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Thermal, structural and electrical studies of the chloro complexes of cobalt, nickel and copper with 1,10-phenanthroline

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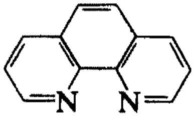
Abstract

The chloro compounds of 1,10-phenanthroline with cobalt, nickel and copper have been prepared in ethanolic solution and have the stoichiometry ML_nCl_2, where $n = 2$ for cobalt and copper and $n = 1$ for nickel. Solid compounds were isolated and characterised by analysis, magnetic moments, and vibrational and electronic spectra. The cobalt and copper compounds have octahedral structures, whereas the nickel compound has a tetrahedral structure. The thermal behaviour of the compounds has been studied using thermogravimetry and differential thermal analysis. During the thermal decomposition processes, intermediate compounds are produced. Electrical conductivity measurements were obtained for the 1,10-phenanthroline and its copper complex. No suitable discs could be obtained for electrical measurements on the cobalt and nickel complexes. The electrical measurements show ohmic behaviour at room temperature, with conductivities of $7.58 \times 10^{-8}\ \Omega^{-1}\ m^{-1}$ for the 1,10-phenanthroline; and $9.10 \times 10^{-8}\ \Omega^{-1}\ m^{-1}$ for the copper complex.

INTRODUCTION

Structural and electrical studies of some first row transition metal complexes with 4,7-phenanthroline have previously been reported [1]. The chloro complexes of cobalt, nickel and copper with 1,10-phenanthroline are discussed in this paper.



1,10-Phenanthroline ($C_{12}H_8N_2$).

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Spectral and magnetic studies have been used to characterise each metal complex and to interpret the type of coordination which takes place with the metal ion. Thermal and electrical studies have been carried out on the 1,10-phenanthroline complexes.

EXPERIMENTAL

Preparation of complexes

1 g of metal chloride and 1 g of 1,10-phenanthroline were dissolved in separate 60 cm^3 portions of boiling ethanol. On mixing, the copper complex precipitated immediately. The cobalt and nickel solutions were refluxed for 6 h, after which the volume of solvent was reduced to facilitate precipitation. All complexes were washed thoroughly with boiling ethanol and air dried. The cobalt complex is orange, the nickel complex is blue and the copper complex is green.

Apparatus

The concentration of the metal ion was obtained using a Perkin-Elmer 373 atomic absorption spectrophotometer and the carbon, hydrogen and nitrogen analyses 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 a 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.

Electrical conduction measurements were performed under d.c. conditions on discs of the compounds which were prepared by compressing powdered samples of the complexes. Each disc was 13 mm in diameter with a thickness of approximately 1 mm. Electrodes 5.9 mm in diameter were formed on the flat surfaces of the discs by applying a silver based conductive paint. Details of the methods used for the electrical measurements have been previously described [2, 3].

RESULTS AND DISCUSSION

The complexes prepared are listed in Table 1. The analytical results agree with the proposed formulae.

The d–d bands in the electronic reflectance spectra and the magnetic moments of the compounds are listed in Table 2. The position of the bands in the spectra and the magnetic moments of the cobalt and nickel complexes indicate that the cobalt ion is in an octahedral environment, whereas the nickel ion is in a tetrahedral environment [4]. The copper complex has a single broad band in its electronic spectrum between 10 000 and 15 000 cm^{-1}, suggesting that the copper atoms are in an octahedral environment [5]. The magnetic moment for this compound was found to be 2.02 BM, indicating an orbital contribution to the magnetic moment.

The energies of the main bands in the IR spectra of 1,10-phenanthroline and its metal complexes are listed in Table 3, together with the descriptions and assignments. The IR spectra of the complexes are almost identical to the spectrum of 1,10-phenanthroline in the region

TABLE 1

Analyses (%) of compounds

Compound		M	C	N	H
$Co(C_{12}H_8N_2)_2Cl_2$	Theory	12.02	58.79	11.42	3.28
	Found	11.57	58.23	10.96	2.91
$Ni(C_{12}H_8N_2)Cl_2$	Theory	18.94	46.52	9.04	2.60
	Found	18.37	46.04	8.73	2.47
$Cu(C_{12}H_8N_2)_2Cl_2$	Theory	12.83	58.25	11.32	3.25
	Found	12.61	58.04	10.96	3.01

TABLE 2

Electronic spectra and magnetic moments

Compound	Band position (cm^{-1})	d–d Transition	μ (BM)
$Co(C_{12}H_8N_2)_2Cl_2$	9174	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	5.01
	19801	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	
$Ni(C_{12}H_8N_2)Cl_2$	4066	$^3T_1(F) \rightarrow {}^3T_2(F)$	3.64
	10638	$^3T_1(F) \rightarrow {}^3A_2(F)$	
	16806	$^3T_1(F) \rightarrow {}^3T_1(P)$	
$Cu(C_{12}H_8N_2)_2Cl_2$	12500	$^2E_g(D) \rightarrow {}^2T_{2g}(D)$	1.82

TABLE 3

IR spectra (4000–200 cm^{-1})

Compound	Ring vibrations	ν(M–Cl)	ν(M–N)
$C_{12}H_8N_2$	1575(s), 1492(s)	–	–
$Co(C_{12}H_8N_2)_2Cl_2$	1579(s), 1510(s)	272(m)	230(m)
$Ni(C_{12}H_8N_2)Cl_2$	1580(s). 1512(s)	301(s)	236(w)
$Cu(C_{12}H_8N_2)_2Cl_2$	1582(s), 1512(s)	280(m)	230(w)

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

4000–600 cm^{-1} except for the bands due to the vibrations of the aromatic ring, which move to higher wavenumbers on forming complexes. This suggests that one or both of the aromatic nitrogen atoms are bonded to a metal ion [5]. The ν(M–Cl) bands in the IR spectra of the cobalt and copper compounds show that the metal ions are in an octahedral environment whereas the bands in the spectrum of the nickel compound

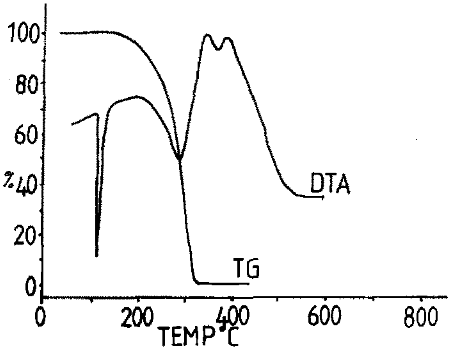

Fig. 1. TG and DTA trace for 1,10-phenanthroline; sample weight = 10.95 mg.

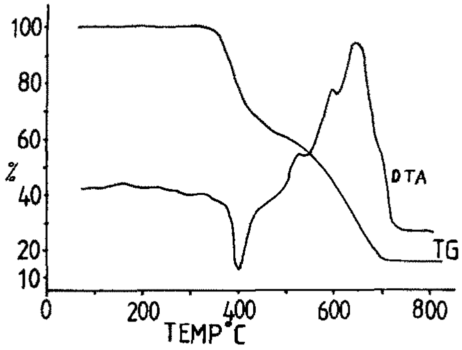

Fig. 2. TG and DTA trace for $Co(C_{12}H_8N_2)_2Cl$; sample weight = 8.68 mg.

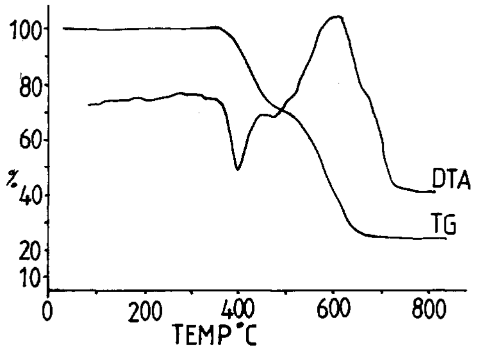

Fig. 3. TG and DTA trace for $Ni(C_{12}H_8N_2)Cl_2$; sample weight = 10.55 mg.

show that it is a tetrahedral environment [4, 5]. Metal–nitrogen bands are also reported in Table 3.

The fact that the compounds were isolated from solution as powders and not as single crystals meant that no complete structure determination could be made. However, spectroscopic and magnetic data enables a prediction to be made regarding the structures of the compounds. In the cobalt and copper complexes, the metal is coordinated octahedrally by four nitrogen atoms (two nitrogen atoms from different 1,10-phenanthroline molecules) and two chloride ions. In the nickel complex, the nickel atom is coordinated tetrahedrally by two nitrogen atoms of a 1,10-phenanthroline molecule and two chloride ions.

The TG and DTA traces for 1,10-phenanthroline and its chloro complexes with cobalt, nickel and copper are shown in Figs. 1–4. The TG and DTA curves for 1,10-phenanthroline (Fig. 1) show that it is thermally stable in the temperature range 20–120°C. Pyrolytic decomposition commences at 170°C and ends at 325°C with total elimination of the

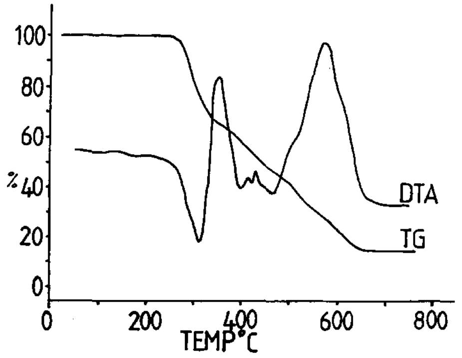

Fig. 4. TG and DTA trace for $Cu(C_{12}H_8N_2)_2Cl_2$; sample weight = 7.97 mg.

TABLE 4

Decomposition processes of the metal complexes

Starting material	Decomposition temp. (°C)	Mass loss (%)		Resulting compound
		Calc.	Found	
$Co(C_{12}H_8N_2)_2Cl_2$	328(endo)	36.8	36.7	$Co(C_{12}H_8N_2)Cl_2$
	500(exo)	83.6	83.3	Co_3O_4
$Ni(C_{12}H_8N_2)Cl_2$	357(endo)	29.1	29.0	$Ni_2(C_{12}H_8N_2)Cl_4$
	486(exo)	75.9	74.8	NiO
$Cu(C_{12}H_8N_2)_2Cl_2$	258(endo)	36.4	37.0	$Cu(C_{12}H_8N_2)Cl_2$
	376(exo)	54.6	54.8	$Cu_2(C_{12}H_8N_2)Cl_4$
	498(exo)	83.9	83.2	CuO

Key: endo = endothermic; exo = exothermic (obtained from DTA curve).

sample. The DTA curve of 1,10-phenanthroline shows an endothermic peak at 117°C corresponding to fusion. The 1,10-phenanthroline decomposes at 120°C producing exothermic peaks. The TG and DTA curves for the chloro complexes of 1,10-phenanthroline with cobalt, nickel and copper are shown in Figs. 2–4. The results of TG and DTA analyses are given in Table 4. The cobalt complex (Fig. 2) undergoes an endothermic reaction with loss of one molecule of phenanthroline, followed by an exothermic reaction with loss of the remaining phenanthroline and finally chlorine to give Co_3O_4. The nickel compound undergoes an endothermic reaction with loss of half a molecule of phenanthroline, followed by an exothermic reaction with loss of the remaining phenanthroline and chlorine to give NiO. The copper compound (Fig. 3) undergoes an endothermic reaction with loss of one molecule of phenanthroline. This is followed by exothermic reactions in which half a molecule of phenanthroline then the remaining half molecule of phenanthroline and chlorine are lost to give CuO.

The room temperature current (I) versus voltage (V) characteristics were obtained under conditions of rising and falling voltage in both polarities. The two currents measured were found to agree within 10%, indicating that the electrodes were not rectifying. The electrical conductivities of only the ligand and the copper complex were measured because no suitable discs could be prepared for the cobalt and nickel complexes.

The room temperature conductivity of the free ligand was $7.58 \times 10^{-8}\,\Omega^{-1}\,m^{-1}$, whilst for the copper complex the conductivity was $9.10 \times 10^{-8}\,\Omega^{-1}\,m^{-1}$. The I–V characteristic for both the ligand and the copper complex exhibit ohmic behaviour. Although the copper complex shows a higher conductivity than the free ligand, the absence of electrical information from the cobalt and nickel complexes precludes any suggestion that this is due to the presence of the metal ion.

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