Structural and thermal studies of the chloro complexes of cobalt, nickel and copper with 4-aminobenzoyl hydrazide and an assessment of their suitability as anti-static additives for polyethylene

J.R. Allan[a], A.R. Gardner[a], B. McCloy[a] and W.E. Smith[b]

[a] *Department of Applied Chemical and Physical Studies, Napier University, Edinburgh (UK)*
[b] *Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow (UK)*

(Received 3 March 1992)

Abstract

The preparation and some properties of the complexes of 4-aminobenzoyl hydrazide with the chlorides of cobalt, nickel and copper are described. Compounds of stoichiometry $Co(C_7H_9N_3O)_2Cl_2$, $Co(C_7H_9N_3O)Cl_2$, $Ni(C_7H_9N_3O)Cl_2$ and $Cu_2(C_7H_9N_3O)Cl_4$ were obtained. Spectral and magnetic studies have been used to provide information about the stereochemistry of the compounds. The compounds $Co(C_7H_9N_3O)_2Cl_2$, $Ni(C_7H_9N_3O)Cl_2$ and $Cu_2(C_7H_9N_3O)Cl_4$ have polymeric octahedral structures, whereas the compound $Co(C_7H_9N_3O)Cl_2$ has a polymeric tetrahedral structure. The thermal behaviour of the complexes has been studied by thermogravimetry and differential thermal analysis. The compounds $Co(C_7H_9N_3O)Cl_2$, $Co(C_7H_9N_3O)_2Cl_2$ and $Cu_2(C_7H_9N_3O)Cl_4$ decompose to give intermediate compounds before the metal oxide is formed. The compound $Ni(C_7H_9N_3O)Cl_2$ decomposes to give nickel chloride and then nickel 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

Polymeric materials, due to their outstanding properties, have extensive commercial applications. However, in certain applications there can be problems such as the build-up of static electricity. In the case of polyethylene, during the moulding process the molten polymer is in contact with metal surfaces and the separation process which takes place can lead to high voltage charge. The accumulation of this static electricity on the surface of the polymer can often be observed by the build-up of

---

dust and dirt. 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 4-aminobenzoyl hydrazide as anti-static agents for polyethylene. 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 4-aminobenzoyl hydrazide and its metal complexes has also been carried out.

NH$_2$

CONHNH$_2$
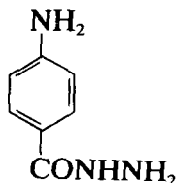
4-Aminobenzoyl hydrazide (C$_7$H$_9$N$_3$O)

EXPERIMENTAL

Preparation of the complexes

The chloro complexes of cobalt, nickel and copper with 4-aminobenzoyl hydrazide 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 4-aminobenzoyl hydrazide (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 pink, the nickel complex green and the copper complex was brown.

In addition, a blue cobalt complex was isolated by adding 25 cm^3 of a warm solution of 4-aminobenzoyl hydrazide (0.01 mol in ethanol) to 25 cm^3 of a warm solution of hydrated metal halide (0.02 mol in ethanol). The precipitation and filtering procedure was the same as above.

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

Each metal complex, the 4-aminobenzoyl hydrazide ligand 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 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. Most have the formula $MLCl_2$, with one of the cobalt complexes being ML_2Cl_2.

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

TABLE 1

Analyses of compounds (%)

Compound	Colour		Metal	Carbon	Nitrogen	Hydrogen
$Co(C_7H_9N_3O)_2Cl_2$	Pink	Theory	13.64	38.89	19.45	4.20
		Found	13.60	38.85	19.15	4.14
$Co(C_7H_9N_3O)Cl_2$	Blue	Theory	20.97	29.92	14.95	3.23
		Found	20.96	29.89	14.64	3.31
$Ni(C_7H_9N_3O)Cl_2$	Green	Theory	20.90	29.95	14.97	3.23
		Found	20.80	29.82	14.93	3.60
$Cu_2(C_7H_9N_3O)Cl_4$	Brown	Theory	30.26	20.01	10.00	2.16
		Found	29.83	19.62	10.17	2.36

TABLE 2

Electronic spectra and magnetic moments

Compound	Band position (cm^{-1})	d–d Transition	μ (BM)
$Co(C_7H_9N_3O)_2Cl_2$	9402	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(F)$	4.95
	18691	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	
	26315 sh	CT^a	
$Co(C_7H_9N_3O)Cl_2$	7092	$^4A_2(F) \rightarrow {}^4T_1(F)$	4.46
	16806	$^4A_2(F) \rightarrow {}^4T_1(P)$	
$Ni(C_7H_9N_3O)Cl_2$	8620	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	3.23
	14705	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	
	26316	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	
$Cu_2(C_7H_9N_3O)Cl_4$	12820	$^2E_g(D) \rightarrow {}^2T_{2g}(D)$	1.52

^{a} Metal to ligand charge transfer.

$Co(C_7H_9N_3O)_2Cl_2$ and $Ni(C_7H_9N_3O)Cl_2$ suggest that the metal atoms are in an octahedral environment [1, 2]. The magnetic moment and position of the bands for $Co(C_7H_9N_3O)Cl_2$ are indicative of the cobalt atoms being in a tetrahedral environment [2]. The copper compound has a broad absorption band between 10 000 and 15 000 cm^{-1}, suggesting an octahedral environment for the copper atoms [1]. The magnetic moment for this compound is lower than that expected for the spin-only value and is indicative of some copper–copper interaction in the compound.

The wavenumbers of the IR absorption bands for 4-aminobenzoyl hydrazide and its metal complexes are shown in Table 3 together with their description and assignments. The IR spectrum of 4-aminobenzoyl hydrazide shows two bands at 3420 and 3340 cm^{-1} which correspond to the N–H vibrations of the amine group. On complexation these bands are observed to move to lower wavenumbers, indicating that the nitrogen atom is coordinating to a metal ion [3].

TABLE 3

Infrared spectra (4000–200 cm^{-1})

Compound	$v(NH_2)$	$v(NH-NH_2)$	$v(C=O)$	$v(M-Cl)$	$v(M-N)$
$C_7H_9N_3O$	3420 (s), 3340 (s)	1004 (m)	1618 (s)	–	–
$Co(C_7H_9N_3O)_2Cl_2$	3410 (s), 3326 (s)	1020 (m)	1640 (s)	250 (m)	232 (w)
$Co(C_7H_9N_3O)Cl_2$	3324 (s), 3300 (s)	1012 (m)	1646 (s)	338 (s)	235 (w)
$Ni(C_7H_9N_3O)Cl_2$	3320 (s), 3240 (s)	1010 (m)	1648 (s)	256 (m)	232 (w)
$Cu_2(C_7H_9N_3O)Cl_4$	3360 (s), 3250 (s)	1024 (m)	1648 (s)	260 (m)	229 (w)

Key: s, strong; m, medium; w, weak.

The band at around 1630 cm^{-1} in the IR spectra of 4-aminobenzoyl hydrazide and its metal complexes is assigned to the $\nu(C=O)$ vibration. The increase in the wavenumber of the absorption frequency in the metal complexes of this carbonyl group suggests that no coordination is taking place through the oxygen to the metal ions [4]. The $\nu(N-N)$ vibration in the complexes moves to a higher wavenumber when comparison is made between the IR spectra of the complexes and of the 4-aminobenzoyl hydrazide. This indicates that bonding is taking place between a nitrogen atom of the N–N group and the metal ions [5]. The metal–halogen and metal–nitrogen bands are 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 complexes $Co(C_7H_9N_3O)Cl_2$, $Ni(C_7H_9N_3O)Cl_2$ and $Cu_2(C_7H_9N_3O)Cl_4$ in polar and non-polar solvents indicates that they have polymeric structures [1]. In the compound $Co(C_7H_9N_3O)Cl_2$, the cobalt ions exist in a tetrahedral environment where each is linked to a pair of chloride ions and where the polymeric chain is produced by one bond to the nitrogen atom of an NH_2 group in the aminobenzoyl hydrazide, and the other bond is through the N–N group of that ligand. The compound $Ni(C_7H_9N_3O)Cl_2$ consists of parallel chains of nickel atoms bonded to halogens with the aminobenzoyl hydrazide molecules as bridging units between adjacent chains, forming a sheet structure. In the copper compound, the arrangement is similar, except that it consists of two parallel chains of copper atoms bonded to halogens with the aminobenzoyl hydrazide molecules as bridging units. In the non-polymeric compound $Co(C_7H_9N_3O)_2Cl_2$, the cobalt ion is in an octahedral environment. Two molecules of the aminobenzoyl hydrazide are bonded to the cobalt ion through the nitrogen atom of the NH_2 group and through a
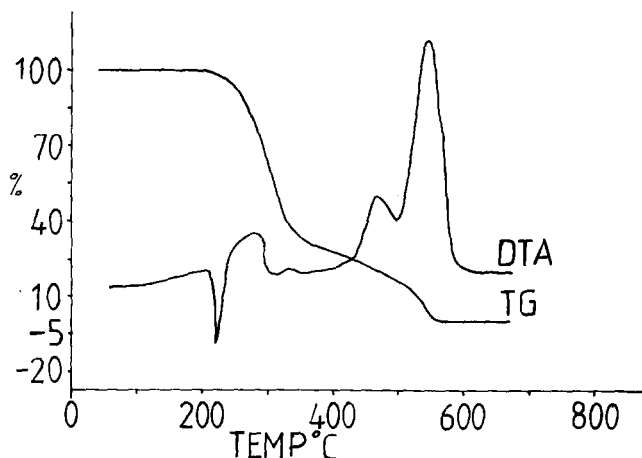

Fig. 1. TG and DTA trace for $C_7H_9N_3O$. Sample weight = 10.28 mg.

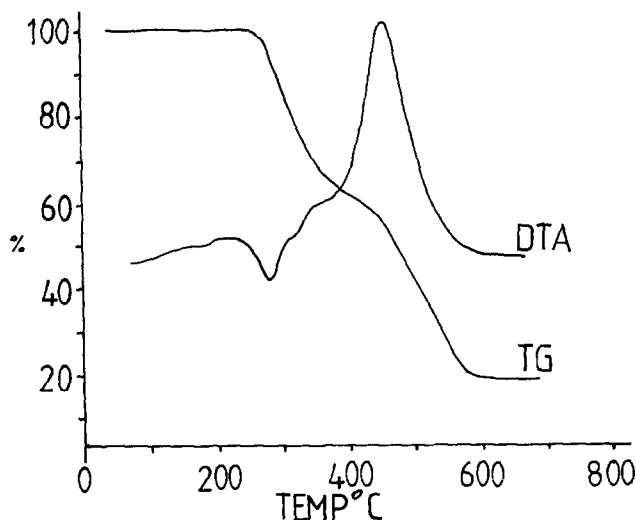Fig. 2. TG and DTA trace for Co(C₇H₉N₃O)₂Cl₂. Sample weight = 9.36 mg.

nitrogen atom of the N–N group in each aminobenzoyl hydrazide molecule. The octahedral environment is completed by the bonding of two chloride ions.

The TG and DTA traces for 4-aminobenzoyl hydrazide and its cobalt, nickel and copper complexes are shown in Figs 1–5. The TG trace for 4-aminobenzoyl hydrazide, Fig. 1, shows that this compound is thermally stable in the 20–198°C range. Its pyrolytic decomposition starts at 198°C and finishes at around 580°C with the total elimination of the sample. The DTA trace displays an endothermic peak at 225°C corresponding to fusion. The decomposition of 4-aminobenzoyl hydrazide produces exothermic effects in the DTA trace. The TG and DTA traces for the complexes formed between 4-aminobenzoyl hydrazide and the chlorides of cobalt, nickel and copper are given in Figs 2–5. The thermal
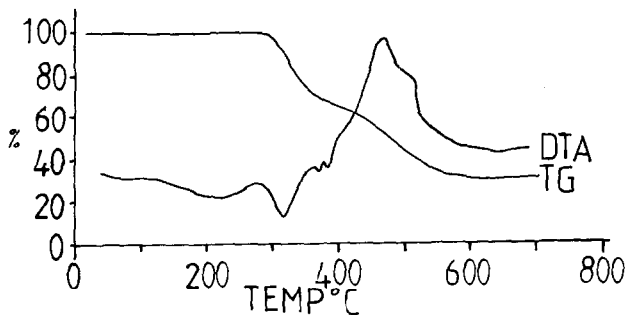

Fig. 3. TG and DTA trace for Co(C₇H₉N₃O)Cl₂. Sample weight = 7.98 mg.
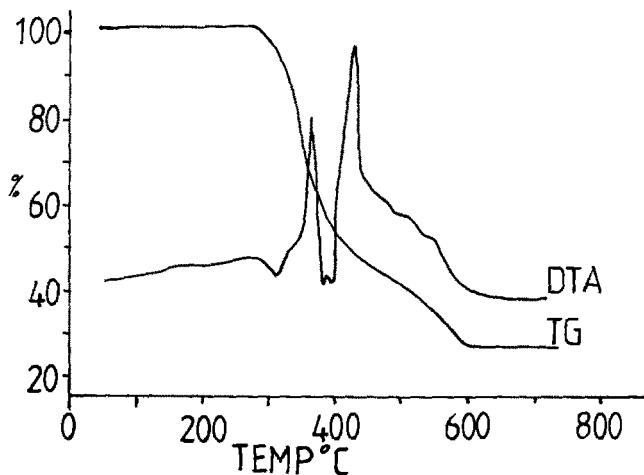
Fig. 4. TG and DTA trace for $Ni(C_7H_9N_3O)Cl_2$. Sample weight $= 8.64$ mg.

decomposition schemes for the complexes are:

$$Co(C_7H_9N_3O)_2Cl_2 \xrightarrow{Endo} Co(C_7H_9N_3O)Cl_2 \xrightarrow{Exo} Co_3O_4$$

$$Co(C_7H_9N_3O)Cl_2 \xrightarrow{Endo} Co_3(C_7H_9N_3O)Cl_6 \xrightarrow{Exo} Co_3O_4$$

$$Ni(C_7H_9N_3O)Cl_2 \xrightarrow{Endo} NiCl_2 \xrightarrow{Exo} NiO$$

$$Cu_2(C_7H_9N_3O)Cl_4 \xrightarrow{Endo} Cu_4(C_7H_9N_3O)Cl_8 \xrightarrow{Exo} CuO$$
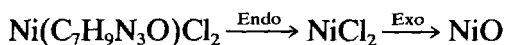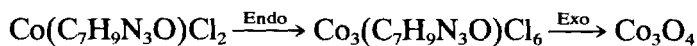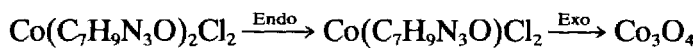
The observed weight losses for these processes compare favourably with the theoretical values in Table 4.
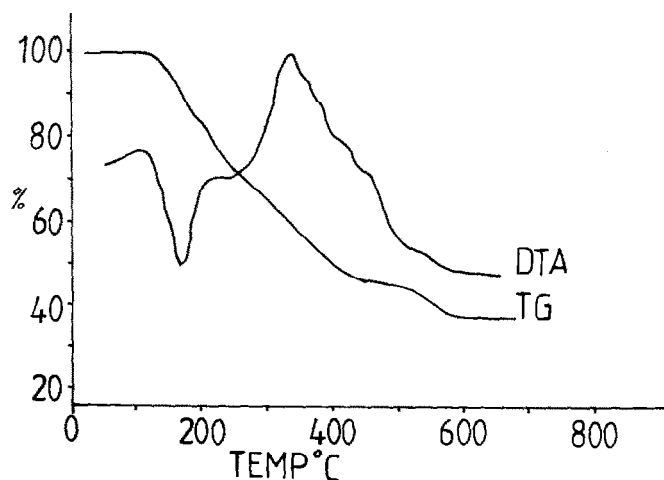
Fig. 5. TG and DTA trace for $Cu_2(C_7H_9N_3O)Cl_4$. Sample weight $= 9.09$ mg.

TABLE 4

Decomposition processes of the metal complexes

Starting material	Decomposition temp. (°C)	% Mass loss		Resulting compound
		Calc.	Found	
$Co(C_7H_9N_3O)_2Cl_2$	250 (Endo)	35.0	34.6	$Co(C_7H_9N_3O)Cl_2$
	376 (Exo)	81.4	81.0	Co_3O_4
$Co(C_7H_9N_3O)Cl_2$	292 (Endo)	35.8	35.6	$Co_3(C_7H_9N_3O)Cl_6$
	404 (Exo)	71.4	71.0	Co_3O_4
$Ni(C_7H_9N_3O)Cl_2$	282 (Endo)	53.8	53.4	$NiCl_2$
	450 (Exo)	73.4	73.0	NiO
$Cu_2(C_7H_9N_3O)Cl_4$	112 (Endo)	18.0	17.8	$Cu_4(C_7H_9N_3O)Cl_8$
	201 (Exo)	62.2	62.0	CuO

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

The high-density polyethylene (HDPE) samples containing the metal complexes $Co(C_7H_9N_3O)Cl_2$, $Ni(C_7H_9N_3O)Cl_2$ and $Cu_2(C_7H_9N_3O)Cl_4$ and the commercial anti-static additive have lower surface resistivities, higher surface conductivities, than the pure HDPE, the HDPE containing 4-aminobenzoyl hydrazide and the HDPE containing the metal complex $Co(C_7H_9N_3O)_2Cl_2$. This was so when measured both at 0 and 336 h after moulding, as can be seen in Table 5. The charge-decay measurements (Table 5), which gave an indication of how quickly charge is dissipated from the surface of the polymer, show that the metal complexes do not possess the same degree of charge migration properties as the commercial anti-static agent. However, surface resistivity measurements for the metal complexes $Co(C_7H_9N_3O)Cl_2$, $Ni(C_7H_9N_3O)Cl_2$ and $Cu_2(C_7H_9N_3O)Cl_4$,

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
$C_7H_9N_3O$/HDPE	1.32×10^{17}	1.32×10^{17}	>120	>120
Commercial additive/HDPE	1.32×10^{13}	7.52×10^{13}	1.0	1.0
$Co(C_7H_9N_3O)_2Cl_2$/HDPE	1.88×10^{17}	1.88×10^{17}	>120	>120
$Co(C_7H_9N_3O)Cl_2$/HDPE	7.52×10^{16}	5.64×10^{16}	>120	>120
$Ni(C_7H_9N_3O)Cl_2$/HDPE	2.44×10^{16}	1.88×10^{16}	>120	>120
$Cu_2(C_7H_9N_3O)Cl_4$/HDPE	9.40×10^{16}	3.76×10^{16}	>120	>120

[a] Time after moulding (h).

after 336 h, show that migration of charge to the surface of the polymer occurs and anti-static properties are observed. It would appear that the anti-static properties of these compounds are related to their polymeric structures because the compound $Co(C_7H_8N_3O)_2Cl_2$ which has a discrete octahedral structure showed no anti-static behaviour.

REFERENCES

1 J.R. Allan, N.D. Baird and A.L. Kassyk, J. Therm. Anal., 16 (1979) 79.
2 J.R. Allan and G.M. Baillie, J. Therm. Anal., 14 (1978) 291.
3 J.R. Allan, B.R. Carson, D.L. Gerrard and S. Hoey, Thermochim. Acta, 153 (1989) 173.
4 J.R. Allan, J.G. Bonner, H.J. Bowley and D.L. Gerrard, Thermochim. Acta, 141 (1989) 227.
5 A. Braibante, F. Dallavalle, M.A. Pellinghelli and E. Leporati, Inorg. Chem., 7 (1968) 1430.