

## Thermal, structural and electrical studies of the chloro complexes of cobalt, nickel and copper with 4,7-phenanthroline

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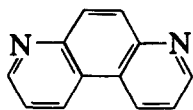
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### Abstract

The chloro compounds of 4,7-phenanthroline with cobalt, nickel and copper have been prepared in ethanolic solution and have stoichiometry  $MCl_2$ . Solid compounds were isolated and characterised by elemental analyses, magnetic moments, vibrational and electronic spectra. The cobalt and nickel compounds have tetrahedral structures, whereas the copper compound has an octahedral structure. The thermal behaviour of the compounds has been studied using thermogravimetry and differential thermal analysis. An intermediate compound is observed in the decomposition of the cobalt complex. Electrical conductivities at room temperature are reported and all compounds display ohmic behaviour. The ligand molecules make a major contribution to the conduction process.

### INTRODUCTION

Structural and electrical studies of some first row transition metal complexes with 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline have previously been reported [1]. The chloro complexes of cobalt, nickel and copper with 4,7-phenanthroline are discussed in this paper.



4,7-Phenanthroline ( $C_{12}H_8N_2$ ).

Spectral and magnetic studies have been used to characterise each

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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 4,7-phenanthroline complexes.

## EXPERIMENTAL

### *Preparation of complexes*

Metal chloride (1 g) and 4,7-phenanthroline (1 g) were dissolved in separate 60 cm<sup>3</sup> 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 and nickel complexes are blue, and the copper complex is grey.

### *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<sup>-1</sup>) and polyethylene discs (600–200 cm<sup>-1</sup>) with a Perkin-Elmer model 598 IR spectrophotometer.

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)<sub>4</sub>] 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<sup>-1</sup>. 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. The discs were 13 mm in diameter with thicknesses 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 complexes have the stoichiometry of  $M(C_{12}H_8N_2)Cl_2$ .

The d-d bands in the electronic reflectance spectra and the magnetic moments of the compounds are listed in Table 2. For the cobalt and nickel compounds, the position of the bands in the spectra and the magnetic moments indicate that the metal atoms are 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 is lower than the spin only value, indicating some spin-spin magnetic interaction in the compound.

The energies of the main bands in the IR spectra of 4,7-phenanthroline and its metal complexes are listed in Table 3, together with the descriptions and assignments. The IR spectra of the complexes are almost

TABLE 1  
Analyses (%) of compounds

Compound		M	C	N	H
$Co(C_{12}H_8N_2)Cl_2$	Theory	19.00	46.48	9.03	2.59
	Found	18.96	46.11	8.85	2.57
$Ni(C_{12}H_8N_2)Cl_2$	Theory	18.94	46.52	9.04	2.60
	Found	18.79	46.12	8.90	2.47
$Cu(C_{12}H_8N_2)Cl_2$	Theory	20.19	45.80	8.90	2.56
	Found	19.96	46.25	9.24	2.69

TABLE 2  
Electronic spectra and magnetic moments

Compound	Band position ( $cm^{-1}$ )	d-d Transition	$\mu$ (BM)
$Co(C_{12}H_8N_2)Cl_2$	9091	${}^4A_2(F) \rightarrow {}^4T_2(F)$ ${}^4A_2(F) \rightarrow {}^4T_1(P)$	4.32
	16129 } 17241 }		
$Ni(C_{12}H_8N_2)Cl_2$	8772	${}^3T_1(F) \rightarrow {}^3T_2(F)$ ${}^3T_1(F) \rightarrow {}^3A_2(F)$	3.87
	16000 } 17182 }		
$Cu(C_{12}H_8N_2)Cl_2$	12048	${}^2E_g(D) \rightarrow {}^2T_{2g}(D)$	1.62

TABLE 3  
IR Spectra (4000–200  $\text{cm}^{-1}$ )

Compound	Ring vibrations	$\nu(\text{M-Cl})$	$\nu(\text{M-N})$
$\text{C}_{12}\text{H}_8\text{N}_2$	1582(s), 1490(s)	–	–
$\text{Co}(\text{C}_{12}\text{H}_8\text{N}_2)\text{Cl}_2$	1587(s), 1502(s)	304(s), 280(m)	238(m)
$\text{Ni}(\text{C}_{12}\text{H}_8\text{N}_2)\text{Cl}_2$	1588(s), 1499(s)	308(s), 282(m)	232(m)
$\text{Cu}(\text{C}_{12}\text{H}_8\text{N}_2)\text{Cl}_2$	1590(s), 1497(s)	274(m)	260(w)

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

identical to the spectrum of 4,7-phenanthroline in the region 4000–600  $\text{cm}^{-1}$ , 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]. Metal–halogen and metal–nitrogen bands observed for each complex in the region 600–200  $\text{cm}^{-1}$  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. It is suggested that the cobalt and nickel complexes have bimetallic structures. The tetrahedral environment for each of the metal ions is obtained from two bridging chloride ions, one terminal chloride ion and a nitrogen atom from an aromatic ring. The copper complex consists of parallel chains of copper atoms bonded to halogen atoms, with the 4,7-phenanthroline molecules as bridging units between adjacent chains, forming a sheet structure.

The TG and DTA traces for 4,7-phenanthroline and its chloro complexes with cobalt, nickel and copper are shown in Figs. 1–4. The TG and DTA curves for 4,7-phenanthroline (Fig. 1) show that it is thermally

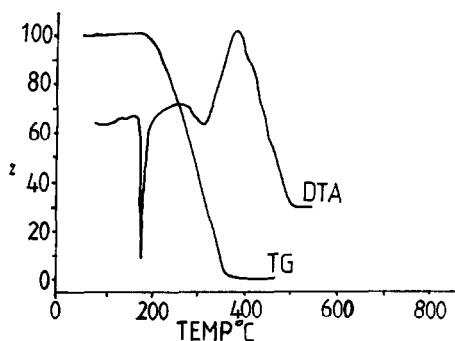


Fig. 1. TG and DTA traces for 4,7-phenanthroline. Sample weight = 10.22 mg.

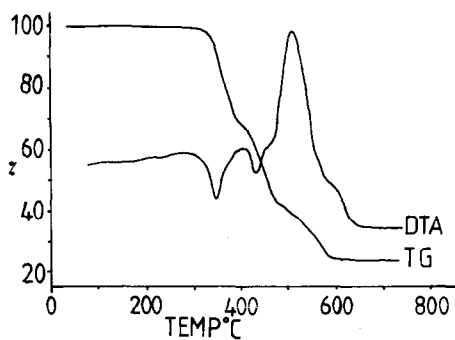


Fig. 2. TG and DTA traces for  $\text{Co}(\text{C}_{12}\text{H}_8\text{N}_2)\text{Cl}_2$ . Sample weight = 9.38 mg.

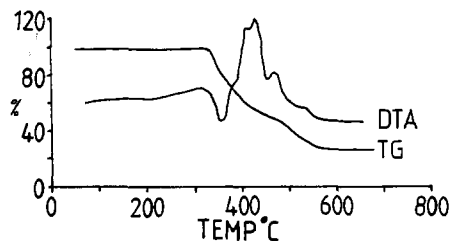


Fig. 3. TG and DTA traces for  $\text{Ni}(\text{C}_{12}\text{H}_8\text{N}_2)\text{Cl}_2$ . Sample weight = 7.50 mg.

stable in the temperature range 20–176°C. Pyrolytic decomposition commences at 176°C and ends at 370°C with total elimination of the sample. The DTA curve of 4,7-phenanthroline shows an endothermic peak at 172°C corresponding to fusion. The TG and DTA curves for the chloro complexes of 4,7-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  $\text{Co}(\text{C}_{12}\text{H}_8\text{N}_2)\text{Cl}_2$  undergoes an endothermic reaction to give  $\text{Co}_2(\text{C}_{12}\text{H}_8\text{N}_2)\text{Cl}_2$ . A further endothermic reaction occurs yielding  $\text{CoCl}_2$ , followed by an exothermic reaction and formation of  $\text{Co}_3\text{O}_4$ . The nickel and copper compounds first undergo endothermic reactions

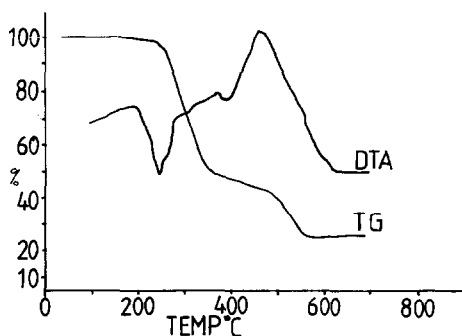


Fig. 4. TG and DTA traces for  $\text{Cu}(\text{C}_{12}\text{H}_8\text{N}_2)\text{Cl}_2$ . Sample weight = 8.22 mg.

TABLE 4  
Decomposition processes of the metal complexes

Starting material	Decomposition temp. (°C)	Mass loss (%)		Resulting compound
		Calc.	Found	
Co(C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> )Cl <sub>2</sub>	259(endo)	29.1	29.6	Co <sub>2</sub> (C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> )Cl <sub>4</sub>
	318(endo)	58.1	58.0	CoCl <sub>2</sub>
	342(exo)	74.1	75.0	Co <sub>3</sub> O <sub>4</sub>
Ni(C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> )Cl <sub>2</sub>	560(endo)	58.1	57.2	NiCl <sub>2</sub>
	598(exo)	75.9	74.02	NiO
Cu(C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> )Cl <sub>2</sub>	538(endo)	57.3	57.1	CuCl <sub>2</sub>
	564(exo)	74.7	75.2	CuO

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

with loss of phenanthroline to give metal chlorides, which in turn react exothermally to give the metal oxides.

The measured room temperature electrical conductivities ( $\sigma$ ) of the compounds and the uncomplexed ligand are shown in Table 5. The room temperature current ( $I$ ) versus voltage ( $V$ ) characteristics were obtained under conditions of rising and falling voltage in both polarities. The four currents measured were found to agree within 10% and were usually closer than this, indicating that the electrodes were not rectifying. The  $I$ - $V$  characteristics of all compounds were found to be linear throughout the voltage range studied, indicating that the electrical conduction was ohmic. The electrical conductivities (Table 5) are calculated from the gradients of the  $I$ - $V$  plots and with the assumption that the current flow is perpendicular to the electrodes.

Comparison of the room temperature conductivities of the compounds with that of the free ligand suggests that the coordinated metal ion and its stereochemistry play no part in the conduction process, and that the conduction pathway is via the ligand molecules. Indeed, from the

TABLE 5  
Room temperature electrical conductivities

Compound	$\sigma$ ( $\Omega^{-1} \text{ m}^{-1}$ ) <sup>a</sup>
C <sub>12</sub> H <sub>8</sub> N <sub>2</sub>	$4.25 \times 10^{-8}$
Co(C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> )Cl <sub>2</sub>	$3.98 \times 10^{-8}$
Ni(C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> )Cl <sub>2</sub>	$2.50 \times 10^{-8}$
Cu(C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> )Cl <sub>2</sub>	$3.96 \times 10^{-8}$

<sup>a</sup> Room temperature conductivity (20°C).

electrical conductivity data presented in Table 5, it would appear that complexation of the ligand with cobalt, nickel and copper has a detrimental effect on the conductivity. Such an observation would be expected if the conduction pathway was predominantly through overlap of suitable orbitals of adjacent ligand molecules, which on complexation would be unable to form a molecular orbital conduction path owing to increased intermolecular distances.

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