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THERMAL STUDIES ON MALEIC ACID COMPOUNDS OF MANGANESE(II), COBALT(II), NICKEL(II), COPPER(II) AND ZINC(II)

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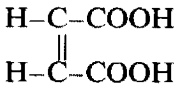
ABSTRACT

Compounds have been prepared from aqueous solutions using the carbonates of manganese, cobalt, nickel and zinc with maleic acid. The copper compound was prepared from aqueous solution using the sulphate and maleic acid. The compounds are all hydrated. The stereochemical configurations of the compounds have been deduced using spectral and magnetic properties. The metal atoms have been found to be in an octahedral environment. The thermal decomposition of the compounds has been studied using thermogravimetry and differential thermal analysis. The compounds have been found to undergo decomposition with loss of water molecules, followed by the organic ligand, to give the metal oxides.

INTRODUCTION

This work is a continuation and extension of previously reported studies on pyridine monocarboxylic acids and the first row transition elements [1,2]. The present investigation is concerned with the complexes formed between manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) with maleic acid.



$$\begin{array}{l}\mathrm{H{-}C{-}COOH}\\ \quad\Vert\\ \mathrm{H{-}C{-}COOH}\end{array}$$

Maleic acid ($C_4O_4H_4$)

The thermal decomposition of the compounds has been studied using thermogravimetry (TG) and differential thermal analysis (DTA). Information regarding the stereochemistry of the compounds has been obtained using electronic spectra, infrared spectra and magnetic measurements.

Complexes of copper(II) and maleic acid have been previously reported in the literature [3].

EXPERIMENTAL

Preparation of the complexes

5 g of maleic acid was dissolved in hot water and the metal carbonate was added in small amounts with stirring until effervescence ceased and the solution was neutral to pH testing. The solution was filtered, the filtrate evaporated until the volume had decreased, and the complex precipitated. The precipitated complex was filtered, washed with water and dried. All of the complexes were prepared by this method, the exception being $Cu(C_4O_4H_2) \cdot H_2O$ which was prepared by the method in ref. 3.

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 $Hg[Co(SCN)_4]$ as calibrant. Each magnetic moment has been corrected for diamagnetism using Pascal's constants [4].

The thermal analyses were carried out on a Stanton Redcroft model STA 781 thermobalance. Thermogravimetry and differential thermal analysis curves were obtained at a heating rate of 10 °C min^{-1} in static air. The curves are not a direct copy of those obtained from the instrument, the temperatures quoted have been obtained from a chart produced by the manufacturer. In all cases, the 20–500 °C temperature range was studied.

The concentration of the metal ion was obtained using a Perkin–Elmer model 373 atomic absorption spectrophotometer; the carbon and hydrogen analysis was determined using a Carlo Erba Elemental Analyser.

RESULTS AND DISCUSSION

The compounds which have been prepared are listed in Table 1. The elemental analyses agree with the given formulae of the compounds. All of the compounds have water molecules present.

In Table 2, the main bands in the infrared spectra are listed. The bands in the region 3700–2800 cm^{-1} are assigned to the ν(0–H) vibration of water [2]. In the manganese and cobalt complexes, both the carboxyl and carboxylate groups are found to co-exist from the appearance of bands in the region 1685–1680 cm^{-1} and 1580–1570 cm^{-1}, assigned to both groups, respectively, whereas in the nickel, copper and zinc complexes only one band is

TABLE 1

Analyses of metal complexes and magnetic moments

Compounds	Theory (%)			Experimental (%)			μ (B.M)
	Carbon	Hydrogen	Metal	Carbon	Hydrogen	Metal	
$Mn(C_4O_4H_3)_2 \cdot 4H_2O$	26.89	3.92	15.38	26.24	3.01	14.96	6.26
$Co(C_4O_4H_3)_2 \cdot 5H_2O$	25.33	4.22	15.55	24.66	3.92	14.81	5.19
$Ni(C_4O_4H_2) \cdot 2H_2O$	22.99	2.87	28.12	23.29	3.02	27.78	3.01
$Cu(C_4O_4H_2) \cdot H_2O$	24.56	2.06	32.48	24.62	2.10	32.40	1.98
$Zn(C_4O_4H_2) \cdot 2H_2O$	22.31	2.81	30.35	22.99	1.92	29.61	—

TABLE 2

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

Compounds	ν(O–H) (H_2O)	ν(COOH)	ν(COO^-)	ν(C–O)	ν(M–O)
$C_4O_4H_4$		1700 (s)		1455 (m)	
$Mn(C_4O_4H_3)_2 \cdot 4H_2O$	3700–2800 (br, s)	1683 (s)	1575 (s)	1440 (m)	250 (w)
$Co(C_4O_4H_3)_2 \cdot 5H_2O$	3700–2800 (br, s)	1681 (s)	1572 (s)	1432 (m)	260 (w)
$Ni(C_4O_4H_2) \cdot 2H_2O$	3700–2800 (br, s)		1574 (s)	1445 (m)	270 (w)
$Cu(C_4O_4H) \cdot H_2O$	3700–2900 (br, s)		1575 (s)	1445 (m)	250 (w)
$Zn(C_4O_4H) \cdot 2H_2O$	3700–2800 (br, s)		1578 (s)	1436 (m)	244 (w)

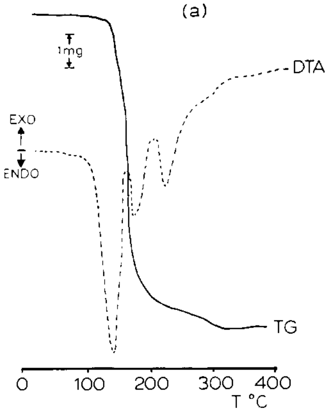
br, broad; s, strong; m, medium; w, weak.

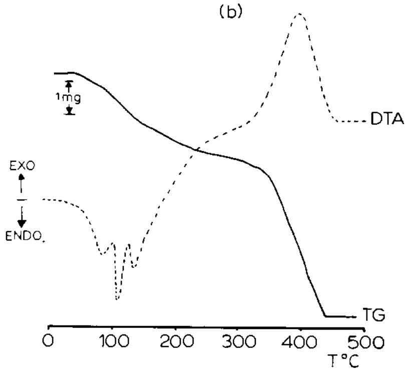
found in the range 1580–1570 cm^{-1} showing that only carboxylate groups are coordinated to the metal in these complexes [5,6]. The ν(M–O) vibrations have been identified for each of the compounds and are listed in Table 2. They would suggest a six-coordinate environment for the metal ion in each of the compounds [7]. The electronic spectra, Table 3, and the magnetic measurements, Table 1, for the cobalt and nickel compounds support the suggestion of an octahedral environment for the metal ions [2]. In the electronic spectrum of the manganese compound, no bands due to d–d transitions were observed. The compound has a magnetic moment of 6.26

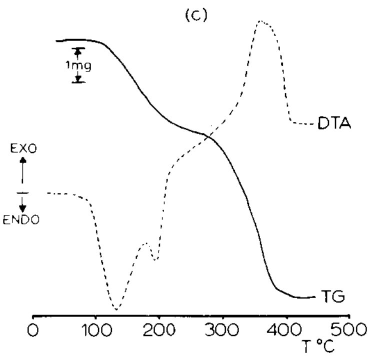
TABLE 3

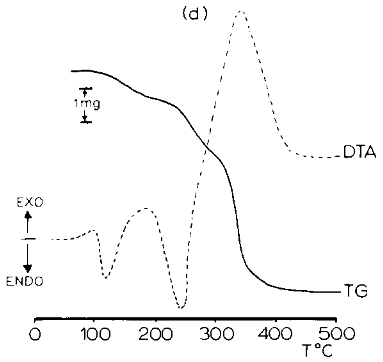
Electronic spectra for some of the isolated compounds

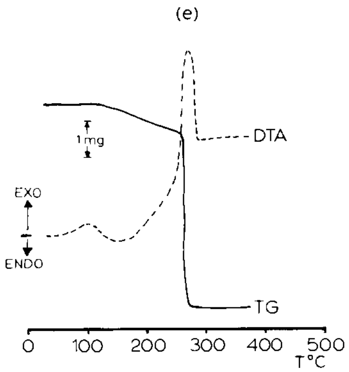
Compounds	Peak position (cm^{-1})	d–d transition
$Co(C_4O_4H_3)_2 \cdot 5H_2O$	7936	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$
	19047	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
$Ni(C_4O_4H_2) \cdot 2H_2O$	8620	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
	15267	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$
	25000	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$
$Cu(C_4O_4H_2) \cdot H_2O$	14430	${}^2E_g(D) \rightarrow {}^2T_{2g}(D)$











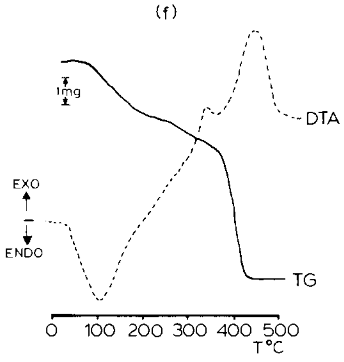


Fig. 1(a). TG/DTA curves for maleic acid, sample weight = 8.90 mg.

Fig. 1(b). TG/DTA curves for $Mn(C_4O_4H_3)_2 \cdot 4H_2O$, sample weight = 8.90 mg.

Fig. 1(c). TG/DTA curves for $Co(C_4O_4H_3)_2 \cdot 5H_2O$, sample weight = 9.49 mg.

Fig. 1(d). TG/DTA curves for $Ni(C_4O_4H_2) \cdot 2H_2O$, sample weight = 9.68 mg.

Fig. 1(e) TG/DTA curves for $Cu(C_4O_4H_2) \cdot H_2O$, sample weight = 9.67 mg.

Fig. 1(f). TG/DTA curves for $Zn(C_4O_4H_2) \cdot 2H_2O$, sample weight = 14.00 mg.

B.M. The copper compound has a broad band in its electronic spectrum at 14430 cm^{-1}, suggesting an octahedral environment for the copper atom as square planar copper(II) compounds show two absorption bands of near equal intensity in the region 15000–18000 cm^{-1} [8,9]. The magnetic moment for this compound is 1.98 B.M. The insolubility of the complexes in both polar and non-polar solvents would suggest the presence of polymeric structures for the compounds [2]. The fact that the compounds were isolated as powders and not as single crystals means that no complete structure determination can be made. However, the spectroscopic and magnetic data enable us to predict that in the compounds the metal ion is in an octahedral environment. It is suggested that for the manganese and cobalt compounds each metal atom is bonded to two anions of the type $C_4O_4H_3^-$ 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 metal to give a coordination number of six and a layer-type polymeric structure. In the nickel, copper and zinc complexes, it is suggested that in each layer the complex exists as a dimeric structure. The two carboxylate groups on each maleate anion are coordinated to the transition metal to give a chelate seven-membered ring. 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 in each of the compounds.

The TG and DTA traces for maleic acid and the complexes with manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) are given in Fig. 1 (a)–(f). The TG/DTA curves for maleic acid show that its pyrolitic decomposition begins at 125 °C and finishes at 320 °C with total elimination of the sample. The DTA curve of the maleic acid shows an endothermic peak at 138 °C due to melting. The acid then decomposes immediately producing endothermic peaks at 180° and 218 °C. The TG and DTA curves for the complexes are similar. They undergo endothermic reactions with loss

TABLE 4

Dehydration processes for the compounds

Process	Peak Temperature (°C)	Thermal nature of transformation	Weight loss (%)		Enthalpy (kJ mol^{-1})
			Calc.	Found	
$Mn(C_4O_4H_3)_2 \cdot 4H_2O \rightarrow Mn(C_4O_3H_3)_2$	108	ENDO	20.04	19.77	111
$Co(C_4O_4H_3)_2 \cdot 5H_2O \rightarrow Co(C_4O_3H_3)_2$	130	ENDO	23.74	24.13	285
$Ni(C_4O_4H_2) \cdot 2H_2O \rightarrow Ni(C_4O_4H_2) \cdot H_2O$	134	ENDO	8.62	8.05	35
$\rightarrow Ni(C_4O_4H_2)$	254	ENDO	9.44	12.39	80
$Cu(C_4O_4H_2) \cdot H_2O \rightarrow Cu(C_4O_4H_2)$	147	ENDO	9.20	8.57	70
$Zn(C_4O_4H_2) \cdot 2H_2O \rightarrow Zn(C_4O_4H_2)$	100	ENDO	16.72	15.71	68

TABLE 5

Decomposition processes of the maleic acid and metal complexes

Process	Temperature range (° C)	Thermal nature of transformation	Residue (%)	
			Calc.	Found
$C_4O_4H_4$ → pyrolitic process	125–320	ENDO	—	—
$Mn(C_4O_4H_3)_2 \rightarrow Mn_3O_4$	226–447	EXO	21.16	22.47
$Co(C_4O_4H_3)_2 \rightarrow Co_3O_4$	204–428	EXO	21.87	22.12
$Ni(C_4O_4H_2) \rightarrow NiO$	180–494	EXO	35.79	34.09
$Cu(C_4O_4H_2) \rightarrow CuO$	132–282	EXO	40.66	40.20
$Zn(C_4O_4H_2) \rightarrow ZnO$	199–428	EXO	45.36	47.86

of water molecules followed by an exothermic reaction and loss of the organic ligand to give the metal oxide. The observed weight losses for these processes compare favourably with the theoretical values, see Table 4, the exception being the nickel complex where it is suggested that it is a two-stage process with some maleic acid also being lost in the second stage of the dehydration process. This could explain the strong endothermic peak which appears at 253° C in the DTA curve. The dehydration enthalpies have been calculated and are given in Table 4. The decomposition of the anhydrous complexes follows immediately after the dehydration processes and the residual weights are in good agreement with the values required for metallic oxides (Table 5).

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