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# Preparation, structural characterisation and thermal analysis studies of methacrylic acid complexes of cobalt(II), nickel(II) and copper(II)

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## Abstract

Compounds of methacrylic acid with cobalt(II), nickel(II), and copper(II) have been prepared in aqueous solution. The compounds have stoichiometries $Co(C_4H_5O_2)_2H_2O$; $Ni(C_4H_5O_2)_2 1.5H_2O$ and $Cu(C_4H_5O_2)(OH)$ and polymeric octahedral structures. Thermal decomposition studies show that the hydrated compounds lose water followed by the organic ligands to give the metal oxides. The copper compound decomposes with loss of the organic ligand and the OH group to give the metal oxide.

## INTRODUCTION

Acrylates and methacrylates are widely used in the polymer industry as their monomers are usually versatile building blocks which can easily polymerise or copolymerise with a variety of monomers. Methacrylates differ from acrylates in that the $\alpha$ hydrogen of the acrylate is replaced by a methyl group that imparts the stability to methacrylic acid polymers. In this paper we discuss the preparation, structural characterisation and thermal analysis studies of the metal complexes formed between methacrylic acid $H_2C{=}C(CH_3)COOH$ and the transition metals cobalt(II), nickel(II) and copper(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. A thermal stability study of the methacrylate complexes has been carried out.

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## EXPERIMENTAL

### *Preparation of the metal complexes*

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

### *Apparatus and measurements*

The concentration of the 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 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 static air. In all cases the 20–1000°C temperature range was studied.

## RESULTS AND DISCUSSION

The results for the elemental analysis of the compounds isolated from aqueous solution are listed in Table 1. The compounds have stoichiometries of $Co(C_4H_5O_2)_2H_2O$; $Ni(C_4H_5O_2)_21.5H_2O$ and $Cu(C_4H_5O_2)(OH)$.

TABLE 1

Analyses of compounds

| Compounds | | Metal/% | Carbon/% | Hydrogen/% |
|---|---|---|---|---|
| $Co(C_4H_5O_2)_2H_2O$ | Theory | 22.74 | 37.08 | 4.66 |
| | Found | 22.57 | 36.43 | 4.40 |
| $Ni(C_4H_5O_2)_21.5H_2O$ | Theory | 22.94 | 37.55 | 5.12 |
| | Found | 22.44 | 36.75 | 4.75 |
| $Cu(C_4H_5O_2)(OH)$ | Theory | 38.38 | 29.02 | 3.65 |
| | Found | 38.19 | 28.62 | 3.50 |

TABLE 2

Infrared spectra, (4000–200 cm$^{-1}$)

| Compound | $\nu_{O-H}(H_2O)$ | $\nu$(COOH) | $\nu$(C–C) | $\nu(COO^-)$ | $\nu$(M–O) |
|---|---|---|---|---|---|
| $C_4H_5O_2$ | | 1696(s) | 1640(s) | | |
| $Co(C_4H_5O_2)_2H_2O$ | 3450–3240(br,s) | | 1646(w) | 1575(s) | 332(s) |
| $Ni(C_4H_5O_2)_2 1.5H_2O$ | 3520–3200(br,s) | | 1642(w) | 1571(s) | 315(w) |
| $Cu(C_4H_5O_2)(OH)$ | | | 1646(w) | 1560(s) | 295(w) |

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

In Table 2 the main bands in the vibrational spectra (4000–200 cm$^{-1}$) are listed. The spectra of the hydrated compounds show broad, strong absorption bands in the 3540–3200 cm$^{-1}$ region, indicating the presence of water of crystallisation. The bands in the 1640–1646 cm$^{-1}$ region are assigned to the $\nu$(C=C) vibration. Since a shift to lower wavenumbers is not observed on complexation for the C=C vibration it is concluded that bonding does not take place between the $\pi$-electron system and the metal ions [1]. The spectra of the complexes confirm the absence of free carboxylic acid groups. The usual reduction in $\nu(COO^-)$ compared to the free –COOH is observed on complexation [1]. A band at 915 cm$^{-1}$ in the spectrum of the copper compound indicates the presence of bridging OH groups [2]. Metal–oxygen vibrations have been identified and are listed for the compounds.

The electronic spectra and magnetic moments (see Table 3) would suggest that for the cobalt and nickel compounds the metal ions are in an octahedral environment [3]. The copper compound has a band in its electronic spectrum between 10 000 and 15 000 cm$^{-1}$ indicating an octahedral environment for the copper atoms [3]. The magnetic moment for the compound is higher than the spin only value of 1.73 BM and would indicate

TABLE 3

Electronic spectra

| Compounds | Band position/cm$^{-1}$ | d–d transition | $\mu$/BM |
|---|---|---|---|
| $Co(C_4H_5O_2)_2H_2O$ | 8264 | ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ | 5.14 |
| | 16393 | ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ | |
| | 20000 | ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ | |
| $Ni(C_4H_5O_2)_2 1.5H_2O$ | 9090 | ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ | 3.71 |
| | 15152 | ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ | |
| | 25510 | ${}^3T_{2g}(F) \rightarrow {}^3T_{1g}(P)$ | |
| $Cu(C_4H_5O_2)(OH)$ | 14285 | ${}^2E_g(D) \rightarrow {}^2T_{2g}(D)$ | 1.86 |

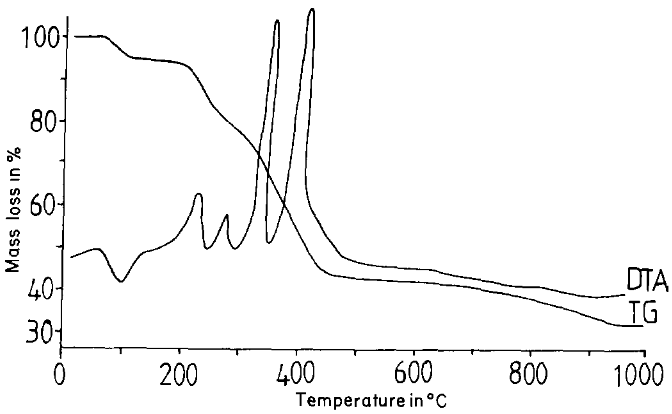

Fig. 1. TG and DTA traces for $Co(C_4H_5O_2)_2H_2O$. Sample mass, 7.39 mg.

some orbital contribution to the magnetic moment. The insolubility of the metal complexes in both polar and non-polar solvents would suggest they have polymeric structures [3].

Because the metal complexes were isolated as powders and not as single crystals from aqueous solutions, a complete structural determination cannot be made. However, the spectroscopic and magnetic data enable us to predict that in the compounds $Co(C_4H_5O_2)_2H_2O$ and $Ni(C_4H_5O_2)_2$ $1.5H_2O$ a planar arrangement exists of carboxylate groups from two different methacrylate 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 each metal atom and a polymeric structure. In the copper compound the copper atoms are

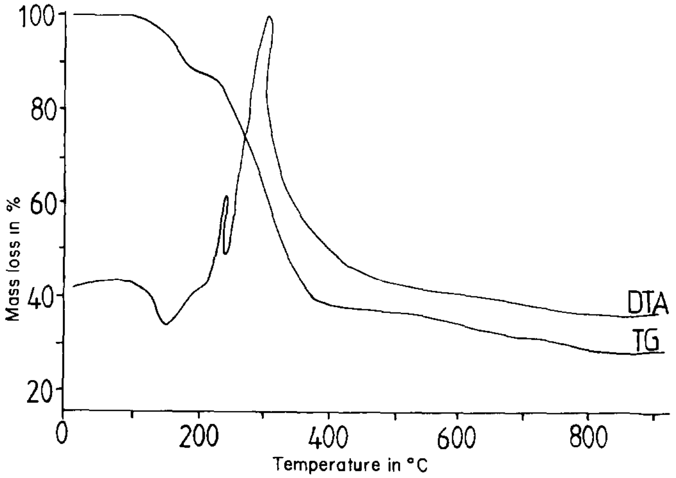

Fig. 2. TG and DTA traces for $Ni(C_4H_5O_2)_2 1.5H_2O$. Sample mass, 9.93 mg.

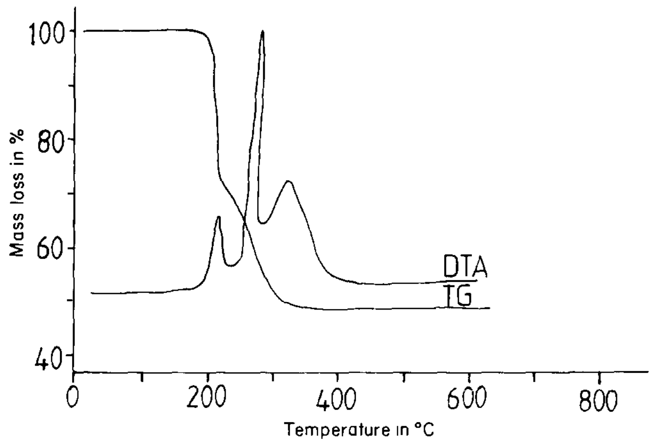

Fig. 3. TG and DTA traces for $Cu(C_4H_5O_2)(OH)$. Sample mass, 9.84 mg.

surrounded in a square plane or approximately so by four oxygen atoms, two from the bridging hydroxyl groups and two from a carboxylate group. Each copper atom is bonded to oxygen atoms in adjacent planes to give a six coordinate environment for the copper and polymer structure.

TG and DTA traces for the metal complexes are shown in Figs. 1–3. The cobalt and nickel complexes undergo an exothermic reaction with loss of water. The dehydration process in each case takes place in one step. The observed mass losses for these processes compare favourably with theoretical values (Table 4). Decomposition of the anhydrous complexes follows, with loss of the organic ligands and the formation of the metal oxides (Table 5). In the DTA traces these decomposition processes correspond to exothermic effects. The copper compound undergoes exothermic reactions with loss of the organic ligand and OH to give copper oxide. The observed values for the decomposition of the anhydrous complexes to their metal oxides compare favourably to the calculated values in Table 5.

TABLE 4

Dehydration processes of metal complexes

| Process | Decomp. temp./°C | Thermal nature of trans- formation [a] | Mass loss/% | |
|---|---|---|---|---|
| | | | Theory | Found |
| $Co(C_4H_5O_2)_2H_2O \rightarrow Co(C_4H_5O_2)_2$ | 58 | Endothermic | 6.95 | 6.90 |
| $Ni(C_4H_5O_2)_2 1.5H_2O \rightarrow Ni(C_4H_5O_2)_2$ | 89 | Endothermic | 10.56 | 10.26 |

[a] Found from DTA trace.

TABLE 5

Decomposition processes of metal complexes

| Process | Decomp. temp./°C | Thermal nature of transformation | Mass loss/% | |
|---|---|---|---|---|
| | | | Theory | Found |
| $Co(C_4H_5O_2)_2 \rightarrow Co_3O_4$ | 155 | Exothermic | 62.08 | 62.10 |
| $Ni(C_4H_5O_2)_2 \rightarrow NiO$ | 203 | Exothermic | 60.62 | 60.10 |
| $Cu(C_4H_5O_2)(OH) \rightarrow CuO$ | 170 | Exothermic | 51.95 | 51.60 |

In summary, the decomposition processes are

$Co(C_4H_5O_2)_2H_2O \rightarrow Co(C_4H_5O_2)_2 \rightarrow Co_3O_4$

$Ni(C_4H_5O_2)_2 1.5H_2O \rightarrow Ni(C_4H_5O_2)_2 \rightarrow NiO$

$Cu(C_4H_5O_2)(OH) \rightarrow CuO$

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