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

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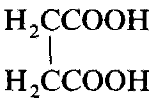
ABSTRACT

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

INTRODUCTION

Succinic acid is a dicarboxylic acid with one type of donor site, the oxygen atoms of the carboxylic group.



$$\begin{array}{l} H_2CCOOH \\ \quad | \\ H_2CCOOH \end{array}$$

Succinic acid ($C_4H_6O_4$)

This paper reports the thermal analytical studies of succinic acid together with the complexes formed by the acid with the transition metals cobalt, nickel, copper and zinc. 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 thermal stability study of the succinic acid complexes has also been carried out.

EXPERIMENTAL

Preparation of compounds

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

Apparatus

The concentration of the metal ion was determined using 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 as solid diffuse reflectance spectra on a Beckmann Acta MIV spectrophotometer.

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 over a temperature range of 20–800 °C.

RESULTS AND DISCUSSION

The compounds prepared, see Table 1, are hydrated and have stoichiometry $M(C_4H_4O_4) \cdot xH_2O$ where $x = 2$ for cobalt and nickel, and 0.5 for copper and zinc.

TABLE 1

Analyses and magnetic moments of the compounds

Compounds	Colour	Analysis						μ (B.M.)
		Theory (%)			Found (%)			
		Metal	Carbon	Hydrogen	Metal	Carbon	Hydrogen	
$Co(C_4H_4O_4) \cdot 2H_2O$	Mauve	27.92	22.76	3.83	27.47	22.94	3.29	4.43
$Ni(C_4H_4O_4) \cdot 2H_2O$	Green	27.84	22.78	3.83	27.53	23.50	3.08	3.54
$Cu(C_4H_4O_4) \cdot 0.5H_2O$	Turquoise	33.69	25.47	2.68	33.15	25.59	2.94	1.40
$Zn(C_4H_4O_4) \cdot 0.5H_2O$	White	34.33	25.22	2.65	33.86	25.39	2.40	–

$(C_4H_4O_4)^{2-}$ is the succinate di-anion.

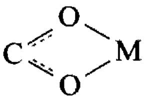
TABLE 2

IR spectra (4000–200 cm^{-1})

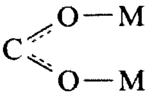
Compound	ν_{O-H} (H_2O)	ν_{COOH}	ν_{COO^-}	ν_{M-O}
$C_4H_6O_4$		1686 (s)	–	–
$Co(C_4H_4O_4)\cdot 2H_2O$	3640–2960 (br, s)		1560 (s)	319 (m)
$Ni(C_4H_4O_4)\cdot 2H_2O$	3680–3000 (br, s)		1562 (s)	286 (w)
$Cu(C_4H_4O_4)0.5H_2O$	3640–3040 (br, s)		1545 (s)	296 (w)
$Zn(C_4H_4O_4)\cdot 0.5H_2O$	3640–3040 (br, s)		1550 (s)	

$C_4H_6O_4$, succinic acid: $C_4H_4O_4^{2-}$, succinate di-anion.
s, Strong; m, medium; br, broad; w, weak.

The main bands in the IR spectra of the compounds are given in Table 2. The compounds all show a strong absorption band in the region 3700–2960 cm^{-1}, ν(O–H), indicating the presence of water of crystallisation [1]. The compounds also show an absorption band in the region 1540–1565 cm^{-1} due to the stretching vibration of the carboxylate groups linked to the metal ions [2]. 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 vibration [3–5]. It has been suggested that bonding of type **II** rather than type **I** is observed [6]



I



II

Metal–oxygen bands have been assigned and are reported for each of the compounds.

The electronic spectrum, see Table 3, and the magnetic measurement, Table 1, suggest that for the cobalt compound the cobalt atom is in a tetrahedral environment [7]. The *Dq* value, Table 3, for the compound is

TABLE 3

Electronic spectra (cm^{-1})

Compound	Peak position	d–d transition	*Dq*	*B*	*β*
$Co(C_4H_4O_4)\cdot 2H_2O$	8130 19048	$^4A_2(F) \rightarrow {}^4T_1(F)$ $\rightarrow {}^4T_1(P)$	441	929	0.96
$Ni(C_4H_4O_4)\cdot 2H_2O$	8620 14598 21309	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ $\rightarrow {}^3T_{1g}(F)$ $\rightarrow {}^3T_{1g}(P)$	862	1022	0.98
$Cu(C_4H_4O_4)\cdot 0.5H_2O$	14492	$^2E_g(D) \rightarrow {}^2T_{2g}(D)$			

consistent with this stereochemistry [8]. The electronic spectrum, Table 3, and the magnetic measurement, Table 1, indicate that for the nickel compound the nickel atom is in an octahedral environment [1]. The *Dq* value, Table 3, for the compound is consistent with this stereochemistry [9]. The β values, Table 3, for the cobalt and nickel compounds show a high degree of ionic character in the metal–ligand bonds in these compounds. The single broad absorption band at 14492 cm^{-1} in the electronic spectrum for the copper compound suggests that the copper atom is in an octahedral environment [1]. The magnetic moment for the compound is 1.4 B.M. suggesting some copper–copper magnetic interaction.

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 nickel, copper and zinc compounds are considered to have a planar arrangement with each carboxylate group on each molecule of the succinate bonded to two different metal atoms to give a chain-like structure. It is also suggested that each metal atom is bonded to metal atoms in adjacent layers by the carboxylate groups of bridging succinate molecules to give a six-coordinate environment for the metal ion. The water molecules are attached by hydrogen bonding in each compound. It is further suggested that the cobalt compound has a dimeric structure with the carboxylate group in each molecule bonded to two different cobalt atoms so that each cobalt atom is in a tetrahedral environment. The water molecules are attached by hydrogen bonding in the compound.

The TG and DTA curves for the succinic acid, Fig. 1, show that it is thermally stable in the temperature range 20–189 °C. Its pyrolytic decomposition starts at 189 °C and finishes at 580 °C with the total elimina-

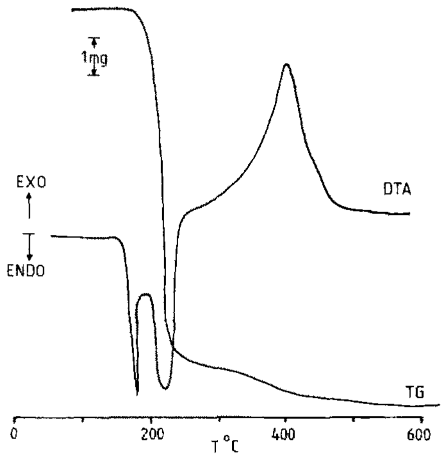


Fig. 1. TG and DTA curves for succinic acid. Sample weight = 11.08 mg.

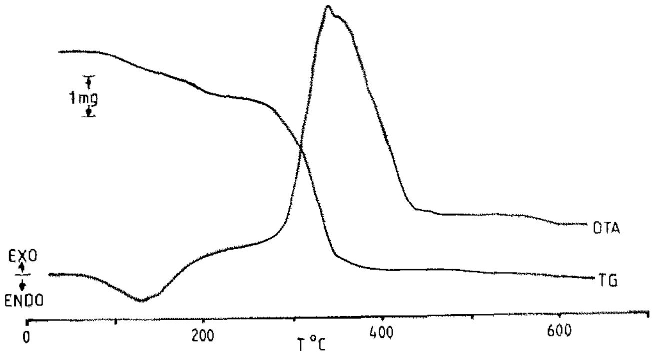


Fig. 2. TG and DTA curves for $Co(C_4H_4O_4)\cdot 2H_2O$. Sample weight = 10.20 mg.

tion of the sample. The DTA curve of succinic acid, Fig. 1, shows an endothermic peak at 185 °C corresponding to fusion. The value of the fusion enthalpy is 83 kJ mol^{-1}. Liquid succinic acid decomposes immediately with an endothermic peak at 216 °C and an exothermic peak at 410 °C. The TG and DTA curves for the compounds formed between succinic acid and cobalt, nickel, copper and zinc are shown 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, see Table 4. The expected endothermic peak for the dehydration processes associated with these compounds was observed in the DTA curve. The dehydration enthalpies have been 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, see Table 5. In the DTA curves these decomposition processes correspond to exothermic effects for the compounds.

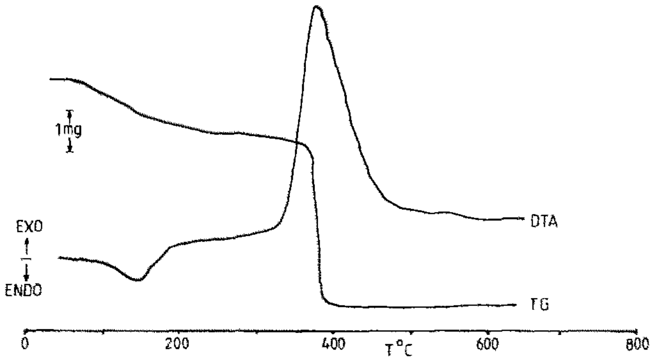


Fig. 3. TG and DTA curves for $Ni(C_4H_4O_4)\cdot 2H_2O$. Sample weight = 9.11 mg.

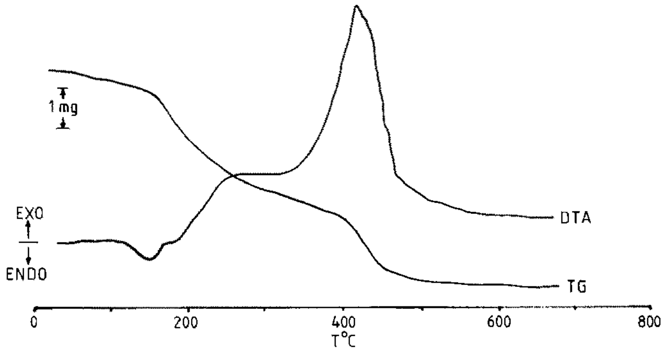


Fig. 4. TG and DTA curves for $Cu(C_4H_4O_4)\cdot 0.5H_2O$. Sample weight = 8.88 mg.

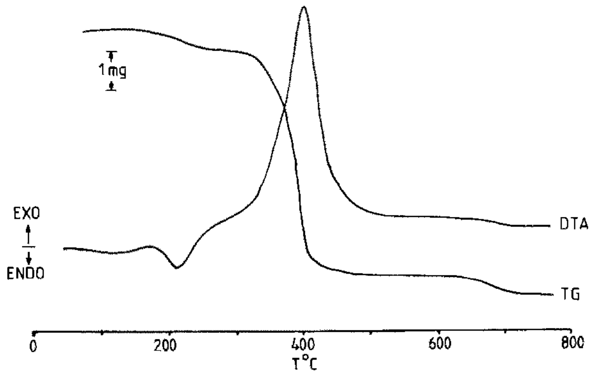


Fig. 5. TG and DTA curves for $Zn(C_4H_4O_4)\cdot 0.5H_2O$. Sample weight = 14.14 mg.

TABLE 4

Dehydration processes of the succinic acid metal complexes

Process	Peak temperature (°C)	Thermal nature of transformation	Weight loss (%)		Enthalpy (kJ mol^{-1})
			Calc.	Found	
$Co(C_4H_4O_4)\cdot 2H_2O \rightarrow Co(C_4H_4O_4)$	130	Endo	17.05	15.89	33
$Ni(C_4H_4O_4)\cdot 2H_2O \rightarrow Ni(C_4H_4O_4)$	143	Endo	17.07	15.68	44
$Cu(C_4H_4O_4)\cdot 0.5H_2O \rightarrow Cu(C_4H_4O_4)$	152	Endo	4.24	4.49	2
$Zn(C_4H_4O_4)\cdot 0.5H_2O \rightarrow Zn(C_4H_4O_4)$	210	Endo	4.72	4.24	9

TABLE 5

Decomposition processes of succinic acid and the anhydrous metal complexes

Process	Temperature range (°C)	Thermal nature of transformation	Residue (%)	
			Calc.	Found
$C_4H_6O_4$ → pyrolytic process	190–580	Endo/exo	–	–
$Co(C_4H_4O_4) \rightarrow Co_3O_4$	246–640	Exo	38.04	38.72
$Ni(C_4H_4O_4) \rightarrow NiO$	280–518	Exo	35.44	36.26
$Cu(C_4H_4O_4) \rightarrow CuO$	181–570	Exo	42.16	42.69
$Zn(C_4H_4O_4) \rightarrow ZnO$	292–780	Exo	42.72	42.49

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