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Structural and thermal studies of the chloro complexes of cobalt, nickel and copper with 2,2-bis(acrylamido)acetic acid and assessment of their suitability as anti-static additives for polyethylene

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Abstract

The preparation and properties of the complexes of 2,2-bis(acrylamido)acetic acid with cobalt, nickel and copper are described. Spectral, magnetic and solubility studies indicate that the complexes have polymeric octahedral structures. The decomposition of each compound has been studied using thermogravimetry and differential thermal analysis. The complexes, which are hydrated, lose water followed by organic ligand to give the metal oxide. The compound 2,2-bis(acrylamido)acetic acid and its metal complexes have been investigated as possible anti-static additives, but were found to be less effective than the commercial compounds. However, there is evidence that they may produce longer lasting anti-static properties.

INTRODUCTION

Polyethylene is a thermoplastic polymer which has a wide commercial application. However, the surface of the polymer is subject to accumulation of static electricity which can discharge to the atmosphere, causing explosion and fire risks. For this reason, anti-static agents such as diglycerides, ethoxylated fatty amines and ammonium salt derivatives [1] are incorporated into the polymer during the moulding process. This paper describes an investigation into the use of the complexes of cobalt, nickel and copper with 2,2-bis(acrylamido)acetic acid, $(H_2C{=}CHCONH)_2CHCO_2H$, as anti-static agents for polyethylene.

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Spectral studies have been used to characterise each of the metal complexes and to interpret the type of coordination which takes place to the metal ion. A thermal stability study of 2,2-bis(acrylamido)acetic acid and its metal complexes has also been carried out.

EXPERIMENTAL

Preparation of complexes

The complexes of cobalt, nickel and copper with 2,2-bis(acrylamido)-acetic acid were prepared by adding 1.5 mmol of hydrated metal carbonate to 200 cm^3 of a warm solution of 2,2-bis(acrylamido)acetic acid (2 mmol in water). Excess metal carbonate was removed by filtration, and the filtrate was heated at 70°C until half of the water had evaporated. The complexes precipitated on cooling and were filtered off, washed with boiling water, and oven dried at 60°C. The cobalt complex was red, the nickel complex was green, and the copper complex was blue.

Preparation of metal complex/high density polyethylene (HDPE) blends

Concentrations of 0.5% (w/w) of each metal complex, 2,2-bis(acrylamido)acetic acid ligand and commercial anti-static agent respectively were preblended with 36 g of HDPE. The preblends were added to a Brabender Plasticorder and mixed at a temperature of 160°C using a rotor speed of 60 r.p.m. After 5 minutes, the blends were removed and compression moulded at 180°C into small plaques (1 mm thick) and films (0.1 mm thick) for subsequent measurement of surface resistivity and charge decay respectively.

Apparatus and measurements

The concentration of the metal ion was obtained using a Perkin-Elmer 373 atomic absorption spectrophotometer. The carbon, hydrogen and nitrogen analyses were made 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}) with a Perkin-Elmer IR spectrophotometer model 598.

The electronic spectra were obtained using a Beckman Acta MIV spectrophotometer to record 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 all cases the 200–800°C range was studied. Surface resistivity measurements were carried out to BS 2782; Part 2; 1976 using a Hewlett-Packard 1600 8A resistivity cell.

Charge decay measurements were carried out using equipment at BP Chemicals Ltd, Grangemouth Research and Development Department, which conformed to BS 2782: Part 2: Method 250C: 1976.

RESULTS AND DISCUSSION

The compounds prepared from aqueous solution are listed in Table 1. The analytical results indicate a stoichiometry for each compound of $ML_2 \cdot xH_2O$, where $x = 3$ for cobalt and nickel, and $x = 6$ for copper.

The wavenumbers of the IR absorption bands for 2,2-bis(acrylamido)-acetic acid and its metal complexes are shown in Table 2, together with the description and assignments. The IR spectrum of the 2,2-bis(acrylamido)acetic acid shows the existence of two bands in the N–H stretching region, not a single band as would be expected for a secondary amide. It is suggested that the doublet is due to the existence of NH_2^+ groups produced by proton transfer from the –COOH group to the –NH– group. The IR spectra of the complexes show strong, broad absorption peaks in the region 3630–2780 cm^{-1}, ν(OH) indicating the presence of water of crystallisation. These broad bands obscure the bands resulting from the NH vibrations of the amide. Each of the complexes was heated on a thermobalance at a fixed temperature until constant weight was obtained to remove the water molecules. The IR spectrum was then obtained for each of the anhydrous compounds, with the resultant N–H and C=O vibrations of the amide group [2] listed in Table 2. The spectra of all the complexes confirm the absence of free carboxylic acid groups. The usual reduction in ν(COO) compared with free COOH is observed, characteristic of bonding type **I** [3].

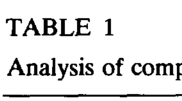

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TABLE 1

Analysis of compounds (%)

Compound		Metal	Carbon	Nitrogen	Hydrogen
$Co(C_8H_9N_2O_4)_2 \cdot 3H_2O$	Theory	11.62	37.88	11.04	4.77
	Found	11.37	37.29	10.74	4.69
$Ni(C_8H_9N_2O_4)_2 \cdot 3H_2O$	Theory	11.58	37.90	11.05	4.77
	Found	11.42	37.47	10.66	4.76
$Cu(C_8H_9N_2O_4)_2 \cdot 6H_2O$	Theory	11.23	33.95	9.90	4.99
	Found	11.33	33.48	9.56	5.12

TABLE 2

Infrared spectra (4000–200 cm^{-1})

Compound	$\nu_{O-H}(H_2O)$	$\nu_{N-H}(NHCO)$	$\nu(COO)$	$\nu(C=C)$	$\nu(M-O)$	$\nu_{N-H}(CONH)$
$C_8H_{10}N_2O_4$	–	3342(s), 3281(s)	1600(s)	1626(m)	–	1664(s)
$Co(C_8H_9N_2O_4)_2 \cdot 3H_2O$	3600–2780(br, s)	3299(s)	1610(s)	1624(sh)	294(s); 283(sh)	1657(s)
$Ni(C_8H_9N_2O_4)_2 \cdot 3H_2O$	3630–2780(br, s)	3280(s)	1612(s)	1622(sh)	296(s); 285(sh)	1652(s)
$Cu(C_8H_9N_2O_4)_2 \cdot 6H_2O$	3620–2800(br, s)	3271(s)	1610(s)	1622(sh)	299(s); 291(sh)	1652(s)

Key: br, broad; s, strong; m, medium; sh, shoulder.

The bands in the 1626–1622 cm^{-1} region are assigned to the $\nu(C{=}C)$ vibration. It is suggested that the C=C group is not involved in bonding with metal ions because a marked shift to a lower wavenumber is not observed on complexation [3]. The metal–oxygen bands listed in Table 2 would suggest that the metal ions in the complexes are in an octahedral environment [3, 4].

The electronic spectra and the magnetic measurements, Table 3, agree with the suggestion that for the cobalt and nickel complexes the metal ions are in an octahedral environment [3]. The single broad absorption band in the electronic spectrum of the copper compound at 12 500 cm^{-1} indicates that the copper atom is also in a octahedral environment [3]. The magnetic moment of 1.52 BM for this compound is indicative of copper–copper magnetic interaction.

Single crystals of the compounds could not be isolated from aqueous solution, thus no definite structures can be described. However, the spectroscopic and magnetic data enable the prediction that the metal ions are in an octahedral environment in the complexes. The poor solubility of the metal complexes in polar and non-polar solvents indicates that they have polymeric structures [3]. It is suggested that the complexes have a planar arrangement, with the carboxylate groups and the carbonyl groups (amide) of two different 2,2-bis(acrylamido)acetate ions bonded to a metal atom to give one layer. The six coordinate environment for each of the metal ions is obtained by oxygen atoms of the carboxylate groups in adjacent layers bonding to the metal to give a polymeric structure. Water molecules are attached by hydrogen bonding.

The TG and DTA traces for 2,2-bis(acrylamido)acetic acid and its cobalt, nickel and copper complexes are shown in Figs. 1–4. The TG trace for 2,2-bis(acrylamido)acetic acid (Fig. 1) shows that this compound is thermally stable in the range 20–186°C. Pyrolytic decomposition starts at 186°C and finishes around 536°C with the total elimination of the sample. The DTA traces displays a sharp exothermic peak followed by further

TABLE 3

Electronic spectra and magnetic moments

Compound	Band position (cm^{-1})	*d–d* transition	μ (BM)
$Co(C_8H_9N_2O_4)_2 \cdot 3H_2O$	8064	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	4.90
	19230	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	
$Ni(C_8H_9N_2O_4)_2 \cdot 3H_2O$	8190	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	3.38
	15150	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	
	25316	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	
$Cu(C_8H_9N_2O_4)_2 \cdot 6H_2O$	12500	$^2E_g(D) \rightarrow {}^2T_{2g}(D)$	1.52

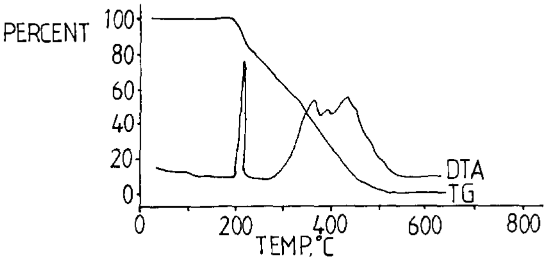

Fig. 1. TG and DTA trace for 2,2-bis(acrylamido)acetic acid. Sample weight = 9.49 mg.

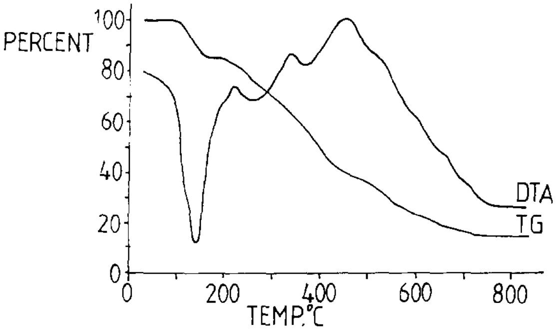

Fig. 2. TG and DTA trace for $Co(C_8H_9N_2O_4)_2 \cdot 3H_2O$. Sample weight = 8.45 mg.

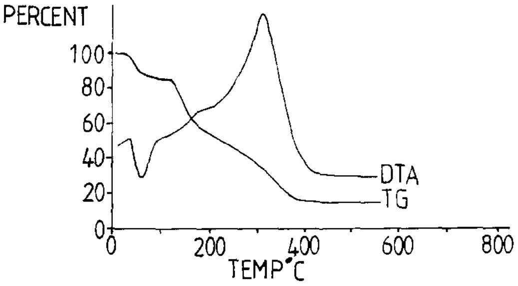

Fig. 3. TG and DTA trace for $Ni(C_8H_9N_2O_4)_2 \cdot 3H_2O$. Sample weight = 9.52 mg.

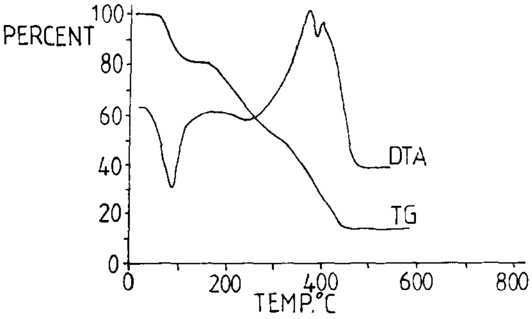

Fig. 4. TG and DTA trace for $Cu(C_8H_9N_2O_4)_2 \cdot 6H_2O$. Sample weight = 8.74 mg.

TABLE 4

Decomposition processes of the metal complexes

Process	Temperature range (°C)	Mass loss (%)	
		Calc.	Found
$C_8H_{10}N_2O_4 \rightarrow$ pyrolytic process	187–253 (EXO)	100	100
$Co(C_8H_9N_2O_4)_2 \cdot 3H_2O \rightarrow Co(C_8H_9N_2O_4)_2$	89–170 (ENDO)	10.6	10.5
$Co(C_8H_9N_2O_4)_2 \rightarrow Co_3O_4$	178–542 (EXO)	86.3	86.1
$Ni(C_8H_9N_2O_4)_2 \cdot 3H_2O \rightarrow Ni(C_8H_9N_2O_4)_2$	32–114 (ENDO)	10.6	10.6
$Ni(C_8H_9N_2O_4)_2 \rightarrow NiO$	124–422 (EXO)	86.3	86.1
$Cu(C_8H_9N_2O_4)_2 \cdot 6H_2O \rightarrow Cu(C_8H_9N_2O_4)_2$	62–142 (ENDO)	19.0	19.1
$Cu(C_8H_9N_2O_4)_2 \rightarrow CuO$	148–508 (EXO)	86.0	85.9

Key: ENDO, endothermic; EXO, exothermic (obtained from DTA curve).

broad exothermic peaks produced during decomposition. The TG and DTA traces for the complexes formed between 2,2-bis(acrylamido)acetic acid and cobalt, nickel and copper are given in Figs. 2–4. The dehydration process in each of the complexes takes place in one step. The observed weight losses for these processes compare favourably with the theoretical values (Table 4). The endothermic peak observed in the DTA traces is as expected for the dehydration processes. Exothermic decomposition of the anhydrous complexes follows the dehydration process, and the residual weights are in good agreement with the theoretical values required for the metal oxides (see Table 5).

The high density polyethylene (HDPE) samples containing the complexes and the commercial anti-static additives have lower surface resistivities than the pure HDPE or the HDPE containing 2,2-

TABLE 5

Electrical properties of HDPE blends

Compound	Surface resistivity (ohms)		Charge decay (S)	
	0^a	336^a	0^a	336^a
HDPE	1.50×10^{17}	9.40×10^{16}	>120	>120
$C_8H_{10}N_2O_4$/HDPE	6.02×10^{16}	1.32×10^{16}	>120	>120
Commercial additive/HDPE	1.32×10^{13}	7.52×10^{13}	1.0	1.0
$Co(C_8H_9N_2O_4)_2 \cdot 3H_2O$/HDPE	1.05×10^{16}	7.52×10^{15}	>120	>120
$Ni(C_8H_9N_2O_4)_2 \cdot 3H_2O$/HDPE	4.70×10^{16}	1.88×10^{16}	>120	>120
$Cu(C_8H_9N_2O_4)_2 \cdot 6H_2O$/HDPE	5.45×10^{16}	5.64×10^{16}	>120	>120

[a] Time after moulding (h).

bis(acrylamido)acetic acid, both initially and 336 hours after moulding (see Table 5). The metal complexes do not reduce the surface resistivity as much as the commercial anti-static additive. The charge decay measurements (Table 5) provide no information about how quickly charge is dissipated from the surface of the HDPE containing the metal complexes.

The commercial additive has a similar performance both initially and 336 hours after moulding. The type of polymer structure described for the metal complexes may be a major contributing factor in inhibiting the migration of charge to the surface of the HDPE. Furthermore, although the commercial additive itself can readily migrate to the surface of the HDPE, migration of the metal complexes will be inhibited in mobility as a result of their polymeric nature.

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