Preparation, structural characterisation, thermal and electrical studies of complexes of cobalt, nickel and copper with *m*-toluidine

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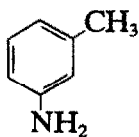*Department of Applied Chemical and Physical Sciences, Napier University, Edinburgh (UK)*

(Received 17 June 1992)

Abstract

The thiocyanate complex of cobalt and the chloro complexes of cobalt, nickel and copper with *m*-toluidine which have been prepared in ethanolic solution have stoichiometry ML_2X_2. The stereochemistry of the complexes has been obtained from spectral and magnetic data. The thiocyanate complex of cobalt and the chloro complexes of nickel and copper have octahedral structures, whereas the chloro complex of cobalt has a tetrahedral structure. Thermal decomposition studies, using thermogravimetry and differential thermal analysis show that intermediate metal complexes are formed for the chloro complexes during their decomposition processes, the metal oxides being finally produced in each case. The thiocyanate complex of cobalt decomposes to give cobalt thiocyanate and finally an oxide of cobalt. The electrical measurements show that the metal complexes exhibit ohmic behaviour and that the metal ion has an important contribution to make to the conduction process.

INTRODUCTION

The compound *m*-toluidine has one donor site for forming bonds with metal ions: the nitrogen atom of the amine group.

m-Toluidine (C_7H_9N)

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In this paper we report studies of the metal complexes formed between cobalt thiocyanate and the chlorides of cobalt, nickel and copper with *m*-toluidine. Spectral and magnetic measurements have been used to characterise each metal complex and to interpret the type of coordination which takes place with the metal ion. The thermal decomposition of the metal complexes along with their electrical conductivities have been studied.

EXPERIMENTAL

Preparation of the metal complexes

The metal salt (1 g) was dissolved in warm ethanol (60 cm³) and *m*-toluidine (6 cm³) was added with stirring. This solution was refluxed for 4 h. On cooling, the metal complexes precipitated. They were filtered, washed with a solution of *m*-toluidine in ethanol and air dried.

Apparatus and measurements

The concentration of metal ion was determined 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 recorded using KBr discs over the wavenumber range 4000–600 cm⁻¹ and using polyethylene discs over the range 600–200 cm⁻¹ on a Perkin-Elmer model 598 IR spectrophotometer.

Electronic spectra were recorded as solid diffuse reflectance spectra using a Beckmann Acta MIV spectrophotometer.

Measurements of magnetic moments were made using the Gouy method with $Hg[Co(SCN)_4]$ as calibrant.

Thermal analysis measurements were made on a Stanton Redcroft STA 1500 thermobalance. Thermogravimetry (TG) and differential thermal analysis (DTA) curves were obtained at a heating rate of 6°C min⁻¹ in static air. The 20–800°C temperature range was studied in all cases.

Electrical conduction measurements were performed under d.c. conditions on discs of the compounds which were prepared by compressing powdered samples of the complexes. These discs were 13 mm in diameter with thicknesses of approximately 1 mm. Electrodes 5.9 mm in diameter were formed on the surfaces of the discs by applying a silver based conductive paint. Details of the methods used for the electrical measurements have been previously described [1, 2].

RESULTS AND DISCUSSION

The compounds isolated from ethanolic solution are listed in Table 1, along with the analytical results. These analyses agree with the given formulae proposed for the compounds.

The molecular magnetic moments and the bands in the electronic spectra of the complexes are listed in Table 2. The position of the bands in the electronic spectra of the cobalt complexes would suggest that in the thiocyanate complex the cobalt ions are in a octahedral environment [3], whereas for the chloro complex the cobalt ions are in a tetrahedral environment [3]. The value obtained for the magnetic moment for each of the complexes supports these suggestions [3]. The position of the bands in

TABLE 1

Analyses (%) of the metal complexes

Compound	Colour		M	C	N	H
$Co(C_7H_9N)_2(NCS)_2$	Pink	Theory	15.13	43.18	14.38	4.65
		Found	15.05	42.87	14.07	4.29
$Co(C_7H_9N)_2Cl_2$	Blue	Theory	17.12	48.85	8.13	5.27
		Found	17.29	48.61	7.89	5.12
$Ni(C_7H_9N)_2Cl_2$	Green	Theory	17.06	48.89	8.14	5.27
		Found	16.88	48.53	8.09	5.01
$Cu(C_7H_9N)_2Cl_2$	Brown	Theory	18.21	48.21	8.03	5.20
		Found	18.09	48.26	8.01	4.92

TABLE 2

Electronic spectra and magnetic measurements

Compound	Band position (cm^{-1})	d–d Transition	μ (BM)
$Co(C_7H_9N)_2(NCS)_2$	9009	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	5.01
	18180	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	
	21739	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	
$Co(C_7H_9N)_2Cl_2$	7547	$^4A_2(F) \rightarrow {}^4T_1(F)$	4.90
	15385	$^4A_2(F) \rightarrow {}^4T_1(P)$	
$Ni(C_7H_9N)_2Cl_2$	8006	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	3.30
	13698	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	
	22988	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	
$Cu(C_7H_9N)_2Cl_2$	14265	$^2E_g(D) \rightarrow {}^2T_{2g}(D)$	1.46

TABLE 3

IR spectra (4000–200 cm^{-1})

Compound	$v(NH_2)$	$v(M-X)$	$v(M-N)$
C_7H_9N	3771(s), 3436(s)	–	–
$Co(C_7H_9N)_2(NCS)_2$	3319(s), 3255(s)	–	272(s), 246(s)
$Co(C_7H_9N)_2Cl_2$	3550(s), 3266(s)	320(s), 300(s)	268(m)
$Ni(C_7H_9N)_2Cl_2$	3320(s), 3238(s)	236(w)	270(m)
$Cu(C_7H_9N)_2Cl_2$	3304(s), 3232(s)	230(w)	282(m)

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

the electronic spectrum of the nickel compound, along with its magnetic moment, would indicate that the nickel atoms are in an octahedral environment [4]. The broad absorption band observed in the electronic spectrum of the copper compound between 10 000 and 15 000 cm^{-1} would suggest that the copper ions are in an octahedral environment [4]. The magnetic moment for the compound is lower than the spin only value, indicating copper–copper magnetic interaction.

The wavenumbers of the IR absorption bands of *m*-toluidine and its metal complexes are given in Table 3 together with the descriptions and assignments. The IR spectrum of *m*-toluidine is very similar to that of its metal complexes in the region 4000–600 cm^{-1}, except that the bands due to the $v(NH_2)$ vibration are shifted to lower wavenumber on the formation of the complexes. This would suggest that the nitrogen atom of the amine group coordinates to a metal ion [5]. In the complex formed between cobalt thiocyanate and *m*-toluidine a band is observed between 2120 and 2100 cm^{-1}, indicating the presence of bridging SCN groups [6].

The $v(M-Cl)$ and $v(M-N)$ bands observed in the 600–200 cm^{-1} region of the IR spectra of the metal complexes are also listed in Table 3.
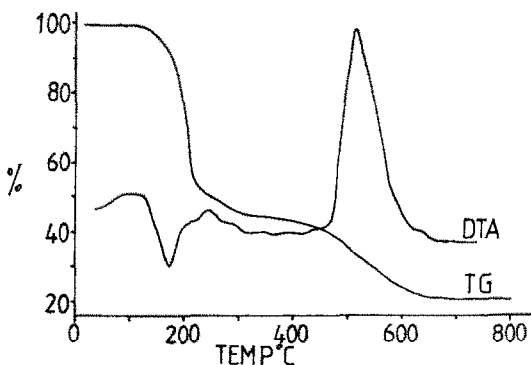
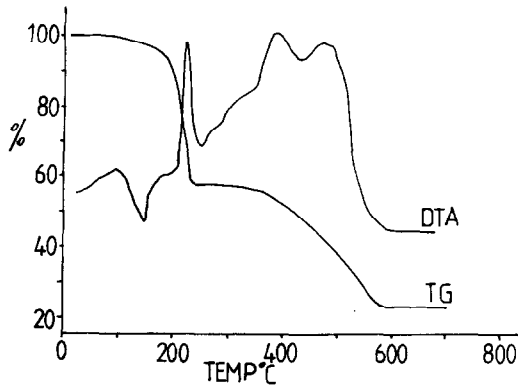Fig. 1. TG and DTA traces for $Co(C_7H_9N)_2(NCS)_2$. Sample weight = 9.76 mg.

Fig. 2. TG and DTA traces for $Co(C_7H_9N)_2Cl_2$. Sample weight = 9.56 mg.

Single crystals of the complexes were not isolated from ethanolic solution. Therefore, without X-ray analysis, no definite structures can be described. However, the spectroscopic and magnetic data suggest that the chloro complexes of nickel and copper and the thiocyanate complex of cobalt have the metal ions in an octahedral environment. The poor solubility of these complexes in both polar and non-polar solvents would suggest that they have polymeric structure [4]. It is thus suggested that the structure of these compounds consists of a chain of metal atoms bonded to X atoms (where X is Cl^- or NCS^-), with the m-toluidine molecules above and below the plane of the M–X chain. The chloro complex of cobalt has a tetrahedral structure, with the cobalt ion bonded to two chloride ions and to two nitrogen atoms from two different molecules of toluidine.

The TG and DTA traces for the metal complexes are shown in Figs. 1–4 and the thermal decomposition data is listed in Table 4. The chloro complexes of cobalt, nickel and copper decompose via intermediate
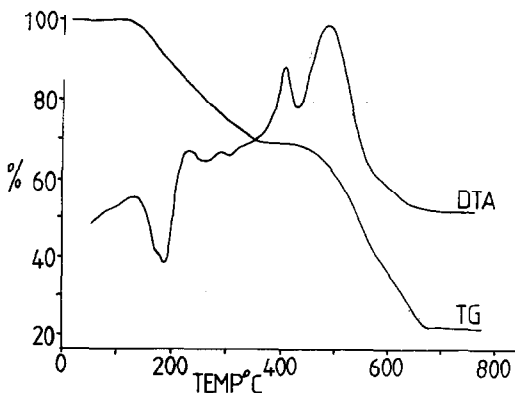

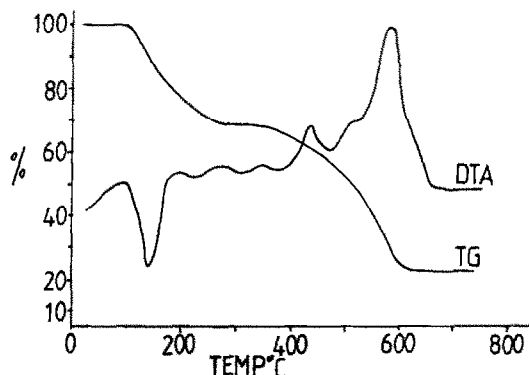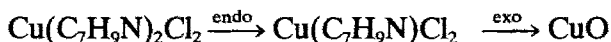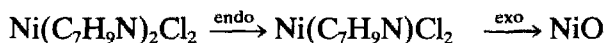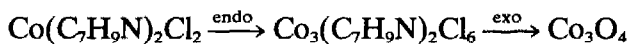Fig. 3. TG and DTA traces for $Ni(C_7H_9N)_2Cl_2$. Sample weight = 9.38 mg.

Fig. 4. TG and DTA traces for $Cu(C_7H_9N)_2Cl_2$. Sample weight = 8.13 mg.

complexes to give the metal oxides. The decomposition scheme is

$$Co(C_7H_9N)_2Cl_2 \xrightarrow{endo} Co_3(C_7H_9N)_2Cl_6 \xrightarrow{exo} Co_3O_4$$

$$Ni(C_7H_9N)_2Cl_2 \xrightarrow{endo} Ni(C_7H_9N)Cl_2 \xrightarrow{exo} NiO$$

$$Cu(C_7H_9N)_2Cl_2 \xrightarrow{endo} Cu(C_7H_9N)Cl_2 \xrightarrow{exo} CuO$$

The thiocyanate complex of cobalt decomposes endothermically with loss of two molecules of *m*-toluidine, followed by an exothermic reaction and loss of chlorine to give Co_3O_4. The observed weight losses for the decomposition processes in each of the compounds compare favourably with the theoretical values listed in Table 4.

The room temperature current (I) versus voltage (V) characteristics

TABLE 4

Thermal decomposition processes of metal complexes

Process	Temp. range (°C)	Thermal nature of the transformation	Weight loss (%)	
			Calc.	Found
$Co(C_7H_9N)_2(NCS)_2 \rightarrow Co(NCS)_2$	110–230	endo	55.1	55.2
$Co(NCS)_2 \rightarrow Co_3O_4$	230–686	exo	16.3	16.2
$Co(C_7H_9N)_2Cl_2 \rightarrow Co_3(C_7H_9N)_2Cl_6$	84–283	endo	41.5	42.0
$Co_3(C_7H_9N)_2Cl_6 \rightarrow Co_3O_4$	283–616	exo	35.2	35.1
$Ni(C_7H_9N)_2Cl_2 \rightarrow Ni(C_7H_9N)Cl_2$	108–400	endo	31.2	31.1
$Ni(C_7H_9N)Cl_2 \rightarrow NiO$	400–696	exo	47.1	47.0
$Cu(C_7H_9N)_2Cl_2 \rightarrow Cu(C_7H_9N)Cl_2$	102–298	endo	30.7	30.6
$Cu(C_7H_9N)Cl_2 \rightarrow CuO$	298–646	exo	46.5	46.6

Key: endo, endothermic; exo, exothermic.

TABLE 5

Room temperature electrical conductivities

Compound	$(\Omega^{-1} m^{-1})$
$Co(C_7H_9N)_2(NCS)_2$	2.83×10^{-8}
$Co(C_7H_9N)_2Cl_2$	2.94×10^{-8}
$Ni(C_7H_9N)_2Cl_2$	6.03×10^{-8}
$Cu(C_7H_9N)_2Cl_2$	7.32×10^{-8}

were obtained under conditions of increasing and decreasing voltage in both polarities. The four currents measured were found to agree within 10%, indicating that the contacts were not rectifying. The $I-V$ relationships for all the complexes studied were found to be linear, indicating ohmic electrical conduction. The electrical conductivity for each complex was determined from the gradient of the $I-V$ characteristic.

The observed room temperature electrical conductivities (σ) of the complexes are given in Table 5. Comparison of the chloro and thiocyanato complexes of cobalt shows that their electrical conductivities are, within experimental error, very similar and hence that their differing stereochemical environments have no effect on conductivity. Examination of the metal chloro complexes shows an increasing trend in electrical conductivity with increasing atomic weight of the coordinated metal ion. As the sterochemistry of the central ion appears to have no contribution to the electrical conductivity than this observed trend indicates that the nature of the metal ion has a significant effect on the elecrical conductivity.

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