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Structural characterisation and thermal analysis studies of the compounds of manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) with poly(acrylic acid)

J.R. Allan[a], J.G. Bonner[a], D.L. Gerrard[b] and J. Birnie[b]

[a] *Department of Applied Chemical and Physical Sciences, Napier Polytechnic, Edinburgh (United Kingdom)*
[b] *British Petroleum Research Centre, Sunbury-on-Thames, Middlesex (United Kingdom)*

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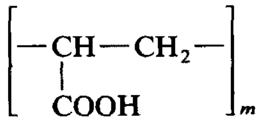
Abstract

The compounds formed by the reaction of poly(acrylic acid) with the carbonates of manganese, cobalt, nickel, copper and zinc in aqueous solution have been prepared. The compounds are all hydrated. Spectral and magnetic properties have been used to deduce the stereochemistry of the compounds. The cobalt and zinc compounds have the metal ions in a tetrahedral environment while the manganese, nickel and copper compounds have the metal ions in an octahedral environment. The thermal behaviour of the compounds has been studied by thermogravimetry and differential thermal analysis. The decomposition studies show that these compounds lose water followed by the organic ligand, to give the metal oxide.

INTRODUCTION

In a previous publication we discussed the stereochemistry and thermal decomposition studies of the complexes of some first-row transition metal ions and acrylic acid [1]. In this paper we report the compounds formed by the reaction of manganese, cobalt, nickel, copper and zinc ions with poly(acrylic acid).



$$\left[-\underset{\displaystyle \mathrm{COOH}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\right]_m$$

poly(acrylic acid)

Spectral and magnetic studies have been used to characterise each compound and to interpret the type of coordination which takes place to the

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metal ion. A study of the thermal stability of each compound was carried out.

EXPERIMENTAL

Preparation of the compounds

Preparation of poly(acrylic acid)

The poly(acrylic acid) (molecular weight 5,000) was supplied by the Aldrich Company, Gillingham, U.K. A solid was obtained by heating the poly(acrylic acid) in a vacuum oven at 90 ° C for 12 hours.

Preparation of the metal compounds

The poly(acrylic acid) (5 g) was dissolved in 50 ml of distilled water. This solution was heated (not boiled) on a hot plate and metal carbonate was added slowly. This was continued until the evolution of carbon dioxide ceased and the solution was no longer acidic. The excess carbonate was removed by filtration and the metal compound was obtained by reducing the volume of the solution on a steam bath.

Apparatus and measurements

The concentration of the metal ions was obtained using a Perkin–Elmer 373 atomic absorption spectrophotometer, and the carbon and hydrogen analysis was determined 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 on a Beckman 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 1500 thermobalance. The TG and 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 analytical results agree with the stoichiometry of the compounds. All of the compounds have water molecules present.

The wavenumbers of the IR absorption bands as well as their descriptions

TABLE 1

Analysis of compounds

Compound [a]	Theory (%)			Found (%)		
	Metal	Carbon	Hydrogen	Metal	Carbon	Hydrogen
$Mn(C_3H_3O_2)_2H_2O$	25.54	33.52	3.72	24.80	33.66	4.64
$Co(C_3H_3O_2)_2 2H_2O$	24.86	30.39	4.26	24.70	30.86	4.45
$Ni(C_3H_3O_2)_2H_2O$	26.82	32.93	3.68	27.30	33.76	3.94
$Cu(C_3H_3O_2)_2(C_3H_4O_2)_3H_2O$	14.4	40.97	4.55	14.70	41.53	4.89
$Zn(C_3H_3O_2)_2H_2O$	29.01	31.96	3.55	28.90	31.68	4.22

[a] $C_3H_3O_2^-$, acrylate ion.

and assignments are given in Table 2. The IR spectra of the complexes show strong, broad absorption bands in the region 3800–2910 cm^{-1}, ν(OH), confirming the presence of water of crystallisation [2]. The usual reduction in $\nu(COO^-)$ compared to free $-CO_2H$, is observed on complexation [3]. The IR spectra of the copper compound also has a band present due to $-CO_2H$, indicating that not all of the $-CO_2H$ groups have undergone complexation. Metal–oxygen bands have been assigned and are listed in Table 2.

The electronic spectra and magnetic moments for the compounds are listed in Table 3. The manganese compound has weak bands at 19400, 25200 and 25500 cm^{-1}. These bands correspond to the d–d transition, ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (G) and ${}^6A_{1g} \rightarrow {}^4A_{1g}$, ${}^4E_g$ (G), and are an indication that the manganese ion is in an octahedral environment [4]. The magnetic moment for the compound is higher than the spin-only value of 5.92 BM. The cobalt compound has bands in its electronic spectrum at 8696 and 18518 cm^{-1}. These bands correspond to the d–d transitions, ${}^4A_2(F) \rightarrow {}^4T_1(F)$ and ${}^4A_2(F) \rightarrow {}^4T_1(P)$, and show that the cobalt atom is in a tetrahedral environment [5].

Further evidence for the cobalt atoms being in a tetrahedral environment

TABLE 2

Infrared spectra (4000–200 cm^{-1})

Compound	ν(O–H)(H_2O)	ν(COOH)	ν(COO–)		ν(M–O)
$Poly(C_3H_4O_2)$ [a]	–	1724 (s)	–	–	–
$Mn(C_3H_3O_2)_2H_2O$ [b]	3760–2915 (br,s) [c]	–	1549 (s)	1413 (s)	260 (w)
$Co(C_3H_3O_2)_2 2H_2O$	3780–3000 (br,s)	–	1554 (s)	1407 (s)	347 (m)
$Ni(C_3H_3O_2)_2H_2O$	3720–3000 (br,s)	–	1570 (s)	1413 (s)	284 (w)
$Cu(C_3H_3O_2)_2(C_3H_4O_2)_3H_2O$	3790–3040 (br,s)	1722 (s)	1566 (s)	1407 (s)	269 (w)
$Zn(C_3H_3O_2)_2H_2O$	3780–2920 (br,s)	–	1593 (s)	1413 (s)	352 (m)

[a] Poly(acrylic acid).
[b] $C_3H_3O_2^-$, acrylate ion.
[c] br, broad; s, strong; m, medium; w, weak.

TABLE 3

Colour, electronic spectra and magnetic moments of the compounds

Compound	Colour	Band position (cm^{-1})	μ (BM)
$Mn(C_3H_3O_2)_2H_2O$	White	19400 25200 25500	5.92
$Co(C_3H_3O_2)_22H_2O$	Blue	6472 15918	4.64
$Ni(C_3H_3O_2)_2H_2O$	Green	8621 14815 25000	2.91
$Cu(C_3H_3O_2)_2(C_3H_4O_2)_3H_2O$		14925	1.64
$Zn(C_3H_3O_2)_2H_2O$	White	–	–

in this compound comes from the magnetic moment which is found to have a value between 4.2 and 4.8 BM, the range normally observed for compounds that have tetrahedral structures [5]. The nickel compound, which has bands in its electronic spectrum at 8621, 14815 and 25000 cm^{-1}, has the nickel atom in an octahedral environment [2]. The bands correspond to the d–d transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$. The magnetic moment for the compound which is in the range 2.8–3.4 BM, further supports the suggestion of an octahedral environment for the nickel ion [2]. The single broad absorption band in the electronic spectrum of the copper compound at 14925 cm^{-1} would suggest that the copper ion is in an octahedral environment [2]. The band corresponds to the d–d transition $^2E_g(D) \rightarrow {}^2T_{2g}(D)$.

The magnetic moment of 1.64 BM for this compound indicates some magnetic spin–spin interaction between the copper atoms. Evidence for the environment of the zinc atom in the zinc compound is obtained from the far-infrared spectrum of the compound. The wavenumber of the Zn–O band in the zinc compound is similar to that normally observed for compounds that have tetrahedral structures [6]. The value for the band is similar to that observed for the cobalt compound which has been postulated as having the cobalt atom in a tetrahedral environment. The bands assigned for the metal–oxygen vibrations of the manganese, nickel and copper compounds agree with the suggestion that the metal atom is in an octahedral environment in these compounds [7].

The fact that the compounds were obtained as powders and not as single crystals means that no complete structure determination can be made. However spectral data for the zinc compound and spectroscopic and magnetic data for the manganese, cobalt, nickel and copper compounds enable us to predict the environment of the metal in each of the compounds. For the manganese and nickel compounds it is suggested that the metal atoms are bonded to carboxylate groups in the same poly(acrylate) chain or to carboxylate groups in different poly(acrylate) chains, to give a planar four-coordinate environment for the metal atoms. A six-coordinate environment for each metal atom is obtained by the metal atom bonding to oxygen atoms of other poly(acrylate) chains. A similar structure is postulated for the copper compound except that as well as the acrylate groups which form the bonds with the copper atoms, there will also be carboxylic acid groups present which will not be involved in bonding with the copper ions. For the cobalt and zinc compounds it is postulated that the metal atoms are bonded to oxygen atoms of different poly(acrylate) chains to give a tetrahedral environment for the metal ions. The water molecules are attached by hydrogen bonding in each of the compounds.

The TG and DTA traces for poly(acrylic acid) are shown in Fig. 1. The pyrolytic decomposition starts at 58° C and finishes at 640° C with total elimination of the sample. The DTA trace shows a glass transition at 87° C, followed by exothermic peaks for the decomposition process. The TG and DTA traces for the polymer–metal complexes formed between poly(acrylic acid) and the transition metals manganese, cobalt, nickel, copper and zinc are given in Figs. 2–6. The dehydration of the complexes starts below 100° C, further supporting the suggestion that the water is present as water of crystallisation [8]. The dehydration of the complexes 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 process associated with these compounds was observed in the DTA traces. The dehydration enthalpies have been calculated and are given in Table 4. 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 metallic oxides, see Table 5.

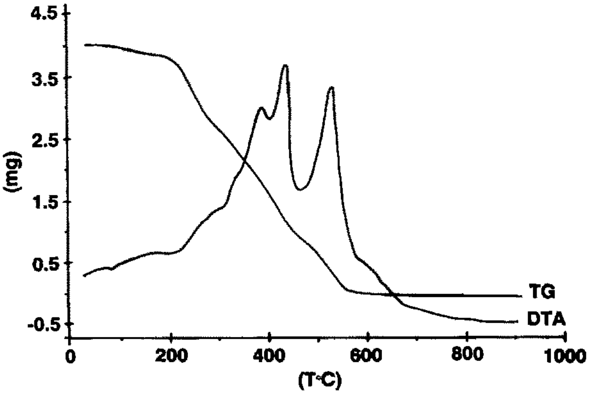

Fig. 1. TG and DTA trace of poly(acrylic acid); sample weight = 4.02 mg.

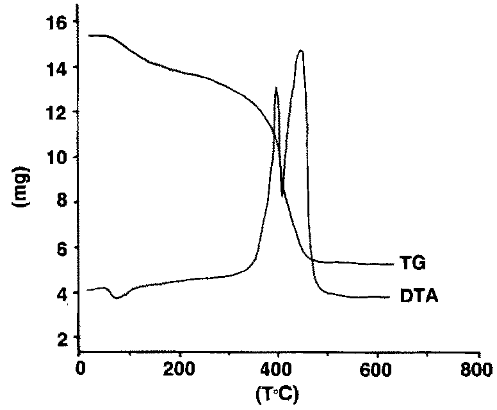

Fig. 2. TG and DTA trace of $Mn(C_3H_3O_2)_2H_2O$; sample weight =15.20 mg.

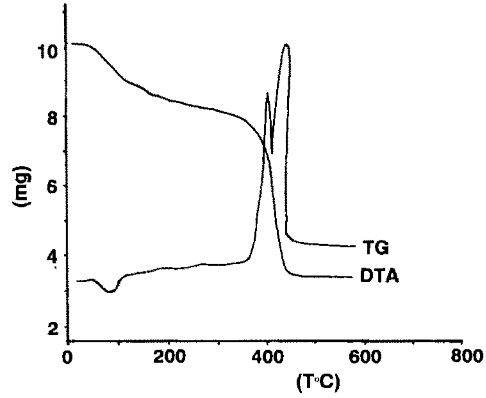

Fig. 3. TG and DTA trace of $Co(C_3H_3O_2)_22H_2O$; sample weight =10.32 mg.

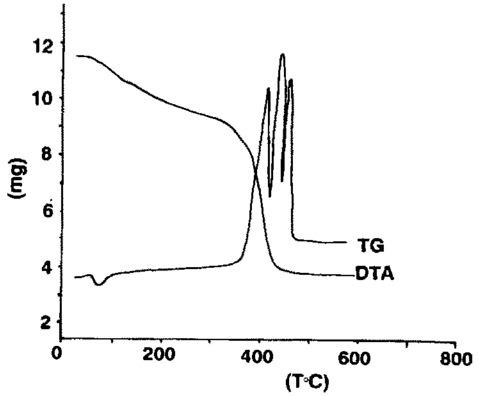

Fig. 4. TG and DTA trace of $Ni(C_3H_3O_2)_2H_2O$; sample weight =11.53 mg.

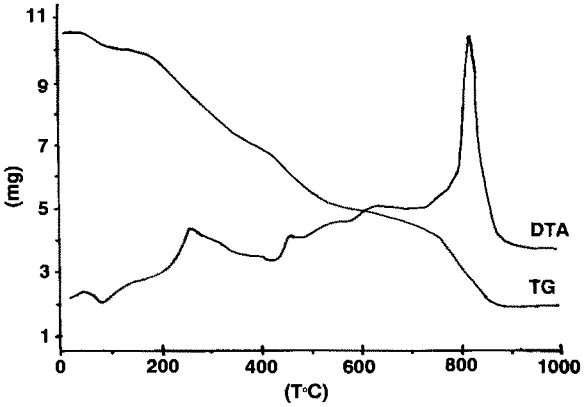

Fig. 5. TG and DTA trace of $Cu(C_3H_3O_2)_2(C_3H_4O_2)_3H_2O$; sample weight = 10.63 mg.

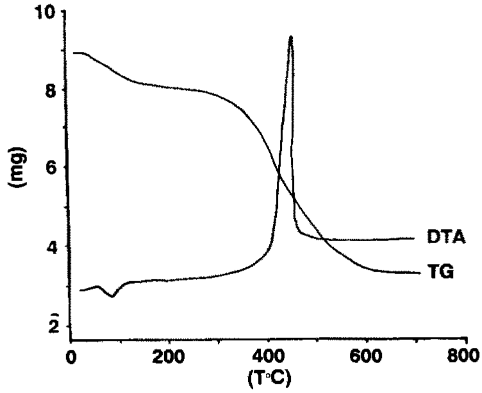

Fig. 6. TG and DTA trace of $Zn(C_3H_3O_2)_2H_2O$; sample weight = 8.96 mg.

TABLE 4

Dehydration process of the poly(acrylic acid) metal compounds

Process [a]	Peak temp. (°C)	Thermal nature of the transformation	Weight loss (%)		Enthalpy (kJ mol^{-1})
			Calc.	Found	
$Mn(C_3H_3O_2)_2H_2O \rightarrow Mn(C_3H_3O)_2$	70	Endo	8.37	7.93	41
$Co(C_3H_3O_2)_22H_2O \rightarrow Co(C_3H_3O_2)_2$	91	Endo	15.39	14.72	67
$Ni(C_3H_3O_2)_2H_2O \rightarrow Ni(C_3H_3O_2)_2$	68	Endo	8.23	8.06	43
$Cu(C_3H_3O_2)_2(C_3H_4O_2)_3H_2O \rightarrow Cu(C_3H_3O_2)_2(C_3H_4O_2)_3$	74	Endo	4.09	4.04	87
$Zn(C_3H_3O_2)_2H_2O \rightarrow Zn(C_3H_3O_2)_2$	79	Endo	7.98	8.12	40

[a] $C_3H_3O_2^-$, acrylate ion; $C_3H_4O_2$, acrylic acid.

TABLE 5

Decomposition process of poly(acrylic acid) and the metal compounds

Process	Temperature range (°C)	Thermal nature of the transformation	Residue (%)	
			Calc.	Found
$C_3H_4O_2$ → pyrolitic process	58–640	Exo	–	–
$Mn(C_3H_3O_2)_2 \rightarrow Mn_2O_3$	176–502	Exo	36.72	36.16
$Co(C_3H_3O_2)_2 \rightarrow Co_3O_4$	168–470	Exo	33.92	33.61
$Ni(C_3H_3O_2)_2 \rightarrow NiO$	136–488	Exo	34.15	33.81
$Cu(C_3H_3O_2)_2(C_3H_4O_2)_3 \rightarrow CuO$	144–886	Exo	18.09	18.36
$Zn(C_3H_3O_2)_2 \rightarrow ZnO$	172–542	Exo	36.10	36.35

In the DTA traces these decomposition processes correspond to exothermic effects for the complexes and these have been indicated in Table 5.

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