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Structural, thermal and electrical studies of the chloro complexes of cobalt, nickel and copper with 4-butylaniline

J.R. Allan *, A.D. Paton, K. Turvey

Department of Applied Chemical and Physical Sciences, Napier University, Edinburgh, UK

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Abstract

The compounds prepared have stoichiometry ML_2Cl_2 (where M is cobalt and copper) and Ni_2LCl_4, where L is the 4-butylaniline ligand. The cobalt and copper compounds have tetrahedral structures while the nickel compound has a polymeric octahedral structure. Thermal analysis studies show that the cobalt and copper compounds decompose with loss of one molecule of 4-butylaniline, followed by the loss of the remaining molecule of 4-butylaniline and all of the original chlorine, to give the metal oxides. The nickel compound decomposes with loss of the 4-butylaniline to give nickel chloride followed by loss of the chlorine to give nickel oxide.

Electrical conductivities at room temperature are reported and all compounds display ohmic conduction. A correlation between the electrical conductivity and stereochemical structure of the complexes has been observed.

Keywords: Cobalt compound; Conductivity; Co-ordination; Copper compound; Decomposition; DTA; IRS; Magnetometry; Nickel compound; TG

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1. Introduction

In this paper, the structural characterisation, and the thermal and electrical studies of the chloro compounds of cobalt, nickel and copper with 4-butylaniline are described.

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* Corresponding author.

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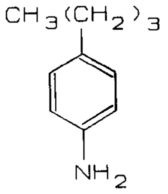

4-Butylaniline ($C_{10}H_{15}N$).

The molecule of 4-butylaniline has one donor site for bonding to metal ions: the nitrogen atom of the amine group. Spectral and magnetic studies were used to characterise each compound and to interpret the type of coordination which takes place to the metal ion. A study of the thermal decomposition of each compound was carried out using thermogravimetry and differential thermal analysis. Studies involving d.c. electrical measurements were used to obtain information about electrical conductivity.

2. Experimental

2.1. Preparation of the compounds

The compounds were prepared as reported in the literature [1].

2.2. 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 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}) on a Perkin-Elmer IR spectrophotometer model 598.

The electronic spectra were obtained on a Beckmann Acta MIV spectrophotometer as solid diffuse spectra.

Magnetic measurements were carried out at room temperature by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant.

Thermal analysis studies were performed using a Stanton-Redcroft model STA 1500 thermobalance. The TG and DTA traces were obtained at a heating rate of 10 K min^{-1}. In all cases, the 20–800°C temperature range was studied.

The electrical measurements carried out on the prepared compounds comprised measuring current as a function of voltage at room temperature to obtain the electrical conductivity σ of the compounds. For such measurements, the compounds were formed into discs of diameter 13 mm and thickness of approximately 1 mm, by compressing the powdered compound in a hydraulic press set to apply a force of 100 kN. The disc thickness was accurately measured by a micrometer. Circular electrodes of known diameter were formed concentrically on the flat faces of the disc by applying silver conductive paint through masks. The disc was then stored in a desiccator for several days before being tested.

The room temperature dark current was measured for a series of applied d.c. voltages using a Keithley 610C electrometer. To test that the electrodes were ohmic and non-blocking, the voltage was increased in stages from zero to 30 V and then decreased in corresponding stages, and this procedure was repeated in reverse polarity. Agreement, within a maximum of ±10%, between the four current readings was regarded as confirmation that the electrodes were not significantly rectifying.

3. Results and discussion

The compounds prepared are listed in Table 1. The analytical results agree with the stoichiometry proposed for the compounds.

The electronic spectra and magnetic measurements are listed in Table 2. The position of the bands in the spectra of the cobalt and copper compounds, together with the magnetic moments, suggest that the metal ions in these compounds are in a tetrahedral environment [2–4]. The position of the bands in the spectrum of the nickel compound and its magnetic moment are indicative of the nickel ions being in an octahedral environment [4].

In Table 3, the main bands in the IR spectra of 4-butylaniline and its metal complexes are listed. The IR spectrum of 4-butylaniline is similar to that of its

Table 1
Analyses of the compounds

Compound		Metal/%	Carbon/%	Nitrogen/%	Hydrogen/%
$Co(C_{10}H_{15}N)_2Cl_2$	Theory	13.75	56.08	6.54	7.05
	Found	13.66	55.69	6.34	6.82
$Ni_2(C_{10}H_{15}N)Cl_4$	Theory	28.27	29.40	3.42	3.70
	Found	28.42	29.49	3.45	3.54
$Cu(C_{10}H_{15}N)_2Cl_2$	Theory	14.67	55.68	6.47	6.98
	Found	14.49	55.23	6.19	6.57

Table 2
Electronic spectra and magnetic moments

Compound	Colour	Band position/cm^{-1}	μ_B/BM
$Co(C_{10}H_{15}N)_2Cl_2$	Blue	6250 15674	4.64
$Ni_2(C_{10}H_{15}N)Cl_4$	Green	8264 13889 23809	3.92
$Cu(C_{10}H_{15}N)_2Cl_2$	Brown	6849 23809	2.03

Table 3
Infrared spectra (4000–200 cm^{-1})

Compound	$\nu(NH_2)/cm^{-1}$		$\nu(M–Cl)/cm^{-1}$	$\nu(M–N)/cm^{-1}$
$C_{10}H_{15}N$	3430(s)	3340(s)	–	–
$Co(C_{10}H_{15}N)_2Cl_2$	3260(s)	3220(s)	320(s)	392(m)
$Ni_2(C_{10}H_{15}N)Cl_4$	3320(s)	3240(s)	252(m)	388(m)
$Cu(C_{10}H_{15}N)_2Cl_2$	3220(s)	3300(s)	300(s)	390(m)

Key: s, strong; m, medium.

complexes in the 4000–600 cm^{-1} region, except for the bands due to the N–H vibrations which move to lower wavenumber on complexation. This indicates that the nitrogen atom of the amine group is bonding to metal ions in these compounds [1]. Metal–nitrogen bands are assigned and reported in Table 3. The metal–chloride bands, also listed in Table 3, agree with the earlier conclusions that the cobalt and copper ions are in tetrahedral environments [5] while the nickel ions are in an octahedral environment [4].

The compounds were isolated from ethanolic solutions as powders. Attempts to obtain single crystals were unsuccessful and, hence, no complete structure determination could be made. However, the information obtained from the spectral and magnetic date enable us to propose structures for the compounds. The cobalt and copper atoms are in a tetrahedral environment, with each metal atom bonded to two chloride ions and to two molecules of 4-butylaniline through the nitrogen atom of the amine group. The poor solubility of the nickel compound in both polar and non-polar solvents would suggest that this compound has a polymeric structure [1]. It is suggested that the nickel compound consists of four layers of Ni–Cl chains in which each chloride ion is acting as a bridge between three nickel atoms with the 4-butylaniline molecules bonded to nickel atoms above and below the plane of the Ni–Cl chains.

The results of the TG and DTA studies are shown in Figs. 1–3 and Table 4. The TG traces for the cobalt and copper compounds show that these compounds decompose with loss of one molecule of 4-butylaniline, followed by loss of the remaining molecule of 4-butylaniline and chlorine to give the metal oxides. The DTA traces show that these processes are accompanied by exothermic reactions. The TG trace for the nickel compound shows that it first loses 4-butylaniline to give nickel chloride, followed by loss of chlorine to produce nickel oxide. The DTA trace shows that the first process involves an endothermic reaction while the second involves exothermic reactions. The observed weight losses for the different processes compare favourably with theoretical values, Table 4. The reaction enthalpy for each of the decomposition processes is also listed in Table 4.

The room-temperature current I versus voltage V characteristics were obtained under conditions of rising and falling voltage in both polarities. The current versus voltage relationships for the prepared complexes of 4-butylaniline with the chlorides of cobalt, nickel and copper were all observed to be linear throughout the voltage

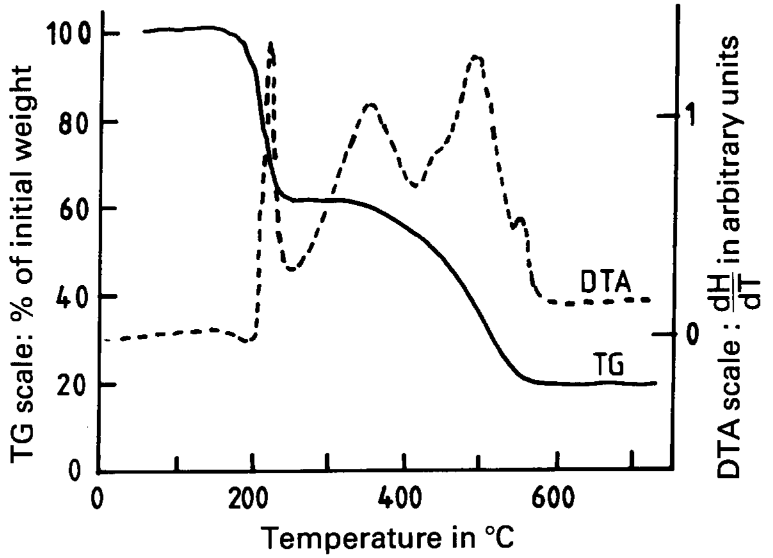

Fig. 1. Thermogravimetric (TG) and differential thermal analysis (DTA) plots for a sample of $Co(C_{10}H_{15}N)_2Cl_2$ of weight 3.34 mg. The DTA plot has the first derivative of enthalpy emission with respect to temperature, dH/dT, as its ordinate; dH/dT is shifted to be zero at the initial temperature.

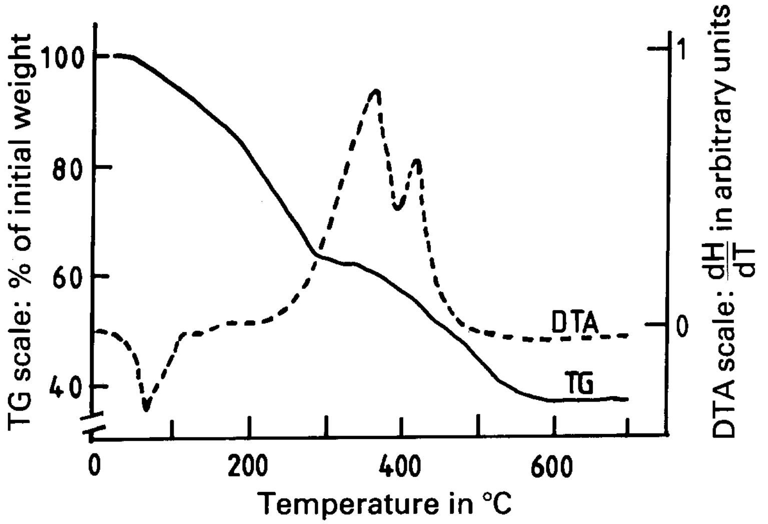

Fig. 2. TG and DTA plots for a sample of $Ni_2(C_{10}H_{15}N)Cl_2$ of weight 11.56 mg. In the DTA plot, dH/dT is shifted to be initially zero.

range investigated, indicating that ohmic electrical conduction predominated. From the mean gradients of the I–V characteristics, the electrical conductivities for the compounds were determined and are shown in Table 5.

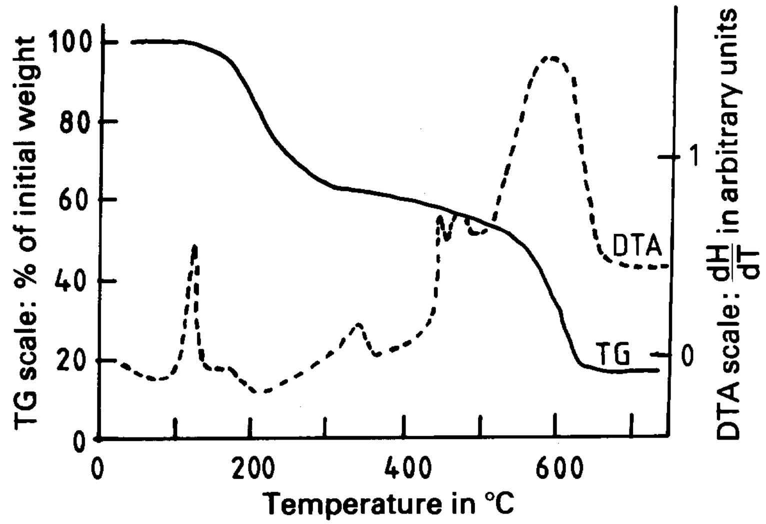

Fig. 3. TG and DTA plots for a sample of $Cu(C_{10}H_{15}N)_2Cl_2$ of weight 8.03 mg. In the DTA plot, d*H*/d*T* is shifted to be initially zero.

Table 4
Thermal decomposition products

Starting material	Decomposition temp./°C	Resulting compound	Weight loss/%		Enthalpy of reaction/ (kJ mol^{-1})
			Calc.	Found	
$Co(C_{10}H_{15}N)_2Cl_2$	148(exo)	$Co(C_{10}H_{15}N)Cl_2$	34.8	34.6	215
	275(exo)	Co_3O_4	46.5	46.4	554
$Ni_2(C_{10}H_{15}N)Cl_4$	38(endo)	$NiCl_2$	36.5	36.2	104
	310(exo)	NiO	26.8	26.6	237
$Cu(C_{10}H_{15}N)_2Cl_2$	98(exo)	$Cu(C_{10}H_{15}N)Cl_2$	34.5	34.4	52
	342(exo)	CuO	47.1	47.0	396

Key: endo, endothermic; exo, exothermic (from DTA trace).

Table 5
Room temperature electrical conductivities of the compounds

Compound	$\sigma/(\Omega^{-1}\ m^{-1})$ [a]
$Co(C_{10}H_{15}N)_2Cl_2$	1.35×10^{-7}
$Ni_2(C_{10}H_{15}N)Cl_4$	5.29×10^{-6}
$Cu(C_{10}H_{15}N)_2Cl_2$	2.23×10^{-8}

[a] Room temperature conductivity (20°C).

The most conductive of the compounds studied was $Ni_2(C_{10}H_{15}N)Cl_4$, followed by $Co(C_{10}H_{15}N)_2Cl_2$ and $Cu(C_{10}H_{15}N)_2Cl_2$. It is considered significant that the nickel compound being the most conductive is the only compound in the present study that has an octahedral polymeric structure. The cobalt and copper compounds are considered to have a tetrahedral stereochemistry and to be monomeric. It is postulated that this structural difference is the reason for the relatively high electrical conductivity of the nickel compound compared with the cobalt and copper compounds. It is suggested that the octahedral polymeric structure of the nickel compound promotes carrier mobility by providing an effective pathway for conduction. The absence of such conduction pathways in the cobalt and copper compounds gives rise to lower electrical conductivity values. A correlation between electrical conductivity and stereochemical structures was recognised in studies of chloro metal complexes of quinoxaline [6].

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