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THE THERMAL, SPECTRAL AND MAGNETIC STUDIES OF MALONIC ACID COMPOUNDS OF SOME TRANSITION METAL IONS

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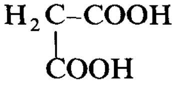
ABSTRACT

Compounds of malonic acid with cobalt, nickel, copper and zinc have been prepared in aqueous solution. The compounds which have been characterised by analyses, magnetic moments, vibrational and electronic spectra have polymeric octahedral structures. The thermal behaviour of these compounds has been studied by thermogravimetry and differential thermal analysis. The compounds which are hydrated lose water of crystallisation followed by organic ligand to give the metal oxide.

INTRODUCTION

Malonic acid and its derivatives are used in medicinal and polymer chemistry [1–9]. It is a dicarboxylic acid with one type of donor site: the oxygen atoms of the carboxylic group.



$$H_2C{-}COOH \atop \quad | \atop \quad COOH$$

Malonic acid ($C_3H_4O_4$)

This paper reports thermal analysis studies of malonic acid together with the complexes formed by the acid and the transition metals cobalt, nickel, copper and zinc. Spectral and magnetic studies were used to characterise each metal complex and to interpret the type of coordination which takes place to the metal ion. A thermal stability study of the malonic acid complexes was carried out.

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EXPERIMENTAL

Preparation of compounds

The compounds were prepared by dissolving the metal carbonate in a hot aqueous solution of malonic 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 IR spectra were obtained using KBr discs (4000–600 cm^{-1}) and polyethylene discs (600–200 cm^{-1}) on 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.

Thermal analysis studies were carried out on a Stanton Redcroft model STA 781 thermobalance. The thermogravimetry (TG) and differential thermal analysis (DTA) curves were obtained at a heating rate of 10 °C min^{-1} in static air and over a temperature range of 20–600 °C.

RESULTS AND DISCUSSION

The compounds prepared (Table 1) are hydrated and have stoichiometry $M(C_3H_2O_4) \cdot xH_2O$ where $x = 1$ for nickel, $x = 2$ for cobalt and zinc and $x = 2.5$ for copper.

TABLE 1

Analysis and magnetic moments of compounds

Compound	Theoretical (%)			Experimental (%)			μ (B.M.)
	M	C	H	M	C	H	
$Co(C_3H_2O_4) \cdot 2\,H_2O$	29.91	18.28	3.06	29.02	17.66	3.01	5.41
$Ni(C_3H_2O_4) \cdot H_2O$	32.84	20.15	2.25	31.91	19.88	2.02	2.87
$Cu(C_3H_2O_4) \cdot 2.5\,H_2O$	30.16	17.10	3.35	29.64	16.41	2.71	1.64
$Zn(C_3H_2O_4) \cdot 2\,H_2O$	32.13	17.71	1.77	31.29	16.94	1.66	–

TABLE 2

Electronic spectral details of prepared compounds

Compound	Peak position (cm^{-1})	d–d transitions	Dq	B	β
$Co(C_3H_2O_4)\cdot 2\,H_2O$	8264	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	938	810	0.84
	19305	$\rightarrow {}^4T_{1g}(P)$			
$Ni(C_3H_2O_4)\cdot H_2O$	8896	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	889	880	0.84
	14925	$\rightarrow {}^3T_{1g}(F)$			
	25000	$\rightarrow {}^3T_{1g}(P)$			
$Cu(C_3H_2O_4)$	15267	${}^2E_g(D) \rightarrow {}^2T_{2g}(D)$			

The electronic spectra (Table 2) and the magnetic measurements (Table 1) suggest that for the cobalt and nickel compounds the metal ion is in an octahedral environment [10]. The Dq values (Table 2) for the compounds are consistent with this stereochemistry [11]. The β values (Table 2) suggest some ionic character in the metal–ligand bonds in these compounds. The single broad absorption band at 15267 cm^{-1} in the electronic spectrum for the copper compound suggests that the copper atom is in an octahedral environment [10]. The magnetic moment for the compound, which is 1.64 B.M. (see Table 1), is indicative of some copper–copper interaction in the compound.

The main bands in the IR spectra of the compounds are given in Table 3. The compounds all show a strong broad absorption band in the region 3710–2960 cm^{-1}, ν(O–H), indicating the presence of water of crystallisation. The compounds show an absorption band at around 1565 cm^{-1} due to the stretching vibration of the carboxylate group linked to the metal ions. An increase in carboxylate resonance leads to single-bond character in the carboxyl group, which is observed as a lowering of the frequency of the C–O stretching vibration [12–14]. Metal–oxygen bands are reported for each of the compounds and indicate a six-coordinate environment for the metal ions [15,16]. The insolubility of the compounds in both polar and non-polar solvents is indicative of polymeric structures [10].

TABLE 3

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

Compound	$\nu_{O-H}(H_2O)$	ν(COOH)	$\nu(COO^-)$	ν(C–O)	ν(M–O)
$C_3H_4O_4$		1742(s)		1312(s)	
$Co(C_3H_2O_4)\cdot 2\,H_2O$	3680–2960(br,s)		1560(s)	1279(s)	282(m)
$Ni(C_3H_2O_4)\cdot H_2O$	3710–2960(br,s)		1563(s)	1280(s)	260(w)
$Cu(C_3H_2O_4)\cdot 2.5\,H_2O$	3601–2962(br,s)		1564(s)	1281(s)	276(m)
$Zn(C_3H_2O_4)\cdot 2\,H_2O$	3610–3060(br,s)		1569(s)	1280(s)	280(w)

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

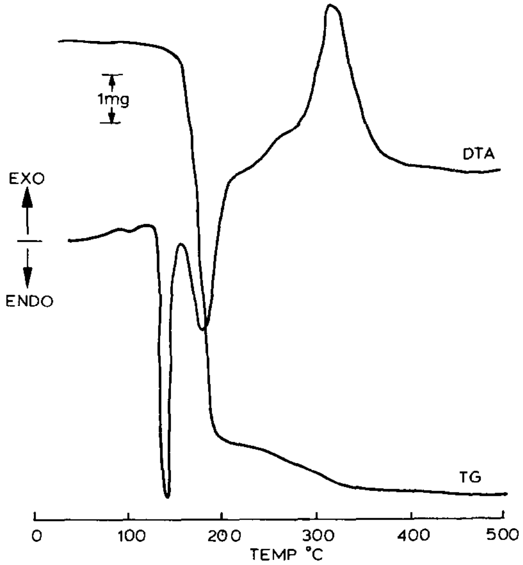

Fig. 1. TG/DTA curve for malonic acid, sample weight = 9.45 mg.

Single crystals of the compounds could not be isolated from solution; thus without X-ray analysis no definite structures can be described. However, the spectroscopic and magnetic data enable us to predict possible structures. The compounds are considered to have a planar arrangement with carboxylate groups on each molecule of the malonate bonded to two different metal atoms to give a chain-like structure. It is also suggested that each metal atom is bonded to oxygen atoms in adjacent layers to give a

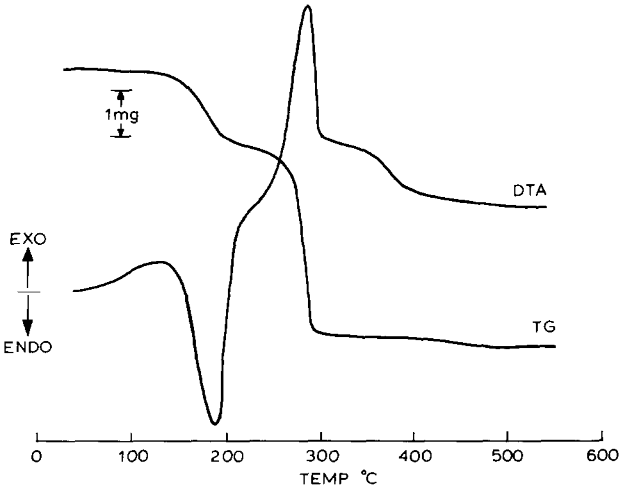

Fig. 2. TG/DTA curve for $Co(C_3H_2O_4)\cdot 2\ H_2O$, sample weight = 9.83 mg.

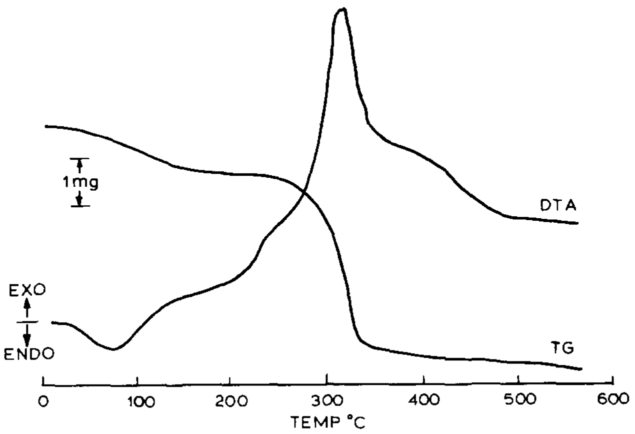

Fig. 3. TG/DTA curve for $Ni(C_3H_2O_4) \cdot H_2O$, sample weight = 9.10 mg.

six-coordinate environment for the metal ion. The water molecules are attached by hydrogen bonding to each structure.

The TG and DTA curves for the malonic acid show that it is thermally stable in the temperature range 20–118 °C. Its pyrolytic decomposition starts at 118 °C and finishes at 486 °C with the total elimination of the sample. The DTA curve of the malonic acid (Fig. 1) shows an endothermic peak at 135 °C corresponding to fusion. The value of the fusion enthalpy is 22 kJ mol^{-1}. Liquid malonic acid decomposes immediately with an endo-

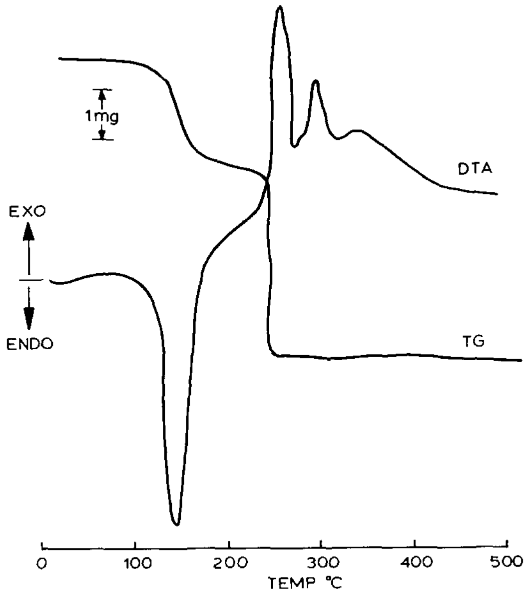

Fig. 4. TG/DTA curve for $Cu(C_3H_2O_4) \cdot 2.5\ H_2O$, sample weight = 9.80 mg.

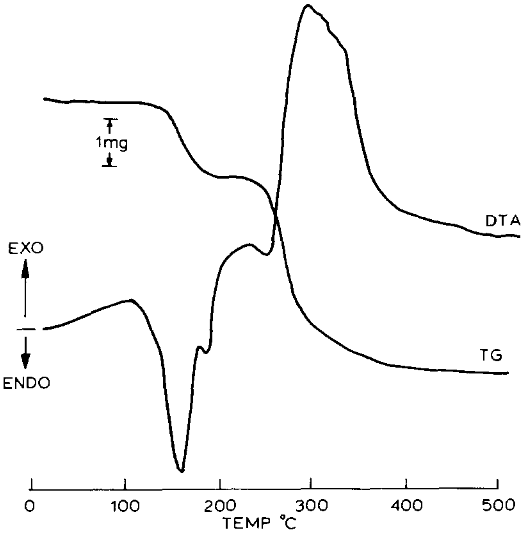

Fig. 5. TG/DTA curve for $Zn(C_3H_2O_4)\cdot 2\,H_2O$, sample weight = 9.76 mg.

TABLE 4

Dehydration processes of the malonic acid metal complexes

Process	Peak temperature (°C)	Thermal nature of transformation	Weight loss (%)		Enthalpy ($kJ\ mol^{-1}$)
			Calc.	Found	
$Co(C_3H_2O_4)\cdot 2\,H_2O \rightarrow Co(C_3H_2O_4)$	192	ENDO	18.27	16.58	85
$Ni(C_3H_2O_4)\cdot H_2O \rightarrow Ni(C_3H_2O_4)$	82	ENDO	14.38	13.18	29
$Cu(C_3H_2O_4)\cdot 2.5\,H_2O \rightarrow Cu(C_3H_2O_4)$	138	ENDO	21.37	20.91	106
$Zn(C_3H_2O_4)\cdot 2\,H_2O \rightarrow Zn(C_3H_2O_4)$	167	ENDO	17.70	17.01	98

TABLE 5

Decomposition processes of malonic acid and the metal complexes

Process	Temperature range (°C)	Thermal nature of transformation	Residue (%)	
			Calc.	Found
$C_3H_4O_4 \rightarrow$ pyrolytic process	118–486	ENDO/EXO	–	–
$Co(C_3H_2O_4) \rightarrow Co_3O_4$	216–502	EXO	40.75	40.69
$Ni(C_3H_2O_4) \rightarrow NiO$	170–550	EXO	41.80	41.75
$Cu(C_3H_2O_4) \rightarrow CuO$	175–420	EXO	37.77	36.73
$Zn(C_3H_2O_4) \rightarrow ZnO$	210–490	EXO	40.01	40.98

thermic peak at 176 °C and an exothermic peak at 316 °C. The TG and DTA curves for the compounds formed between malonic acid and cobalt, nickel, copper and zinc are given in Figs. 2–5. The TG and DTA curves are similar. The dehydration of the compounds takes place in one step. The observed weight losses for these processes compare favourably with the theoretical values given in Table 4. The expected endothermic peak for the dehydration processes associated with these compounds was observed in the DTA curve.

The dehydration enthalpies were calculated and are listed in Table 4. The decomposition of the anhydrous compounds follows immediately after the dehydration process and the residual weights are in good agreement with the values required for the metallic oxides (Table 5). In the DTA curves, these decomposition processes correspond to exothermic effects for the compounds.

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