAL IONS

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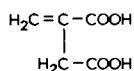
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ABSTRACT

Some new compounds of itaconic acid with manganese(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), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) techniques. The compounds are all hydrated except the copper compound which is anhydrous. Thermal decomposition studies show that the hydrated compounds lose water followed by organic ligand to give the metal oxide. The copper compound loses organic ligand to form copper oxide.

INTRODUCTION

Itaconic acid is used in the polymer industry, particularly in copolymerisation reactions to improve such properties as mechanical shear, adhesion, emulsion stability and dye receptivity [1–6]. The acid has two different donor sites for forming bonds with metal ions: the double bond between the carbon atoms and the oxygen atoms of the carboxylic acid groups.



Itaconic acid (H₂ITAC)

This paper reports on the thermal analysis studies of itaconic acid together with the complexes formed by the acid and the transition metals manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II). Spectral and magnetic studies have been used to characterise each metal complex and to interpret the type of coordination which takes place to the metal ion. A study of the thermal stability of the itaconic acid complexes has been carried out.

EXPERIMENTAL

The compounds were prepared by dissolving the metal carbonate in a hot aqueous solution of itaconic acid. The excess carbonate was removed by filtration. The compound was precipitated by concentrating the solution on a steam bath.

APPARATUS

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

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. Each magnetic moment has been corrected for diamagnetism using Pascal's constants [7].

The thermal analyses studies were carried out on a Stanton Redcroft Model STA 781 thermobalance and a Mettler differential scanning calorimeter (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 $^{\circ}\text{C min}^{-1}$.

RESULTS AND DISCUSSION

The compounds prepared (Table 1) are hydrated and have stoichiometry $\text{M}(\text{ITAC}) \cdot x\text{H}_2\text{O}$ where $x = 1$ for manganese, nickel and zinc; $x = 2$ for cobalt. The copper compound is anhydrous and has stoichiometry $\text{Cu}(\text{HITAC})_2$.

The electronic spectra (Table 2) and the magnetic measurements (Table 1) would suggest that for the cobalt and nickel compounds the metal ion is in an octahedral environment [8]. No information is available on the stereochemistry of the manganese compound from the electronic spectrum and the magnetic moment which is similar to the spin only value. The position of the band in the electronic spectrum of the copper compound would suggest that the copper atom is in an octahedral environment [8]. The magnetic moment for the compound is 1.96 B.M.

TABLE 1

Analysis of compounds and magnetic moments

Compound	Theoretical (%)			Experimental (%)			μ (B.M.)
	M	C	H	M	C	H	
Mn(ITAC)·H ₂ O	27.32	29.84	2.98	27.12	29.66	2.71	5.91
Co(ITAC)·2H ₂ O	26.42	26.90	3.58	25.91	26.42	3.44	4.82
Ni(ITAC)·H ₂ O	28.66	29.29	2.92	28.14	29.42	2.71	3.18
Cu(HITAC) ₂	37.30	19.75	3.18	36.45	19.41	2.87	1.96
Zn(ITAC)·H ₂ O	30.92	28.38	2.83	30.22	27.74	2.43	—

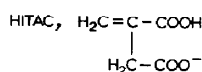
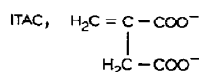


TABLE 2

Electronic spectral details of prepared compounds

Compound	Peak positions (cm ⁻¹)	<i>d-d</i> Transitions
Co(ITAC)·2H ₂ O	8130	⁴ T _{1g} (F) → ⁴ T _{2g} (F)
	19047	→ ⁴ T _{2g} (P)
Ni(ITAC)·H ₂ O	8928	³ A _{2g} (F) → ³ T _{2g} (F)
	14814	→ ³ T _{1g} (F)
	25001	→ ³ T _{1g} (P)
Cu(HITAC) ₂	14814	² E _g (D) → ² T _{2g} (D)

In Table 3 the main bands in the infrared spectrum of the compounds are reported. The manganese, cobalt, nickel and zinc compounds show a strong absorption band in the region 3700–2680 cm⁻¹, $\bar{\nu}_{\text{O-H}}$, indicating the presence of water of crystallisation. The compounds show an absorption band around 1780 cm⁻¹ due to the stretching vibration of the carboxylate group linked to the metal ions. An increase in carboxylate resonance causes single bond character in the carbonyl group which is observed by a lowering of the frequency of the C–O stretching vibration [9–11]. The band at around 1630

TABLE 3

Infrared spectra (4000–200 cm⁻¹) for the isolated compounds

Compounds	$\bar{\nu}_{\text{O-H}}(\text{H}_2\text{O})$	$\bar{\nu}_{\text{COOH}}$	$\bar{\nu}_{\text{C=C}}$	$\bar{\nu}_{\text{COO}^-}$	$\bar{\nu}_{\text{C-O}}$	$\bar{\nu}_{\text{M-O}}$
H ₂ ITAC		1692 (s)	1628 (m)		1438 (m)	
Mn(ITAC)·H ₂ O	3640–2980 (br, s)		1630 (w)	1580 (s)	1390 (m)	260 (vw)
Co(ITAC)·2H ₂ O	3660–2860 (br, s)		1632 (w)	1575 (s)	1380 (m)	240 (vw)
Ni(ITAC)·H ₂ O	3680–2720 (br, s)		1630 (w)	1570 (s)	1403 (m)	280 (vw)
Cu(HITAC) ₂		1700 (m)	1640 (w)	1592 (s)	1406 (m)	258 (w)
Zn(ITAC)·H ₂ O	3700–2910 (br, s)		1635 (w)	1580 (s)	1408 (m)	255 (vw)

br, broad; s, strong; m, medium; w, weak; vw, very weak.

cm^{-1} in each of the compounds is assigned to the $\bar{\nu}(\text{C}=\text{C})$ vibration. It is suggested that coordination does not take place between the π electron system of the $\text{C}=\text{C}$ bond and the metal ions since a change to lower frequency of the $\bar{\nu}(\text{C}=\text{C})$ vibration is not observed in the compounds [12,13]. The IR spectrum of the copper compound which is anhydrous is similar except that a band at 1700 cm^{-1} corresponding to the stretching vibration of a carbonyl group is observed.

Metal-oxygen bands are reported for each of the compounds and would indicate a six coordinate environment for the metal ions [14,15]. The insolubility of the compounds in both polar and non-polar solvents is indicative of polymeric structures [8].

The fact that the compounds were isolated as powders and not as single crystals means that no complete structure determination can be made. However spectroscopic and magnetic data enable us to predict that in the compounds the metal ions are in an octahedral environment. The compounds are considered to have a planar arrangement with the carboxylate groups on each molecule of itaconic acid bonded to two different metal atoms to give a chain like structure. It is further suggested that each metal atom is bonded to oxygen atoms in adjacent layers to give a six coordinate environment for the metal ion. The water molecules are attached by hydrogen bonding to each structure. In the copper compound, $\text{Cu}(\text{HITAC})_2$, for each molecule of itaconic acid, one carboxylate group will be used in

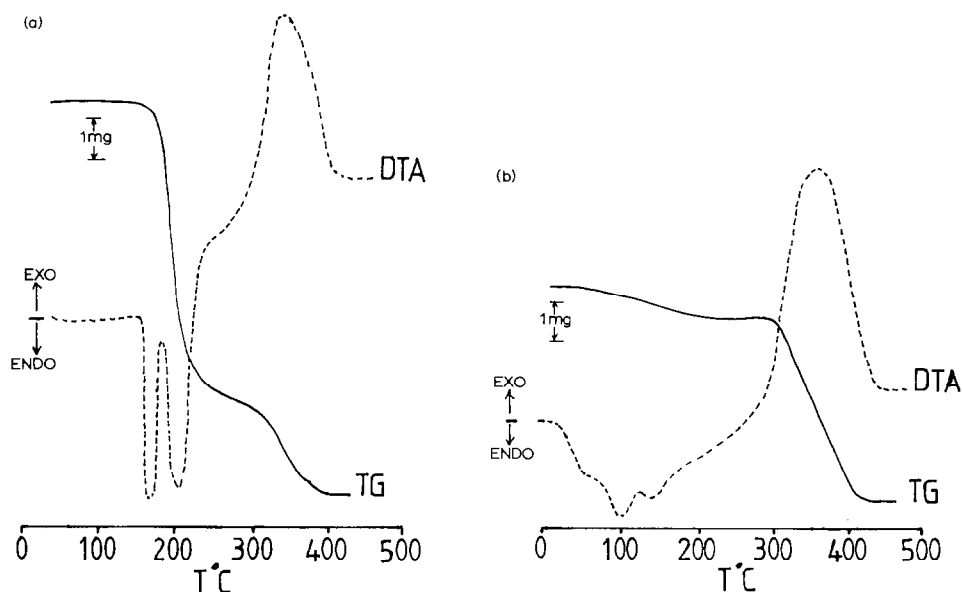


Fig. 1. (a) TG/DTA curve for itaconic acid, sample weight = 9.60 mg; (b) TG/DTA curve for $\text{Mn}(\text{ITAC}) \cdot \text{H}_2\text{O}$, sample weight = 8.56 mg.

forming coordinate bonds to a copper atom to give a planar arrangement similar to that discussed for the previous compounds. It is suggested that each copper atom is bonded to oxygen atoms in adjacent layers to give a six coordinate environment for the copper ion.

The TG, DTA and DSC curves for itaconic acid show that the acid is thermally stable in the temperature range 30–136°C. Its pyrolytic decomposition starts at 136°C and finishes at 400°C with the total elimination of the sample. The DSC curve of the itaconic acid (Fig. 2a) shows an endother-

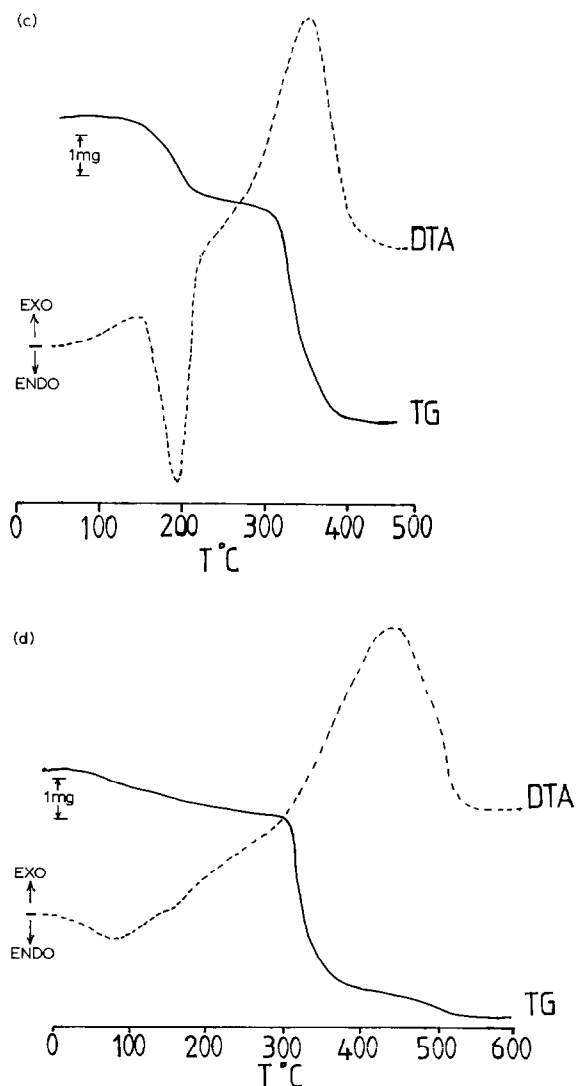


Fig. 1. continued. (c) TG/DTA curve for $\text{Co(ITAC)} \cdot 2\text{H}_2\text{O}$, sample weight = 11.18 mg; (d) TG/DTA curve for $\text{Ni(ITAC)} \cdot \text{H}_2\text{O}$, sample weight = 9.02 mg.

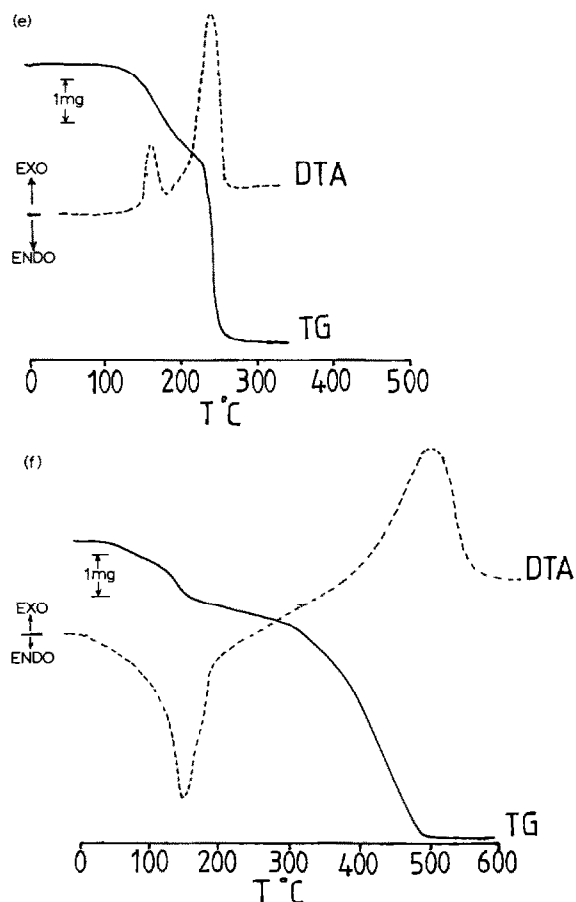


Fig. 1. continued. (e) TG/DTA curve for $\text{Cu}(\text{HITAC})_2$, sample weight 8.56 mg; (f) TG/DTA curve for $\text{Zn}(\text{ITAC}) \cdot \text{H}_2\text{O}$, sample weight 11.95 mg.

mic peak at 171.3°C corresponding to fusion. The value of the fusion enthalpy is 32.2 kJ mol^{-1} . Liquid itaconic acid decomposes immediately with an endothermic peak at 233.4°C . The TG/DTA and DSC curves for the complexes formed between itaconic acid and manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) are given in Figs. 1 and 2. The TG/DTA and DSC curves for the manganese, cobalt, nickel and zinc complexes are similar. 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 and DTA curves. The dehydration enthalpies have been calculated and are given in Table 4. The decomposition of the anhydrous complexes follows immediately after the dehydration process and the residual weights are in good agreement with the values required for the metallic

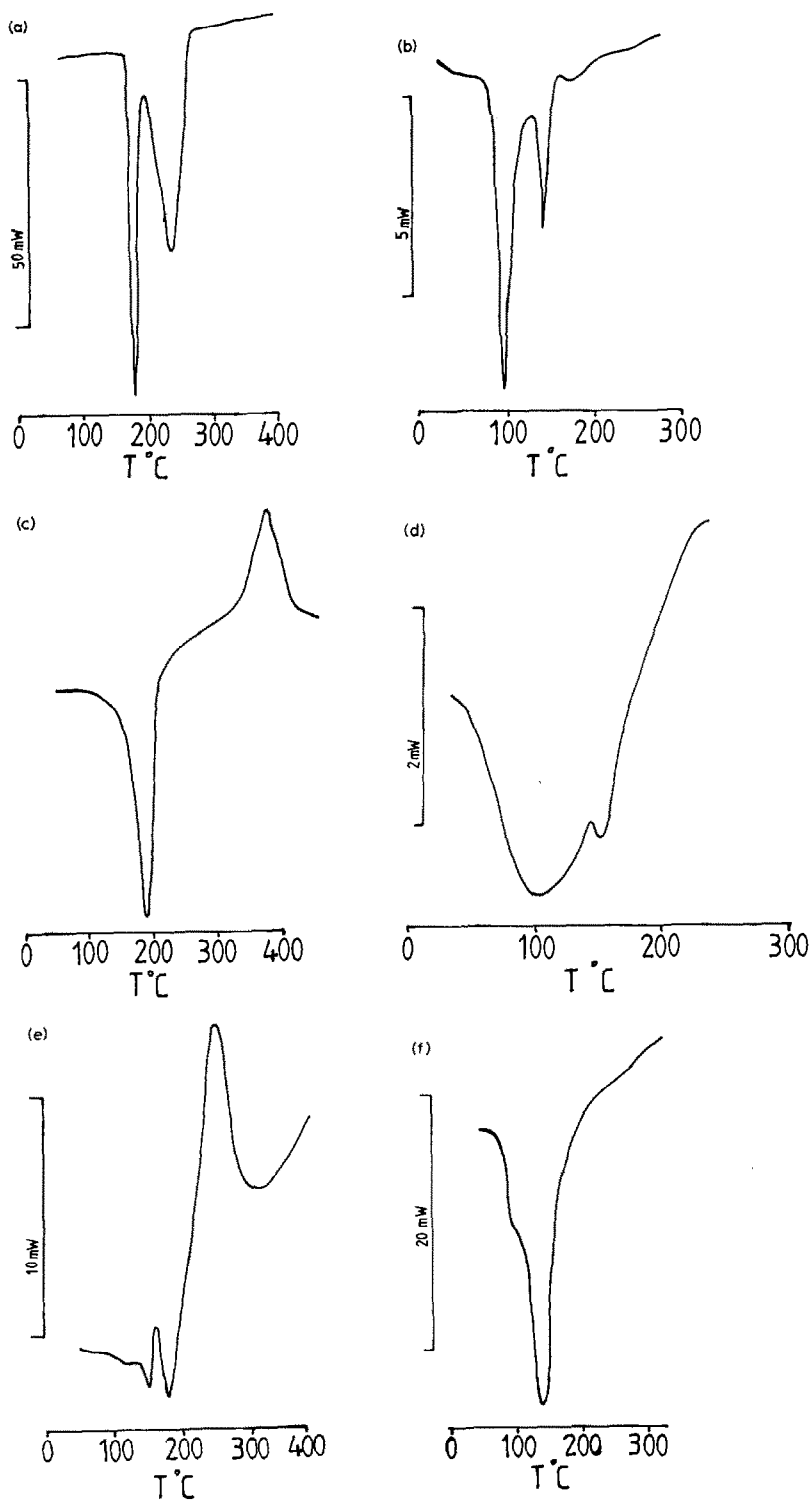


Fig. 2. (a) DSC curve for itaconic acid; (b) DSC curve for $\text{Mn(ITAC)} \cdot \text{H}_2\text{O}$; (c) DSC curve for $\text{Co(ITAC)} \cdot 2\text{H}_2\text{O}$; (d) DSC curve for $\text{Ni(ITAC)} \cdot \text{H}_2\text{O}$; (e) DSC curve for Cu(HITAC)_2 ; (f) DSC curve for $\text{Zn(ITAC)} \cdot \text{H}_2\text{O}$.

TABLE 4

Dehydration processes of the itaconic acid metal complexes

Process	Peak temperature (°C)	Thermal nature of transformation	Weight loss (%)		Enthalpy (kJ mol ⁻¹)
			Calc.	Found	
Mn(ITAC)·H ₂ O → Mn(ITAC)	92.7	Endo	8.95	8.24	13.11
Co(ITAC)·2H ₂ O → Co(ITAC)	189.2	Endo	15.99	15.92	103.91
Ni(ITAC)·H ₂ O → Ni(ITAC)	100.8	Endo	8.78	8.98	20.79
Zn(ITAC)·H ₂ O → Zn(ITAC)	137.1	Endo	8.51	8.36	82.52

TABLE 5

Decomposition processes of itaconic acid and the metal complexes

Process	Temperature range (°C)	Thermal nature of transformation	Residue weight loss (%)	
			Calc.	Found.
H ₂ ITAC → pyrolytic process	136–400	Endo	–	–
Mn(ITAC) → Mn ₃ O ₄	270–409	Exo	35.59	35.71
Co(ITAC) → Co ₃ O ₄	212–428	Exo	35.66	35.77
Ni(ITAC) → NiO	210–512	Exo	36.47	37.69
Cu(HITAC) ₂ → CuO	136–354	Exo	24.72	24.44
Zn(ITAC) → ZnO	215–484	Exo	38.49	39.13

oxides (Table 5). In the DSC and DTA curves, these decomposition processes correspond to exothermic effects for the complexes. The copper compound undergoes exothermic reactions with loss of the organic ligand and the formation of copper oxide.

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