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THERMAL STUDIES ON FUMARIC ACID AND CROTONIC ACID COMPOUNDS OF COBALT(II) AND NICKEL(II)

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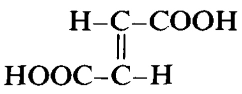
ABSTRACT

Some new compounds of fumaric acid and crotonic acid with cobalt and nickel have been prepared in aqueous solution. These compounds, which have been characterized by analyses, magnetic moments, vibrational and electronic spectra, have polymeric octahedral structures. They are all hydrated, with the exception of the cobalt compound of crotonic acid, which is anhydrous. The thermal behaviour of the compounds has been studied by thermogravimetry and differential thermal analysis. Thermal decomposition studies show that the hydrated compounds lose water followed by organic ligand to give the metal oxide. The anhydrous compound loses organic ligand to give the metal oxide.

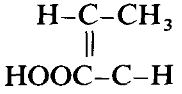
INTRODUCTION

Fumaric acid and crotonic acid are used in the manufacture of adhesives, emulsions, optical fibres, unsaturated polyester resins and compositions [1–10]. The acids have 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.



$$\begin{array}{c}\text{H–C–COOH}\\ \| \\ \text{HOOC–C–H}\end{array}$$

Fumaric acid (H_2fa)



$$\begin{array}{c}\text{H–C–CH}_3\\ \| \\ \text{HOOC–C–H}\end{array}$$

Crotonic acid (Hca)

This paper reports on thermal analysis studies of fumaric acid and crotonic acid, together with the complexes formed by the acids and the transition metals cobalt and nickel. Spectral and magnetic studies have been used to characterize each metal complex and to interpret the type of

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coordination which takes place with the metal ion. The thermal stability of the acid complexes has also been studied.

EXPERIMENTAL

Preparation of compounds

The compounds were prepared by dissolving the metal carbonate in a hot aqueous solution of either fumaric or crotonic acid. The excess carbonate was removed by filtration. The compound was precipitated by concentrating the solution over a steam bath.

Apparatus

The concentration of the metal ion was determined using a Perkin–Elmer 373 atomic absorption spectrophotometer, and the carbon and hydrogen analyses were carried out using a Carlo–Erba elemental analyser.

The IR spectra were obtained using KBr discs (4000–600 cm^{-1}) and polyethylene discs (600–200 cm^{-1}) in a Perkin–Elmer IR spectrophotometer, model 598.

The electronic spectra were obtained on a Beckmann Acta MIV spectrophotometer as solid diffuse reflectance spectra.

Magnetic measurements were carried out by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant. Each magnetic moment was corrected for diamagnetism using Pascal's constants [11].

The thermal analysis studies were carried out on a Stanton–Redcroft model STA 781 thermobalance. Thermogravimetric curves were obtained at a heating rate of 6 °C min^{-1} in static air. In all cases, the temperature range studied was 20–1000 °C.

RESULTS AND DISCUSSION

The compounds isolated from aqueous solution are listed in Table 1. The cobalt and nickel compounds of fumaric acid are hydrated. The nickel compound of crotonic acid is hydrated; the cobalt compound is anhydrous.

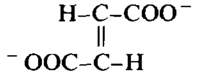
The electronic spectra (listed in Table 2) and the magnetic measurements (listed in Table 1) suggest that the cobalt and nickel ions are in an octahedral environment [12].

The main bands in the IR spectra of the compounds are reported in Table 3. The nickel compound of crotonic acid and the cobalt and nickel compounds of fumaric acid show a strong absorption band in the region 3800–2600 cm^{-1}, ν_{O-H}, indicating the presence of water of crystallization.

TABLE 1

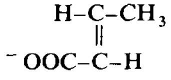
Analyses of compounds and magnetic moments

Compound	Theory (%)			Experimental (%)			μ (B.M.)
	Metal	Carbon	Hydrogen	Metal	Carbon	Hydrogen	
Co(fa)·$0.5H_2O$	32.27	26.39	1.66	32.16	26.02	1.56	4.94
Ni(fa)·$3H_2O$	25.88	21.18	3.55	25.66	21.58	3.33	2.92
$Co(ca)_2$	22.74	37.08	3.89	22.37	37.68	4.23	5.03
$Ni(ca)_2$·$2H_2O$	24.16	39.54	5.80	23.66	39.09	4.92	3.04



$$\begin{array}{c}\mathrm{H{-}C{-}COO^-}\\ \|\\ \mathrm{^-OOC{-}C{-}H}\end{array}$$

fa



$$\begin{array}{c}\mathrm{H{-}C{-}CH_3}\\ \|\\ \mathrm{^-OOC{-}C{-}H}\end{array}$$

ca

TABLE 2

Electronic spectral details of compounds

Compounds	Peak position (cm^{-1})	d–d transition	Dq	B	β
Co(fa)·$0.5H_2O$	8132	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	923	814	0.84
	19230	$\rightarrow {}^4T_{1g}(P)$			
Ni(fa)·$3H_2O$	8771	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	877	909	0.87
	15267	$\rightarrow {}^3T_{1g}(F)$			
	24691	$\rightarrow {}^3T_{1g}(P)$			
$Co(ca)_2$	8130	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	764	920	0.79
	18519	$\rightarrow {}^4T_{1g}(P)$			
$Ni(ca)_2$·$2H_2O$	8787	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	878	869	0.83
	14705	$\rightarrow {}^3T_{1g}(F)$			
	24691	$\rightarrow {}^3T_{1g}(P)$			

TABLE 3

IR spectra (4000–200 cm^{-1}) for the compounds [a]

Compounds	ν_{O-H} (H_2O)	ν_{COOH}	ν_{COO^-}	$\nu_{C=C}$	ν_{C-O}	ν_{M-O}
H_2fa		1700 (s)		1660 (sh)	1426 (s)	
Co(fa)·$0.5H_2O$	3760–2640 (s, br)		1578 (s)	1659 (w)	1399 (s)	286 (s)
Ni(fa)·$3H_2O$	3800–2600 (s, br)		1562 (s)	1658 (w)	1394 (s)	282 (s)
Hca		1702 (s)		1661 (s)	1424 (s)	
$Co(ca)_2$			1550 (s)	1660 (s)	1410 (s)	287 (m)
$Ni(ca)_2$·$2H_2O$	3660–3110 (s, br)		1558 (s)	1660 (s)	1408 (s)	288 (m)

[a] sh, shoulder; br, broad; s, strong; m, medium; w, weak.

The compounds each show an absorption band attributable to the stretching vibration of the carboxylate groups linked to the metal ions. An increase in carboxylate resonance causes single bond character in the carbonyl group, indicated by a reduction in the C=O stretching vibration [13–15]. The band at around 1660 cm^{-1} for each of the compounds is assigned to the ν(C=C) vibration. The ν(C=C) vibration is little different from the values for the free ligand, showing that no bonding has taken place with the metal ions. The slight reduction in the frequency of this signal in the spectra of the complexes is attributable to the effect of d_π–p_π overlap. Metal–oxygen bands, reported for each of the complexes, indicate a six-coordinate environment for the metal ions [16]. The insolubility of the compounds in polar and non-polar solvents is indicative of polymeric structures [12].

As the compounds were isolated as powders rather than single crystals, their structure cannot be determined completely. However, the spectroscopic and magnetic data enable us to predict a possible stereochemistry for the complexes. The complexes formed between fumaric acid and cobalt and nickel are considered to have a planar arrangement with the carboxylate groups on each fumarate di-anion bonded to two different metal atoms to give a chain-like structure. Each metal ion is thus bonded to four oxygen atoms in the plane and to oxygen atoms in adjacent planes, giving a layer structure and a coordination number of six for the metal ion. In the complexes formed between crotonic acid and cobalt and nickel it is suggested that two molecules of the crotonate anion are attached to each metal ion, to give a square planar structure. Each metal ion is thus bonded to four oxygen atoms in the plane. It is further suggested that the complex consists of a layer structure in which each metal ion is bonded to oxygen atoms in adjacent layers, giving a six-coordinate environment for the metal ion. In the hydrated compounds the water molecules are attached by hydrogen bonding. The values for the Racah parameter B and the nephelauxetic ratio β (see Table 2) suggest some electron delocalization between the metal and the ligands.

The TG and DTA curves for fumaric acid and crotonic acid are shown in Figs. 1 and 2. Fumaric acid is thermally stable in the temperature range 20–153° C. Pyrolytic decomposition begins at 153° C and finishes at 407° C with total elimination of the sample. The DTA curve shows an endothermic

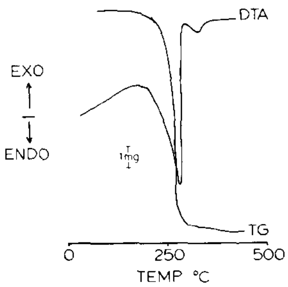


Fig. 1. Simultaneous TG and DTA curves of fumaric acid. Sample mass = 10.54 mg.

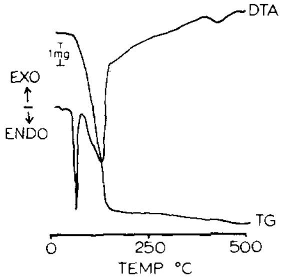


Fig. 2. Simultaneous TG and DTA curves of crotonic acid. Sample mass = 9.00 mg.

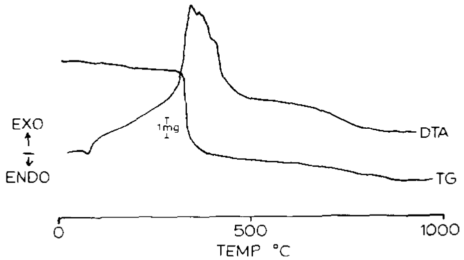


Fig. 3. Simultaneous TG and DTA curves of Co(fa)·$0.5H_2O$. Sample mass = 9.80 mg.

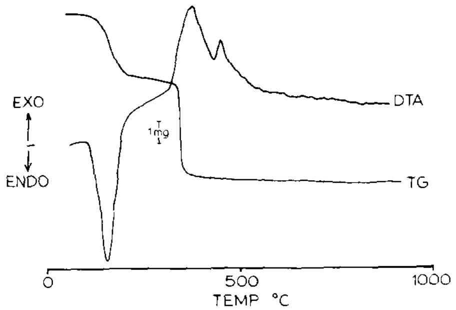


Fig. 4. Simultaneous TG and DTA curves of Ni(fa)·$3H_2O$. Sample mass = 11.85 mg.

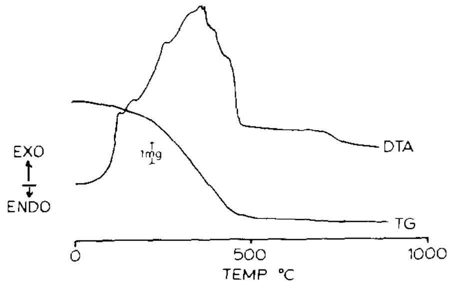


Fig. 5. Simultaneous TG and DTA curves of $Co(ca)_2$. Sample mass = 9.38 mg.

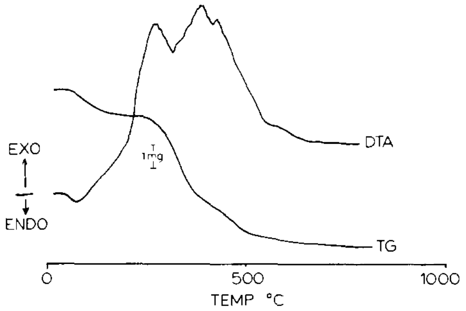


Fig. 6. Simultaneous TG and DTA curves of $Ni(ca)_2 \cdot 2H_2O$. Sample mass = 10.30 mg.

peak at 300 °C owing to melting. The enthalpy of fusion is 102.9 kJ mol^{-1}. The acid then decomposes immediately with an endothermic peak at 326 °C. Crotonic acid is thermally stable in the temperature range 20–45 °C. Pyrolytic decomposition begins at 45 °C and finishes at 486 °C with total elimination of the sample. The DTA curve shows an endothermic peak at 72.4 °C owing to melting. The enthalpy of fusion is 12.28 kJ mol^{-1}. The acid then decomposes immediately with endothermic peaks at 130 °C and 447 °C.

The TG and DTA curves for the complexes of fumaric acid and crotonic acid are shown in Figs. 3–6. The cobalt complex of fumaric acid and the

TABLE 4

Dehydration processes of fumaric acid and crotonic acid complexes

Process	Peak temperature (° C)	Thermal nature of transformation	Weight loss (%)		Enthalpy (kJ mol^{-1})
			Calculated	Found	
$Co(fa) \cdot 0.5H_2O \rightarrow Co(fa)$	132	ENDO	4.94	4.08	9.45
$Ni(fa) \cdot 3H_2O \rightarrow Ni(fa)$	181	ENDO	23.78	23.62	39.07
$Ni(ca)_2 \cdot 2H_2O \rightarrow Ni(ca)_2$	135	ENDO	14.46	12.62	56.75

TABLE 5

Decomposition processes of the fumaric acid and crotonic acid complexes

Process	Temperature range (° C)	Thermal nature of transformation	Residue (%)	
			Calculated	Found
$H_2fa \rightarrow$ pyrolytic process	153–407	ENDO	–	–
Hca → pyrolytic process	45–486	ENDO	–	–
$Co(fa) \rightarrow Co_3O_4$	190–890	EXO	40.09	41.83
$Ni(fa) \rightarrow NiO$	380–815	EXO	32.91	34.59
$Co(ca)_2 \rightarrow Co_3O_4$	40–720	EXO	35.03	35.18
$Ni(ca)_2 \rightarrow NiO$	380–780	EXO	30.01	30.09

nickel complexes of fumaric acid and crotonic acid are hydrated. The dehydration of each complex takes place in one step. The observed weight losses for these processes compare favourably with the theoretical values (see Table 4). The endothermic peak observed in the DTA curves is as expected for the dehydration processes associated with these compounds. The dehydration enthalpies have been calculated and are given in Table 4. 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 oxides (see Table 5). In the DTA curves these decomposition processes correspond to exothermic effects for the complexes. The cobalt complex of crotonic acid, which is anhydrous, undergoes an exothermic reaction with loss of the organic ligand to give Co_3O_4.

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