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THERMAL, SPECTRAL AND MAGNETIC STUDIES OF THE CHLORO COMPLEXES OF COBALT(II), NICKEL(II) AND COPPER(II) WITH PHENETIDINE

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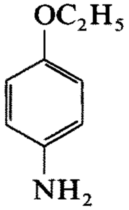
ABSTRACT

The chloro compounds of *p*-phenetidine with cobalt(II), nickel(II) and copper(II) were prepared in ethanolic solution from which solid compounds were isolated. The suggested structure for the cobalt compound is tetrahedral, while for the nickel and copper it is octahedral. The techniques of thermogravimetry and differential thermal analysis show that the compounds dichloro-bis(*p*-phenetidine) cobalt(II) and dichloro-bis(*p*-phenetidine) nickel(II) form intermediate compounds before the metal oxide is produced. The compound dichloro-bis(*p*-phenetidine) copper(II) decomposes with loss of the phenetidine and chlorine and the formation of copper oxide.

INTRODUCTION

This is a continuation of previously reported work on the structural characterisation and thermal-analysis studies of transition-metal complexes of primary amines [1–4]. In this paper we report the thermogravimetry and differential-thermal-analysis studies of the chloro complexes of cobalt, nickel and copper with *p*-phenetidine.



p-Phenetidine ($C_8H_{11}NO$)

0040-6031/90/$03.50

p-Phenetidine is a primary amine with two different types of donor site: the nitrogen atom of the amine group and the oxygen atom of the ether group: for bonding to metal ions. Spectral and magnetic studies were used to characterise each metal complex and to interpret the type of coordination which takes place to the metal ion.

EXPERIMENTAL

Preparation of complexes

The metal(II) halide (0.05 mol) was dissolved in a minimum of boiling ethanol. To the boiling ethanol solution was added an excess of the *p*-phenetidine. The precipitated product was then isolated by filtration and washed with a minimum of ethanol and air dried.

Apparatus

The concentration of the metal ion was measured using a Perkin–Elmer 373 atomic absorption spectrophotometer and the carbon, hydrogen and nitrogen analyses were done 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}) in a Perkin–Elmer IR spectrophotometer model 598. The electronic spectra were recorded on a Beckmann Acta MIV spectrophotometer as solid diffuse reflectance spectra. Magnetic measurements were carried out using the Gouy method using $Hg[Co(SCN)_4]$ as a calibrant.

Thermal-analysis studies were carried out on a Stanton Redcroft model STA 1500 thermobalance. The thermogravimetry (TG) and differential-thermal-analysis (DTA) curves were obtained at a heating rate of $10\,°C\ min^{-1}$ in static air over the temperature range 20–700 ° C.

RESULTS AND DISCUSSION

The analytical results of the complexes are given in Table 1. These analyses agree with the given formulae proposed for the compounds.

The magnetic moments and the bands in the electronic spectra of the complexes isolated from ethanolic solution are listed in Table 2. The position of the bands in the cobalt and nickel compounds would suggest that the cobalt ion is in a tetrahedral environment while the nickel ion is in an octahedral environment [5,6]. The values obtained for the magnetic moments support this suggestion [5,6]. The single broad absorption band at 12195 cm^{-1} in the electronic spectrum for the copper compound suggests that the copper atom is in an octahedral environment [5,6]. The magnetic moment

TABLE 1

Analyses of the compounds

Compound	Theory (%)				Found (%)			
	Metal	C	N	H	Metal	C	N	H
$Co(C_8H_{11}NO)_2Cl_2$ [a]	14.58	47.54	6.93	5.48	14.02	47.21	5.96	5.00
$Co(C_8H_{11}NO)Cl_2$ [b]	22.07	55.98	5.24	4.15	21.74	35.80	5.10	3.96
$Ni(C_8H_{11}NO)_2Cl_2$ [a]	14.53	47.57	6.93	5.49	14.39	46.86	6.32	5.32
$Ni(C_8H_{11}NO)Cl_2$ [b]	21.99	36.02	5.25	4.16	21.48	35.41	4.91	3.80
$Cu(C_8H_{11}NO)_2Cl_2$ [a]	15.54	47.01	6.85	5.42	15.36	46.53	6.83	4.76

[a] Initial compound isolated from solution.

[b] Intermediate compound produced by heating the corresponding initial compound ($C_8H_{11}NO$, phenetidine).

TABLE 2

Electronic spectra and magnetic moments of complexes isolated from solution

Compound	Peak position [a] (cm^{-1})	d–d transition	μ (B.M.)
$Co(C_8H_{11}NO)_2Cl_2$	7407	${}^4A_2(F) \rightarrow {}^4T_1(F)$	4.22
	16000	${}^4A_2(F) \rightarrow {}^4T_1(P)$	
$Ni(C_8H_{11}NO)_2Cl_2$	8700	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	3.01
	143000	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	
	23809 (sh)	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	
$Cu(C_8H_{11}NO)_2Cl_2$	12195	${}^2E_g(D) \rightarrow {}^2T_{2g}(D)$	1.60

[a] sh, Shoulder.

for the compound, 1.60 B.M. (Table 2), is indicative of some copper–copper interaction in the compound.

The wavenumbers of the IR absorption bands for phenetidine and its chloro complexes isolated from ethanolic solution are given in Table 3 together with their descriptions and assignments. The IR spectrum of phenetidine is very similar to that of its complexes in the region 4000–600

TABLE 3

Infra-red spectra of complexes isolated from solution (4000–200 cm^{-1})

Compound	$\nu_s(N-H)$		$\nu_B(N-H)$	ν_{M-Cl}		ν_{M-N}
$C_8H_{11}NO$	3420(s)	3350(s)	1621(s)	–		–
$Co(C_8H_{11}NO)_2Cl_2$	3262(s)	3210(s)	1578(s)	334(s)	312(s)	292(m)
$Ni(C_8H_{11}NO)_2Cl_2$	3310(s)	3230(s)	1589(s)	242(w)		295(m)
$Cu(C_8H_{11}NO)_2Cl_2$	3270(s)	3210(s)	1600(s)	230(w)		294(m)

s, Strong; w, weak; m, medium.

TABLE 4

Thermal-decomposition products

Starting material	Decomposition temperature [a] (°C)	Product	Weight loss (%)	
			Calc.	Found
$Co(C_8H_{11}NO)_2Cl_2$	110 (endo/exo)	$Co(C_8H_{11}NO)Cl_2$	33.93	33.20
	460 (exo)	Co_3O_4	81.46	80.50
$Ni(C_8H_{11}NO)_2Cl_2$	90 (endo)	$Ni(C_8H_{11}NO)Cl_2$	33.95	33.97
	240 (exo)	NiO	81.51	82.33
$Cu(C_8H_{11}NO)_2Cl_2$	97 (endo/exo)	CuO	80.54	80.56

[a] endo, Endothermic; exo, exothermic.

cm^{-1} except that the bands due to the N–H vibrations are shifted to lower frequencies on formation of the complexes. This would suggest that the nitrogen atoms of the amine groups are coordinated to a metal atom [2]. The ν(M–Cl) bands in the spectra of the nickel and copper complexes show that the metal ions are in a six-coordinate environment, while the corresponding bands for the cobalt complex indicate that the cobalt ion is in a four-coordinate environment [5,6].

The insolubility of the nickel and copper compounds in both polar and non-polar solvents is indicative of polymeric structures [5].

Single crystals of the compounds could not be isolated from ethanolic solution, thus without X-ray analysis no definite structures can be described. However, the spectroscopic and magnetic data enable us to predict possible structures. It is thus suggested that the structure of the nickel and copper complexes consists of a chain of metal atoms bonded to chloride ions with the phenetidine molecules bonded by nitrogen atoms to the metal above and below the plane of the metal–chloride chain. The cobalt compound has a tetrahedral structure in which the cobalt ion is bonded to two chloride ions and two nitrogen atoms from each of the phenetidine molecules.

The thermal decomposition data are given in Table 4 and the TG and DTA curves are shown in Figs. 1–3. The dark-blue cobalt compound which has stoichiometry $Co(C_8H_{11}NO)_2Cl_2$ undergoes an endothermic reaction followed by a exothermic reaction with loss of one molecule of phenetidine to give $Co(C_8H_{11}NO)Cl_2$. An exothermic reaction then takes place when the remaining molecule of phenetidine plus the chlorine is lost and the compound Co_3O_4 is formed. The green nickel compound which has stoichiometry $Ni(C_3H_{11}NO)_2Cl_2$ undergoes a endothermic reaction with loss of one molecule of phenetidine to give $Ni(C_8H_{11}NO)Cl_2$ followed by an exothermic reaction with loss of the remaining molecule of phenetidine and chlorine to give NiO. The brown copper compound, $Cu(C_8H_{11}NO)Cl_2$, undergoes a endothermic reaction followed by exothermic reactions, with loss of the two

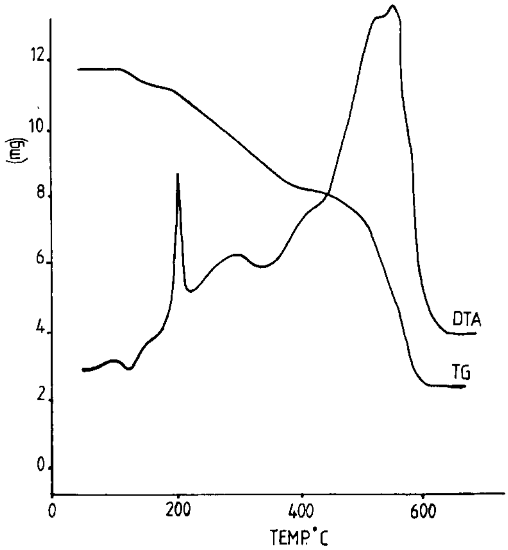


Fig. 1. TG and DTA curves for Co$(C_8H_{11}NO)_2Cl_2$. Sample weight = 11.80 mg.

molecules of phenetidine and the chlorine to give CuO. The compound Co$(C_8H_{11}NO)Cl_2$ has bands in its electronic spectrum at 16 090 and 18 180 cm^{-1}, while the compound Ni$(C_8H_{11}NO)Cl_2$ has bands in its electronic spectrum at 13 300 and 22 300 cm^{-1}. This is characteristic of cobalt(II) and nickel(II) in a distorted-octahedral environment [7,8].

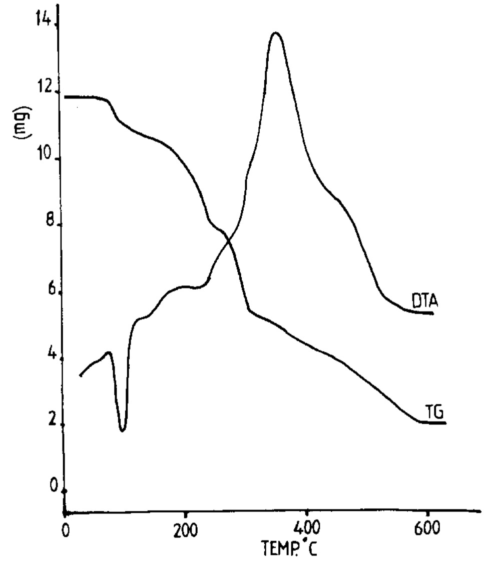


Fig. 2. TG and DTA curves for Ni$(C_8H_{11}NO)_2Cl_2$. Sample weight = 11.89 mg.

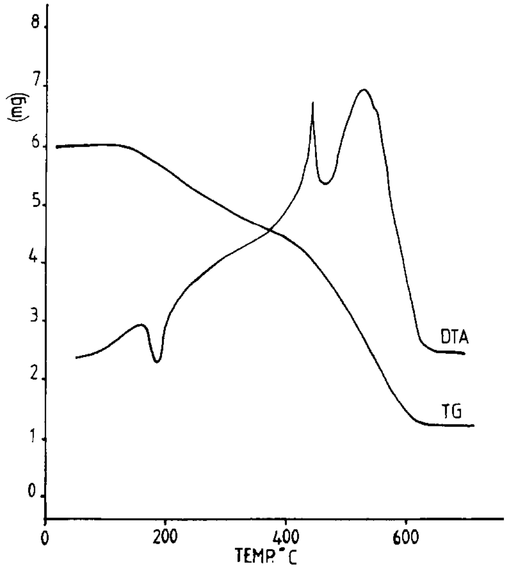


Fig. 3. TG and DTA curves for $Cu(C_8H_{11}NO)_2Cl_2$. Sample weight = 6.02 mg.

The actual structures adopted by these phases are not known, but it is likely that the complexes with smaller amounts of base have lattices in which there is considerable halide bridging as have been previously postulated for pyridine complexes [7,8]. The IR spectra of these compounds would agree with this suggestion since bands due to the ν(N–H) vibrations move to lower wavenumber, while the bands due to the ν(C–O–C) vibration show no change when compared with the free ligand. In spite of the lack of knowledge of precise details, the broad outline of the thermal decompositions is clear and may be summarised as

$$Co(C_8H_{11}NO)_2Cl_2(\text{tet}) \rightarrow Co(C_8H_{11}NO)Cl_2(\text{oct}) \rightarrow Co_3O_4$$

$$Ni(C_8H_{11}NO)_2Cl_2(\text{oct}) \rightarrow Ni(C_8H_{11}NO)Cl_2(\text{oct}) \rightarrow NiO$$

$$Cu(C_8H_{11}NO)_2Cl_2(\text{oct}) \rightarrow CuO$$

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