Structural and thermal studies of the chloro complexes of cobalt, nickel and copper with 2,6-diaminopyridine and an assessment of their suitability as anti-static additives for polyethylene

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Abstract

The preparation and some properties of the complexes of 2,6-diaminopyridine with the chlorides of cobalt, nickel and copper are described. Spectral, magnetic and solubility studies indicate that the cobalt and nickel complexes have polymeric octahedral structures, whereas the copper complex has a tetragonal structure. The thermal behaviour of these complexes has been studied by thermogravimetry and differerential thermal analysis. The thermal decomposition studies show that the compounds decompose with loss of organic ligand and halogen to give the metal oxide. The complexes were 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

During moulding and extrusion processes, molten polyethylene is in contact with metal surfaces and the separation process which takes place can lead to high static charge. The accumulation of this static electricity on the surface of the polymer can give rise to dangerous situations such as fire and explosion hazards due to high energy discharges in air. Furthermore, surface soiling can occur producing items of unacceptable appearance to the consumer. Anti-static agents such as fatty acid mono/diglycerides and ethoxylated fatty amines are used to overcome the static accumulation. This paper describes an investigation into the use of the chloro complexes of cobalt, nickel and copper with 2,6-diaminopyridine as anti-static agents for polyethylene. The ligand has two

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types of donor sites, the nitrogen atom of the aromatic ring and the nitrogen atom of the amine groups.
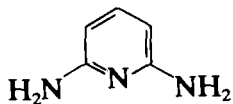
2,6-Diaminopyridine ($C_5H_7N_3$)

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 2,6-diaminopyridine and its metal complexes has also been carried out.

EXPERIMENTAL

Preparation of complexes

The chloro complexes of cobalt, nickel and copper with 2,6-diaminopyridine were prepared by adding 25 cm^3 of a warm solution of hydrated metal halide (0.01 mol in ethanol) to 25 cm^3 of a warm solution of 2,6-diaminopyridine (0.02 mol in ethanol). The complexes precipitated on cooling and were filtered, purified by repeated washing with boiling ethanol, and air dried. The cobalt complex was brown, the nickel complex dark brown and the copper complex was dull grey.

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

Each metal complex, the 2,6-diaminopyridine ligand and a commercial anti-static agent, respectively, (0.5% w/w) were pre-blended with 36 g of HDPE. The pre-blends were added to a Brabender plasticorder and mixed at a temperature of 160°C using a rotor speed of 60 rev min^{-1}. After 5 min, 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 and the carbon, hydrogen and nitrogen analyses were obtained 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 Beckmann 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. The TG and DTA curves were obtained at a heating rate of $10°C\,min^{-1}$. In all cases, the 20–800°C temperature 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 analytical results for the complexes agree with the stoichiometry of the complexes proposed in Table 1.

The molecular magnetic moments and the bands in the electronic spectra of the complexes are listed in Table 2. The energy of the wavenumbers and the magnetic moments for the compounds $Co_2(C_5H_7N_3)Cl_4$ and $Ni(C_5H_7N_3)Cl_2$ suggest that the metal atoms are in an octahedral environment [1]. The values obtained for the magnetic moments support this suggestion [1]. The copper complex has a single broad absorption band at 19,048 which suggests that the copper ion is in a tetragonal arrangement [2]. A magnetic moment of 1.72 BM was obtained for this complex.

The wavenumbers of the IR absorption bands for 2,6-diaminopyridine and its metal complexes are shown in Table 3 together with their description and assignments. The bands due to the ring vibration are found to move to higher wavenumbers on complexation, suggesting that bonding has taken place between the ring nitrogen atom and a metal ion [1]. The bands due to the $v(NH_2)$ vibrations are also observed to move to higher wavenumbers in the complexes. This is indicative of no coordination taking place between the metal and the nitrogen atom of an amine

TABLE 1

Analyses of compounds (%)

Compound		Metal	Carbon	Nitrogen	Hydrogen
$Co_2(C_5H_7N_3)Cl_4$	Theory	31.96	16.28	11.39	1.91
	Found	31.72	15.86	10.95	2.56
$Ni(C_5H_7N_3)Cl_2$	Theory	24.59	25.15	17.60	2.96
	Found	24.46	24.50	17.38	3.34
$Cu(C_5H_7N_3)_2Cl_2$	Theory	18.02	34.05	23.83	4.00
	Found	18.29	33.80	23.64	3.43

TABLE 2

Electronic spectra and magnetic moments

Compound	Band position (cm^{-1})	d–d Transition	μ (BM)
$Co_2(C_5H_7N_3)Cl_4$	6712	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	5.03
	14705	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	
	23256	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	
$Ni(C_5H_7N_3)Cl_2$	6667	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	3.36
	14285	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	
	21739	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	
$Cu(C_5H_7N_3)_2Cl_2$	19048	$^2B_1 \rightarrow {}^2A_1$	1.72

group [3] in the complexes. The bands associated with the $v(M–Cl)$ and $v(M–N)$ vibrations are also listed in Table 3.

Single crystals of the compounds could not be isolated from ethanolic solution, thus no definite structures can be described. However, the spectroscopic and magnetic data enable us to predict possible structures. The poor solubility of the metal complexes in polar and non-polar solvents indicates that they have polymeric structures [1]. It is suggested that the cobalt and nickel complexes have a four- and two-layer chain structure, respectively, in which each halogen atom is acting as a bridge between three metal atoms with the organic ligand in the trans positions [4]. The copper complex has a pseudo-planar structure with long bonds being formed from the copper atom in one plane to the halogen atoms in different planes as is observed in the structure of bispyridine copper(II) chloride [5].

The TG and DTA traces for 2,6-diaminopyridine and its cobalt, nickel and copper complexes are shown in Figs. 1–4. The TG trace for 2,6-diamonopyridine (Fig. 1), shows that this compound is thermally stable in the 20–118°C range. Its pyrolytic decomposition starts at 118°C and finishes at around 580°C with the total elimination of the sample. The DTA trace displays an endothermic peak at 122°C corresponding to

TABLE 3

Infrared spectra (4000–200 cm^{-1})

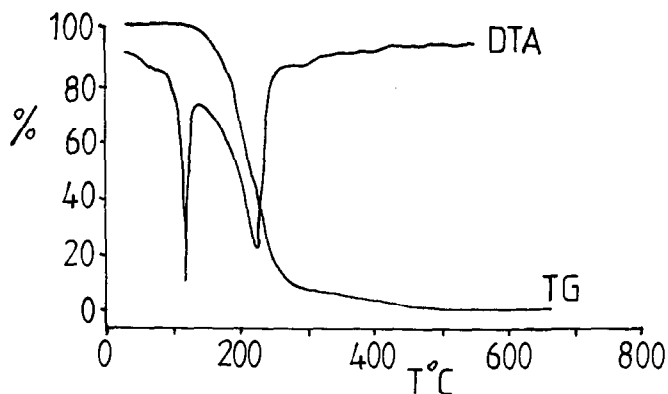| Compound	$v(NH_2)$	Ring vibrations	$v(M–Cl)$	$v(M–N)$
$C_5H_7N_3$	3388 (s), 3128 (s)	1594 (s), 1454 (s)	–	–
$Co_2(C_5H_7N_3)Cl_4$	3548 (s), 3324 (s)	1598 (s), 1458 (s)	270 (w)	216 (w)
$Ni(C_5H_7N_3)Cl_2$	3550 (s), 3329 (s)	1622 (s), 1459 (s)	248 (w)	214 (w)
$Cu(C_5H_7N_3)_2Cl_2$	3405 (s), 3296 (s)	1614 (s), 1462 (s)	245 (w)	210 (w)

Key: s, strong; w, weak.

Fig. 1. TG and DTA trace for $(C_5H_7N_3)$. Sample weight = 9.67 mg.

fusion. The value of the fusion enthalpy is $15 \, kJ \, mol^{-1}$. Liquid 2,6-diaminopyridine decomposes immediately with an endothermic peak at 226°C. The TG and DTA traces for the complexes formed between 2,6-diaminopyridine and the chlorides of cobalt, nickel and copper are given in Figs. 2–4.

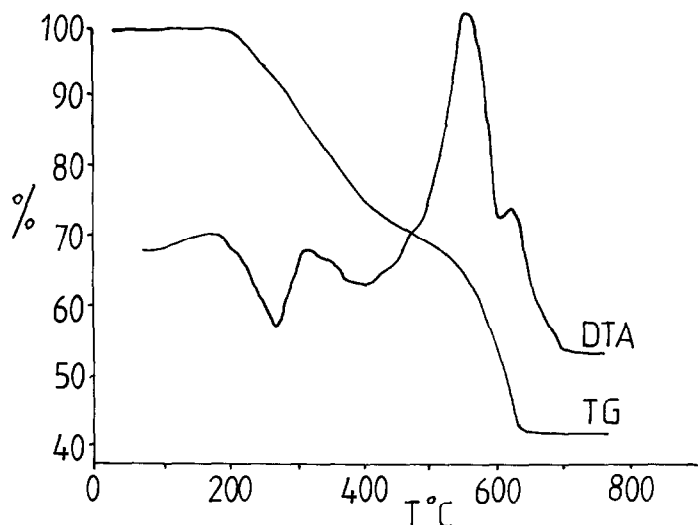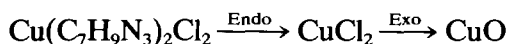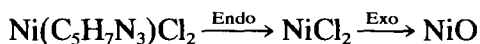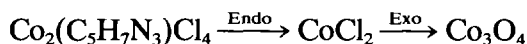The thermal decomposition schemes for the complexes are

$$Co_2(C_5H_7N_3)Cl_4 \xrightarrow{Endo} CoCl_2 \xrightarrow{Exo} Co_3O_4$$

$$Ni(C_5H_7N_3)Cl_2 \xrightarrow{Endo} NiCl_2 \xrightarrow{Exo} NiO$$

$$Cu(C_7H_9N_3)_2Cl_2 \xrightarrow{Endo} CuCl_2 \xrightarrow{Exo} CuO$$

Fig. 2. TG and DTA trace for $Co_2(C_5H_7N_3)Cl_4$. Sample weight = 8.20 mg.
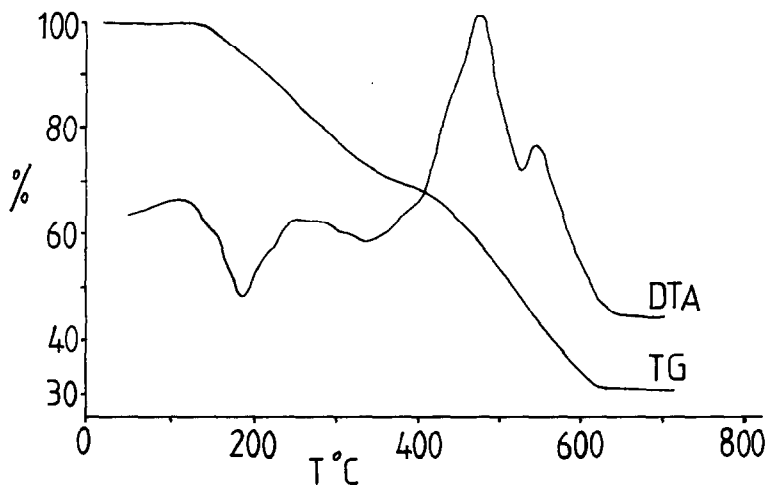
Fig. 3. TG and DTA trace for Ni(C$_5$H$_7$N$_3$)Cl$_2$. Sample weight = 8.64 mg.

The observed weight losses for these processes compare favourably with the theoretical values in Table 4.

The high-density polyethylene (HDPE) samples containing the commercial anti-static additives have lower surface resistivities than the pure HDPE, or the HDPE containing 2,6-diaminopyridine, both initially and 336 h after moulding, Table 5. The metal complexes do not reduce the surface resistivity as much as the commercial anti-static additive. The surface resistivity both 0 h and 336 h after moulding shows a marked improvement in the anti-static properties of the uncomplexed 2,6-diaminopyridine when compared to the complexed 2,6-diaminopyridine. The disappointing results observed for the surface resistivity measurements of the cobalt complex are possibly due to the fewer 2,6-diaminopyridine molecules present in the structure. The charge decay
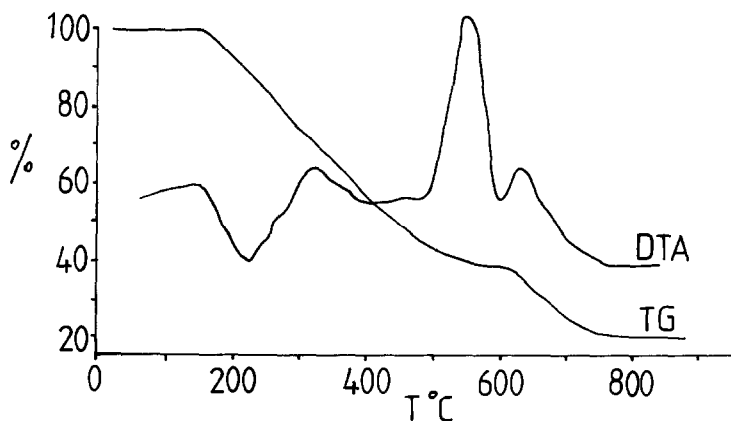

Fig. 4. TG and DTA trace for Cu(C$_7$H$_9$N$_3$)$_2$Cl$_2$. Sample weight = 7.65 mg.

TABLE 4

Decomposition processes of the metal complexes

Process	Temperature range (°C)	% Mass loss	
		Calc.	Found
$C_5H_7N_3 \rightarrow$ pyrolytic process	118–580 (Endo)	100	100
$Co_2(C_5H_7N_3)Cl_4 \rightarrow CoCl_2$	196–468 (Endo)	29.6	29.5
$CoCl_2 \rightarrow Co_3O_4$	468–659 (Exo)	29.8	29.7
$Ni(C_5H_7N_3)Cl_2 \rightarrow NiCl_2$	139–364 (Endo)	29.8	29.7
$NiCl_2 \rightarrow NiO$	364–646 (Exo)	29.8	29.7
$Cu(C_7H_9N_3)_2Cl_2 \rightarrow CuCl_2$	161–558 (Endo)	61.9	61.8
$CuCl_2 \rightarrow CuO$	558–738 (Exo)	15.6	15.4

Key: Endo, endothermic; Exo, exothermic (obtained from DTA curves).

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
$C_5H_7N_3$/HDPE	9.78×10^{15}	5.26×10^{15}	>120	>120
Commercial additive/HDPE	1.32×10^{13}	7.52×10^{13}	1.0	1.0
$Co_2(C_5H_7N_3)Cl_4$/HDPE	1.88×10^{17}	1.88×10^{17}	>120	>120
$Ni(C_5H_7N_3)Cl_2$/HDPE	7.52×10^{16}	5.64×10^{16}	>120	>120
$Cu(C_5H_7N_3)_2Cl_2$/HDPE	2.44×10^{16}	1.88×10^{16}	>120	>120

[a] Time after moulding (h).

measurements, Table 4, provide no information about how quickly charge is dissipated from the surface of the HDPE. This is possibly due to the polymeric structures of the metal complexes which make migration of these compounds to the surface of the HDPE system more difficult.

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