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THERMAL, SPECTRAL AND MAGNETIC STUDIES OF SOME COMPOUNDS OF COBALT(II), NICKEL(II) AND COPPER(II) WITH CINNAMIC ACID

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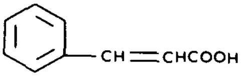
ABSTRACT

Some new compounds of cinnamic acid with cobalt, nickel and copper have been prepared in aqueous solution. The compounds, which have been characterised by analyses, magnetic moments, and 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 of cobalt and nickel are hydrated while the copper compound is anhydrous. Thermal decomposition studies show that the hydrated compounds lose water followed by the organic ligand to give the metal oxide. The copper compound loses the organic ligand to form copper oxide.

INTRODUCTION

Cinnamic acid (see below) 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 group.



Cinnamic acid ($C_9H_8O_2$).

This paper reports the thermal analysis studies of cinnamic acid together with some complexes formed by the acid and the transition metals, cobalt, nickel and copper. 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. Depending on how the transition metal coordinates to the acid, the possibility exists of producing polymer systems containing double bonds.

EXPERIMENTAL

Method A

5 g of cinnamic acid was dissolved in 400 cm^3 of hot water and the metal carbonate was added in small amounts, with stirring until effervescence ceased. The solution was filtered and the filtrate evaporated until the volume had decreased and the complex precipitated. The precipitate was filtered and the product air dried.

Method B

14.8 g of cinnamic acid was added to 1000 cm^3 of boiling water with stirring. To this acid solution was added 5.3 g of sodium carbonate. When the evolution of carbon dioxide was complete, 8.0 g of copper sulphate was added to the solution and a precipitate was produced. The precipitate was filtered and air dried.

Apparatus

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

The IR spectra were obtained using KBr discs (4000–600 cm^{-1}) range and polyethylene discs (600–200 cm^{-1} range) on a Perkin–Elmer IR 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.

The thermal analysis studies were carried out on a Stanton–Redcroft model STA 781 thermobalance. Thermogravimetry (TG) and differential thermal analysis (DTA) curves were obtained at a heating rate of 10 °C min^{-1} in static air. In all cases the 20–1000 °C temperature range was studied.

RESULTS AND DISCUSSION

The compounds prepared are listed in Table 1. The copper complex, $Cu(C_9H_7O_2)_2$, was prepared using method B as a copper(I) complex of unknown stoichiometry was isolated using method A. The cobalt and nickel complexes, which were prepared by method A, have stoichiometry $M(C_9H_7O_2)_2 \cdot 2H_2O$.

TABLE 1

Analyses and magnetic moments of the compounds

Compound	Method of preparation	Colour	Theory (%)			Found (%)			μ (B.M.)
			Metal	Carbon	Hydrogen	Metal	Carbon	Hydrogen	
$Co(C_9H_7O_2)_2 \cdot 2H_2O$	A	Pink	15.13	55.49	4.62	15.42	55.66	4.27	3.65
$Ni(C_9H_7O_2)_2 \cdot 2H_2O$	A	Green	15.08	55.52	4.62	14.94	55.17	4.72	3.18
$Cu(C_9H_7O_2)_2$	B	Blue	17.75	60.42	3.95	17.49	59.87	3.58	1.67

$C_9H_7O_2 = C_6H_5CH{=}CHCOO^-$

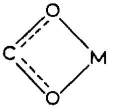
TABLE 2

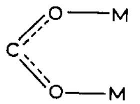
IR spectra (cm^{-1})

Compound	$\bar{\nu}_{O-H}(H_2O)$	$\bar{\nu}_{COOH}$	$\bar{\nu}_{COO^-}$	$\bar{\nu}_{C=C}$	$\bar{\nu}_{C-O}$	$\bar{\nu}_{M-O}$
$C_9H_8O_2$		1682 (s)		1634 (s)	1450 (s)	
$Co(C_9H_7O_2)_2 \cdot 2H_2O$	3700–3100 (br, s)		1549 (s)	1642 (s)	1451 (s)	291 (m)
$Ni(C_9H_7O_2)_2 \cdot 2H_2O$	3680–3000 (br, s)		1521 (s)	1642 (s)	1451 (s)	292 (m), 318 (m)
$Cu(C_9H_7O_2)_2$			1561 (s)	1640 (s)	1451 (s)	296 (m)

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

Table 2 lists the main bands in the IR spectra. The bands in the 3700–3000 cm^{-1} region are assigned to the $\bar{\nu}$(O–H) of water [1]. The bands in the 1634–1642 cm^{-1} region are assigned to the $\bar{\nu}$(C=C) vibration. It is suggested that coordination does not take place between the π-electron system of the C=C bond and the metal ions because a change to lower frequency is not observed in the compounds [2]. The spectra of the complexes confirms the absence of free carboxylic acid groups. The usual reduction in $\bar{\nu}(COO^-)$ compared to free–CO_2H is observed, characteristic of bonding type I rather than II [2].


(I)


(II)

The $\bar{\nu}$(M–O) vibrations have been identified and are listed in Table 2.

The electronic spectra, Table 3, and the magnetic moments, Table 1, would suggest that for the cobalt and nickel compounds the metal ion is in an octahedral environment [1]. The magnetic moment for the cobalt compound is 3.65 B.M. which is lower than that normally observed for octahedral cobalt compounds. However Stoufer et al. have reported com-

TABLE 3

Electronic spectra (cm^{-1})

Compound	Peak positions	d–d transitions
$Co(C_9H_7O_2)_2 \cdot 2H_2O$	8065	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$
	18867	$\rightarrow {}^4T_{1g}(P)$
$Ni(C_9H_7O_2)_2 \cdot 2H_2O$	8621	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
	14815	$\rightarrow {}^3T_{1g}(F)$
	25000	$\rightarrow {}^3T_{1g}(P)$
$Cu(C_9H_7O_2)_2$	14815	$^2E_g(D) \rightarrow {}^2T_{2g}(D)$

pounds which have an octahedral structure and which have magnetic moments of around 3.70 B.M. [3]. The low magnetic moment is considered to be due to interaction between the ${}^4T_{1g}$ and ${}^2E_g$ states [4]. The copper compound, $Cu(C_9H_7O_2)_2$, has a broad absorption band between 10000 and 15000 cm^{-1}. This suggests an octahedral environment for the copper atom [2]. The broadness of the band results from Jahn–Teller distortion which is due to an odd number of electrons in the $d_{x^2-y^2}$ orbital [5]. The band is made up of composite bands involving transitions from the other d-orbitals to the $d_{x^2-y^2}$ orbital. The magnetic moment for the copper compound is lower than that expected from the spin-only value and would suggest some copper–copper magnetic interaction in the compound [6].

The insolubility of the compounds in both polar and non-polar solvents would suggest that they have polymeric structures [1].

The fact that the compounds were isolated as powders and not as single crystals from the aqueous solutions means that a complete structure determination can not be made. However the spectroscopic and magnetic data enable us to predict that in the compounds $Co(C_9H_7O_2)_2 \cdot 2H_2O$, $Ni(C_9H_7O_2)_2 \cdot 2H_2O$ and $Cu(C_9H_7O_2)_2$ the metal ions are in an octahedral environment. It is suggested that the compounds have a planar arrangement with the carboxylate groups of two different cinnamate ions bonded to a metal atom to give one layer. It is further suggested that each metal is bonded to oxygen atoms in adjacent layers to give a six-coordinate environ-

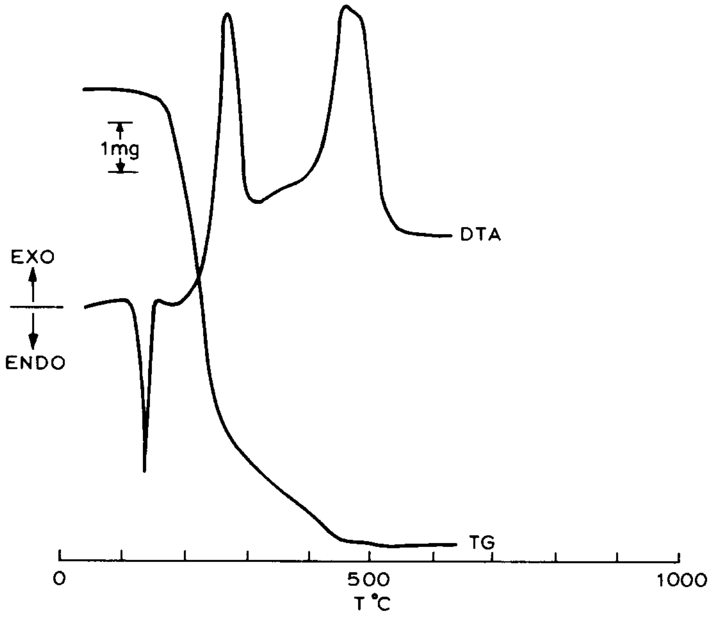


Fig. 1. TG/DTA curves for cinnamic acid, sample weight 8.84 mg.

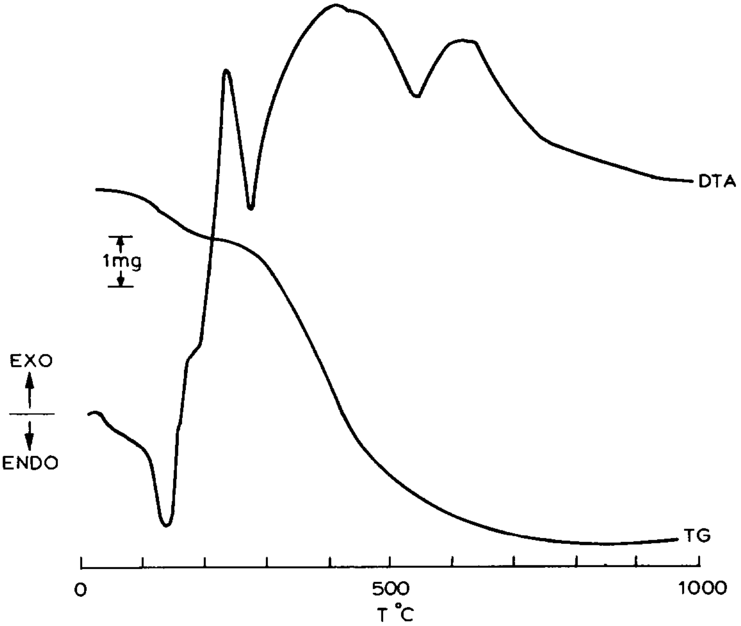


Fig. 2. TG/DTA curves of $Co(C_9H_7O_2)_2 \cdot 2H_2O$, sample weight 8.70 mg.

ment for the metal ion and a polymeric structure. The water molecules in the hydrated compounds are attached by hydrogen bonding.

The TG and DTA traces for cinnamic acid and the complexes with cobalt, nickel and copper are given in Figs. 1–4. The TG curve for cinnamic

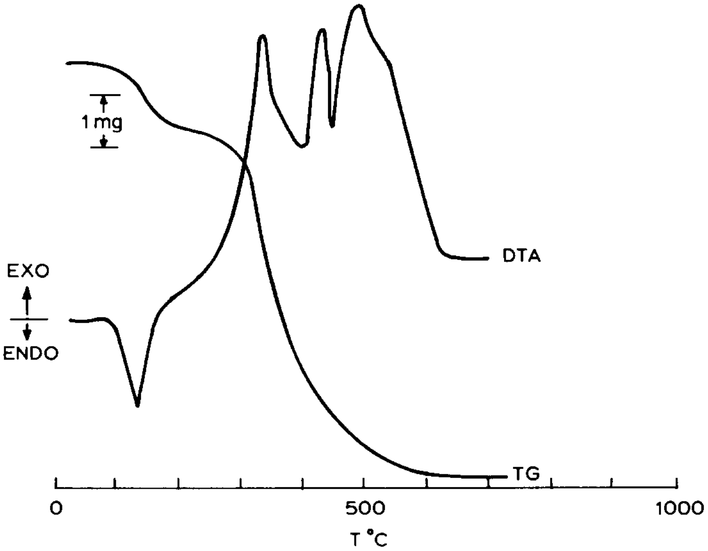


Fig. 3. TG/DTA curves of $Ni(C_9H_7O_2)_2 \cdot 2H_2O$, sample weight 9.66 mg.

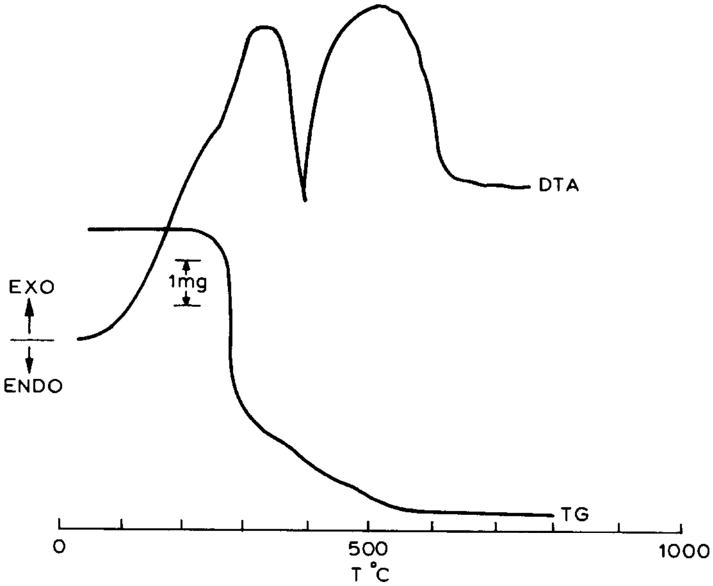


Fig. 4. TG/DTA curves of $Cu(C_9H_7O_2)_2$, sample weight 7.10 mg.

acid shows that the acid is thermally stable in the temperature range 20–122°C. Its pyrolitic decomposition begins at 122°C and finishes at 525°C with the total elimination of the sample. The DTA curve of the cinnamic acid shows an endothermic peak at 133°C due to melting. The enthalpy of fusion is 4.9 kJ mol^{-1}. The acid then decomposes immediately producing exothermic peaks at 244 and 438°C respectively.

The TG and DTA curves for the complexes formed between cinnamic acid and cobalt(II), nickel(II) and copper(II) are given in Figs. 2–4. The dehydration process in each of the complexes $Co(C_9H_7O_2)_2 \cdot 2H_2O$ and $Ni(C_9H_7O_2)_2 \cdot 2H_2O$ 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.

TABLE 4

Dehydration processes of the metal complexes

Process	Peak temp (°C)	Thermal nature of trans-formation	Weight loss (%)		Enthalpy (kJ mol^{-1})
			Calc.	Found	
$Co(C_9H_7O_2)_2{\cdot}2H_2O \rightarrow Co(C_9H_7O_2)_2$	140	Endo	9.24	8.51	19.3
$Ni(C_9H_7O_2)_2{\cdot}2H_2O \rightarrow Ni(C_9H_7O_2)_2$	142	Endo	9.25	10.67	28.4

TABLE 5

Decomposition processes of the cinnamic acid and the metal complexes

Process	Temp. range (°C)	Thermal nature of transformation	Residue (%)	
			Calc.	Found
$C_9H_8O_2 \rightarrow$ pyrolytic process	122–525	Exo	–	–
$Co(C_9H_7O_2)_2 \rightarrow Co_3O_4$	172–820	Exo	20.61	20.68
$Ni(C_9H_7O_2)_2 \rightarrow NiO$	150–560	Exo	19.20	19.66
$Cu(C_9H_7O_2)_2 \rightarrow CuO$	220–816	Exo	22.16	22.53

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 metal oxides, see Table 5. In the DTA curves these decomposition processes correspond to exothermic effects for the complexes. The compound $Cu(C_9H_7O_2)_2$ undergoes exothermic reactions with loss of the organic ligand to give CuO.

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