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Preparation, structural characterisation and thermal analysis studies of vinylacetic acid compounds of some first row transition metals

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Abstract

Compounds of vinylacetic acid with cobalt(II), nickel(II), copper(II) and zinc(II) have been prepared in aqueous solution. The cobalt, nickel and copper compounds have stoichiometry $M(C_4H_5O_2)_2H_2O$ while the zinc compound has stoichiometry $Zn(C_4H_5O_2)_2$. The compounds have polymeric structures. Thermal decomposition studies on the compounds show that those compounds which are hydrated lose a water molecule followed by the organic ligand to give the metal oxide. The zinc compound forms an intermediate compound before decomposing to the metal oxide.

INTRODUCTION

Vinylacetic acid, $H_2C{=}CHCH_2COOH$, has two different donor sites for forming bonds with metal ions: the double bond between carbon atoms and the oxygen atoms of the carboxylic acid group. This paper reports the preparation, structural characterisation and thermal analysis studies of the metal complexes formed between vinylacetic acid and the transition metals cobalt(II), nickel(II), copper(II) and zinc(II). Spectral and magnetic studies have been used to determine the environment of the metal ions in these compounds 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

Preparation of the metal complexes

Vinylacetic acid was added to boiling water and the metal carbonate was added until a neutral solution was obtained. This solution was then reduced in volume on a water bath to precipitate the metal complex. The complex was filtered, washed with distilled water and dried in a vacuum oven.

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Apparatus and measurements

The concentrations of the metal ions were determined using a Perkin-Elmer 373 atomic absorption spectophotometer; 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} range) and polyethylene discs (600–200 cm^{-1} range) on a Perkin-Elmer IR spectrophotometer model 598. The electronic spectra were obtained on a Beckman Acta MIV 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 1500 thermobalance. Thermogravimetry (TG) and differential thermal analysis (DTA) traces were obtained at a heating rate of 10°C min^{-1} in stable air. In all the cases the 20–800°C range was studied.

RESULTS AND DISCUSSION

The elemental analyses for the metal complexes are listed in Table 1. The cobalt, nickel and copper complexes have the stoichiometry $M(C_4H_5O_2)_2H_2O$ while the zinc complex has stoichiometry of $Zn(C_4H_5O_2)_2$, where $C_4H_5O_2$ is vinylacetate.

In Table 2 the main bands in the IR spectra are listed. The bands in the 3680–3120 cm^{-1} region are assigned to the ν(O–H) of water, and the bands in the 1646–1648 cm^{-1} region are assigned to the ν(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

TABLE 1

Analyses of compounds

Compound		Metal/%	Carbon/%	Hydrogen/%
$Co(C_4H_5O_2)_2H_2O$	Theory	23.84	38.88	4.89
	Found	23.69	38.57	4.28
$Ni(C_4H_5O_2)_2H_2O$	Theory	23.77	38.88	4.89
	Found	23.66	38.59	4.59
$Cu(C_4H_5O_2)_2H_2O$	Theory	25.24	38.17	4.80
	Found	25.01	38.02	3.99
$Zn(C_4H_5O_2)_2$	Theory	27.75	40.79	4.27
	Found	27.42	41.76	4.27

TABLE 2

Infrared spectra 4000–200 cm^{-1}

Compounds	$\nu_{O-H}(H_2O)$	ν(COOH)	ν(C=C)	$\nu(COO^-)$	ν(M–O)
$C_4H_6O_2$	–	1714(s)	1647(w)	–	–
$Co(C_4H_5O_2)_2H_2O$	3680–3140(br,s)		1648(w)	1573(s)	260(w)
$Ni(C_4H_5O_2)_2H_2O$	3680–3188(br,s)		1646(w)	1563(s)	265(w)
$Cu(C_4H_5O_2)_2H_2O$	3680–3120(br,s)		1646(sh)	1587(s)	253(w)
$Zn(C_4H_5O_2)_2$			1646(sh)	1569(s)	284(w)

Key: br, broad; s, strong; w, weak; sh, shoulder.

wavenumbers is not observed on complexation [1]. The spectra of the metal complexes confirm the absence of free carboxylic acid groups. The usual reduction in the COO^- vibration compared to the $-CO_2H$ vibration on the complexation is observed [1]. Metal–oxygen bands are reported for each of the compounds in Table 2 and indicate that the cobalt, nickel, copper and zinc atoms in their compounds are in an octahedral environment [2].

The electronic spectra and the magnetic moments (Table 3) for the cobalt and nickel compounds agree with the suggestion that the metal atoms are in an octahedral environment [3]. The copper compound has a broad adsorption band between 10 000 and 15 000 cm^{-1}. This indicates that the copper atoms are in an octahedral environment [3]. The broadness of the band is a result of Jahn Teller distortion which is due to an odd number of electrons in the $d_{x^2-y^2}$ orbital [4]. The band is made up of composite bands involving transitions from the d orbitals to the $d_{x^2-y^2}$ orbital [4]. The magnetic moment for the copper compound is lower than that expected for the spin only value and would suggest some copper–copper magnetic interaction in the compound. The insolubility of the compounds in both polar and non-polar solvents would suggest that they have polymeric structures [3].

The fact that the compounds were isolated as powders and not as single crystals from the aqueous solutions means that no complete structure

TABLE 3

Electronic spectra

Compound	Band position/cm^{-1}	d–d transition	μ/BM
$Co(C_4H_5O_2)_2H_2O$	8064	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	5.19
	18939	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	
$Ni(C_4H_5O_2)_2H_2O$	8403	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	3.39
	14705	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	
	24813	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	
$Cu(C_4H_5O_2)_2H_2O$	14619	$^2E_g(D) \rightarrow {}^2T_{2g}(D)$	1.48

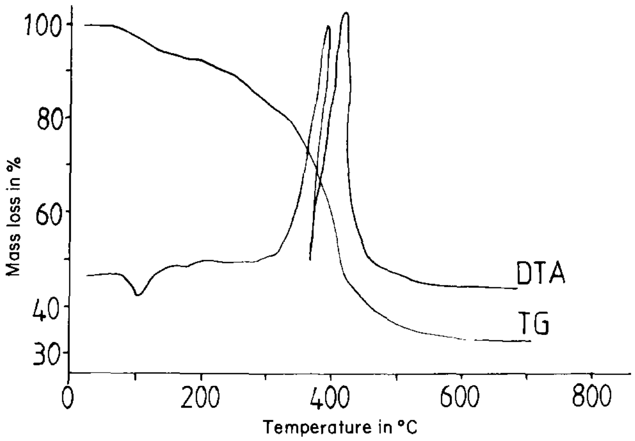

Fig. 1. TG and DTA traces for $Co(C_4H_5O_2)_2H_2O$. Sample 9.68 mg.

determination using X-ray studies could be made. However, the spectroscopic and magnetic data enable us to predict possible structures. The compounds are considered to have a planar arrangement with the carboxylate groups of two different vinylacetate ions bonded to a metal atom to give one layer. 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 and a polymeric structure. The water molecules are attached by hydrogen bonding in the cobalt, nickel and copper compounds.

The TG and DTA traces for the metal complexes are shown in Figs. 1–4. The cobalt, nickel and copper complexes undergo an endothermic reaction with loss of a water molecule. The observed mass losses for the dehydration processes compare favourably with the theoretical values given in Table 4.

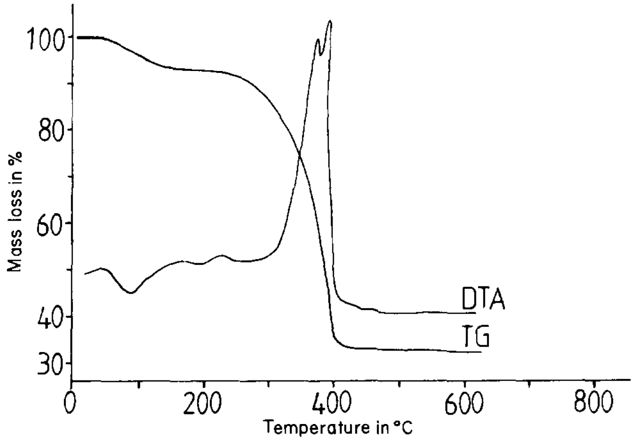

Fig. 2. TG and DTA traces for $Ni(C_4H_5O_2)_2H_2O$. Sample mass, 9.96 mg.

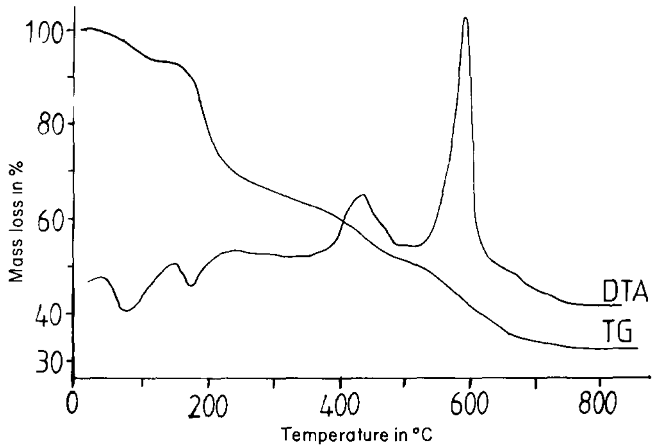

Fig. 3. TG and DTA traces for $Cu(C_4H_5O_2)_2H_2O$. Sample mass, 8.45 mg.

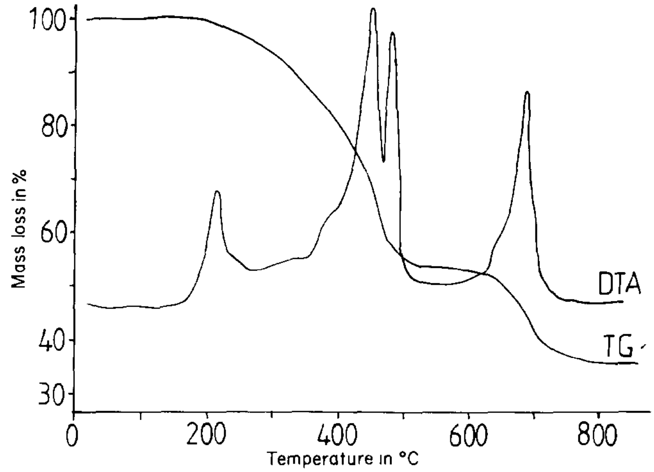

Fig. 4. TG and DTA traces for $Zn(C_4H_5O_2)_2$. Sample mass, 9.76 mg.

TABLE 4

Dehydration processes of metal complexes

Process	Decomp. temp./ °C	Thermal nature of trans-formation [a]	Mass loss/%	
			Theory	Found
$Co(C_4H_5O_2)_2H_2O \rightarrow Co(C_4H_5O_2)_2$	66	Endothermic	7.29	7.30
$Ni(C_4H_5O_2)_2H_2O \rightarrow Ni(C_4H_5O_2)_2$	36	Endothermic	7.29	7.26
$Cu(C_4H_5O_2)_2H_2O \rightarrow Cu(C_4H_5O_2)_2$	29	Endothermic	7.15	7.10

[a] Found from DTA trace.

TABLE 5

Decomposition processes of metal complexes

Process	Decomp. temp./ °C	Thermal nature of trans-formation [a]	Mass loss/%	
			Theory	Found
$Co(C_4H_5O_2)_2 \rightarrow Co_3O_4$	196	Exothermic	60.23	60.18
$Ni(C_4H_5O_2)_2 \rightarrow NiO$	198	Exothermic	62.46	62.44
$Cu(C_4H_5O_2)_2 \rightarrow CuO$	130	Exothermic	61.26	61.20
$Zn(C_4H_5O_2)_2 \rightarrow$				
$Zn(C_4H_5O_2)_{0.5} \rightarrow$	170	Exothermic	54.18	54.20
ZnO	572	Exothermic	11.28	11.30

[a] Found from DTA trace.

The removal of the water molecules in each of the complexes is then followed by exothermic reactions and loss of organic ligands to give the metal oxide in each case (Table 5). The anhydrous zinc complex would appear to undergo a two stage decomposition process when the observed mass losses are compared to the theoretical values (Table 5). The TG traces show that this compound loses one and a half molecules of organic ligand followed by half a molecule of organic ligand to give the metal oxide. The DTA trace shows that each of these processes involves exothermic reactions.

In summary, the decomposition schemes are

$$Co(C_4H_5O_2)_2H_2O \xrightarrow{\text{endo}} Co(C_4H_5O_2)_2 \xrightarrow{\text{exo}} Co_3O_4$$

$$M(C_4H_5O_2)_2H_2O \xrightarrow{\text{endo}} M(C_4H_5O_2)_2 \xrightarrow{\text{exo}} MO$$

where M = Ni or Cu, and

$$Zn(C_4H_5O_2)_2 \xrightarrow{\text{endo}} Zn(C_4H_5O_2)_{0.5} \xrightarrow{\text{exo}} ZnO$$

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