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THERMAL STUDIES ON THE CHLORO COMPOUNDS OF COBALT(II), NICKEL(II) AND COPPER(II) WITH 4-AMINOQUINALDINE

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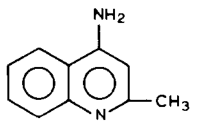
ABSTRACT

Some new chloro compounds of cobalt, nickel and copper with 4-aminoquinaldine were prepared. The compounds are all hydrated. Spectral and magnetic properties were used to deduce the stereochemistry. The complexes have polymeric octahedral structures. The thermal behaviour of the complexes was studied by TG and DTA. Thermal decomposition studies show that these compounds lose water followed by the organic ligand to give the metal oxide.

INTRODUCTION

In this work, the structural properties and the thermal analysis studies of the chloro compounds of cobalt, nickel and copper with 4-aminoquinaldine are described and discussed. The molecule of 4-aminoquinaldine has two possible coordination sites: the amino group and the ring nitrogen atom.



4-aminoquinaldine ($C_{10}H_{10}N_2$)

Spectral and magnetic studies were used to characterize each complex and to interpret the type of coordination which takes place to the metal ion. A study of the thermal stability of each compound was carried out. No thermal decomposition data has been reported in the literature for any of these compounds.

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EXPERIMENTAL

Preparation of the metal compounds

The chloro complexes of cobalt, nickel and copper with 4-aminoquinaldine were prepared by adding 25 cm^3 of a hot solution of 4-aminoquinaldine (0.02 mol in ethanol) to 25 cm^3 of a hot solution of the hydrated metal halide (0.01 mol in ethanol). The complexes, which precipitated on cooling, were filtered and purified by repeated washing with boiling ethanol followed by drying at 40 °C in air.

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} on a Perkin–Elmer IR spectrophotometer Model 598.

The electronic spectra were obtained on a Beckmann Acta MIV spectrophotometer as 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 781 thermobalance. The TG and DTA curves were obtained at a heating rate of 10 °C min^{-1} in static air. In all cases the 20–1000 °C temperature range was studied.

RESULTS AND DISCUSSION

The compounds prepared are listed in Table 1. The analytical results agree with the stoichiometry of the compounds. All of the compounds have water molecules present.

The wavenumbers of the IR absorption bands as well as their descriptions and assignments are given in Table 2. The IR spectra of the complexes show strong, broad absorption bands in the region 3700–2400 cm^{-1}, ν(OH), confirming the presence of water of crystallization. These broad bands obscure the bands resulting from the $\nu(NH_2)$ vibrations. Hence each of the complexes was heated on a thermobalance at a fixed temperature until constant weight was obtained to remove the water molecules. The IR spectra were then obtained for each of the anhydrous compounds (Table 2). In the region 3560–3140 cm^{-1}, the ν(N–H) vibrations in the complexes move to higher wavenumbers when comparison is made in this region between the IR spectra of the complexes and the 4-aminoquinaldine. These observations suggest that there is no coordination through the nitrogen of the amino

TABLE 1

Analysis and magnetic moments of the compounds

Compounds	Colour	Theory (%)				Found (%)				μ (BM)
		M	C	N	H	M	C	N	H	
$Co(C_{10}H_{10}N_2)_2Cl_2 \cdot 2H_2O$	Turquoise	12.22	49.80	11.62	5.03	12.40	49.72	11.47	4.66	5.24
$Ni(C_{10}H_{10}N_2)_2Cl_2 \cdot 1.5H_2O$	Green	12.41	50.77	11.85	4.91	12.77	50.41	11.72	4.81	3.26
$Cu(C_{10}H_{10}N_2)_2Cl_2 \cdot 2.5H_2O$	Green	12.81	48.43	11.29	5.09	13.00	48.02	11.09	5.24	1.62

$C_{10}H_{10}N_2$ = 4-aminoquinaldine.

TABLE 2

IR spectra (4000–200 cm^{-1})

Compound	$\nu_{O-H}(H_2O)$	ν_{NH_2}	Ring vibrations	ν_{M-X}	ν_{M-N}
$C_{10}H_{10}N_2$	–	3428(s), 3285(s)	1645(s), 1575(s), 1505(s)	–	–
$Co(C_{10}H_{10}N_2)_2Cl_2 \cdot 2H_2O$	3680–2400(br,s)	–	1650(s), 1596(s), 1512(s)	–	–
$Co(C_{10}H_{10}N_2)_2Cl_2$	–	3560(s), 3325(s), 3150(s)	1650(s), 1596(s), 1512(s)	274(vw)	336(m)
$Ni(C_{10}H_{10}N_2)_2Cl_2 \cdot 1.5H_2O$	3700–2500(br,s)	–	1648(s), 1602(s), 1510(s)	–	–
$Ni(C_{10}H_{10}N_2)_2Cl_2$	–	3330(s), 3148(s)	1648(s), 1602(s), 1510(s)	245(vw)	338(m)
$Cu(C_{10}H_{10}N_2)_2Cl_2 \cdot 2.5H_2O$	3690–2340(br,s)	–	1640(s), 1594(s), 1510(s)	–	–
$Cu(C_{10}H_{10}N_2)_2Cl_2$	–	3520(s), 3320(s), 3150(s)	1640(s), 1594(s), 1510(s)	206(vw)	336(m)

br = broad; s = strong; m = medium, vw = very weak.

TABLE 3

Electronic spectra (cm^{-1})

Compound	Peak position	d–d Transitions	*Dq*	*B*	*β*
$Co(C_{10}H_{10}N_2)_2Cl_2 \cdot 2H_2O$	8333	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	860	783	0.81
	16949	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$			
	19802	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$			
$Ni(C_{10}H_{10}N_2)_2Cl_2 \cdot 1.5H_2O$	8064	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	806	901	0.86
	14705	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$			
	25000	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$			
$Cu(C_{10}H_{10}N_2)_2Cl_2 \cdot 2.5H_2O$	15748	$^2E_g(D) \rightarrow {}^2T_{2g}(D)$			

group of the 4-aminoquinaldine and the metal [1]. The IR spectrum of the 4-aminoquinaldine is almost identical to that of its complexes in the region 2000–625 cm^{-1}, except for the bands due to the ring vibrations of the aromatic ring which move to higher wavenumbers. This would suggest that coordination is taking place between the metal and the nitrogen atom in the aromatic ring [2]. Metal–chloride and metal–nitrogen bands are assigned for the complexes and are reported in Table 2.

The electronic spectra (Table 3) and the magnetic measurements (Table 1) would suggest that for the cobalt and nickel compounds the metal ion is in an octahedral environment [2,3]; the values for *Dq* are in agreement with this suggestion [4]. The values for *β* show a degree of ionic character in the metal–ligand bonds. The single broad absorption band in the electronic spectrum of the copper compound at 15748 cm^{-1} would suggest that the copper ion is in an octahedral environment [5]. The magnetic moment of 1.62 BM for this compound would suggest the presence of some copper–copper interaction [6].

The poor solubility of the compounds in both polar and non-polar solvents is indicative of polymeric structures [2].

The fact that the compounds were isolated from ethanolic solution as powders and not as single crystals means that no complete structure determination can be made. However, spectroscopic and magnetic data enable us to predict that the metal ions are in an octahedral environment in the compounds. It is thus postulated that the structure of the compounds is a chain of metal atoms bonded to halogens with the 4-aminoquinaldine molecules above and below the plane of the metal–halogen chain to give a polymeric structure. It is further suggested that the water molecules are attached to the structure by hydrogen bonding.

The TG and DTA traces for 4-aminoquinaldine and its cobalt, nickel and copper compounds are given in Figs. 1–4. The TG trace for 4-aminoquinaldine (Fig. 1) shows that this compound is thermally stable in the 20–170 °C range. Its pyrolitic decomposition starts at 170 °C and finishes around

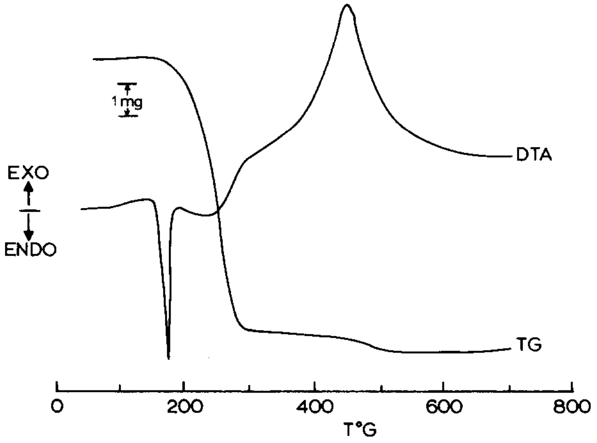

Fig. 1. TG and DTA trace for 4-aminoquinaldine. Sample weight = 9.00 mg.

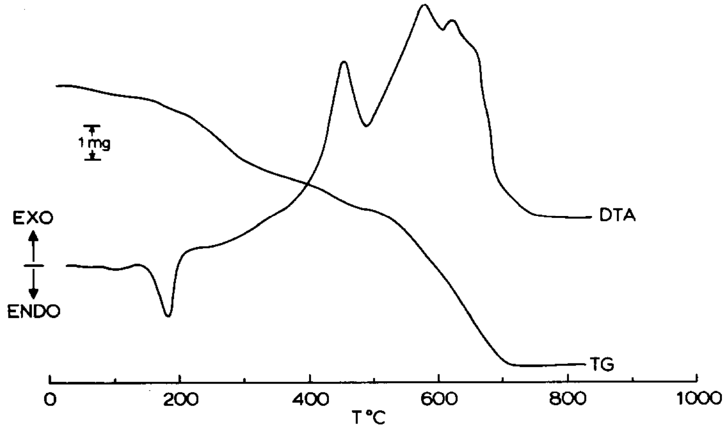

Fig. 2. TG and DTA trace for $Co(C_{10}H_{10}N_2)_2Cl_2 \cdot 2H_2O$. Sample weight = 9.78 mg.

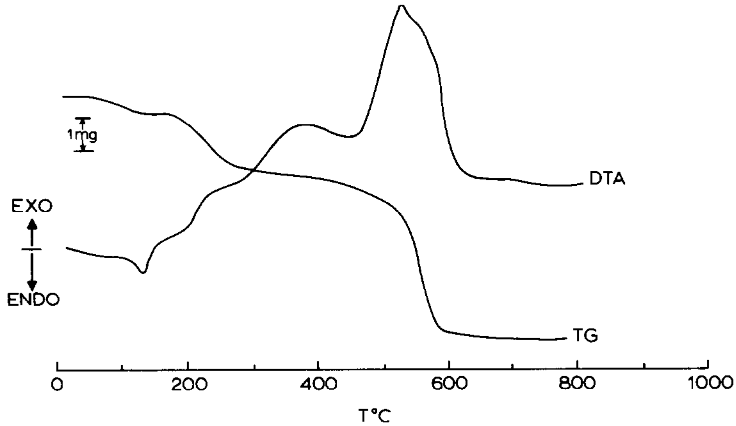

Fig. 3. TG and DTA trace for $Ni(C_{10}H_{10}N_2)_2Cl_2 \cdot 1.5H_2O$. Sample weight = 9.10 mg.

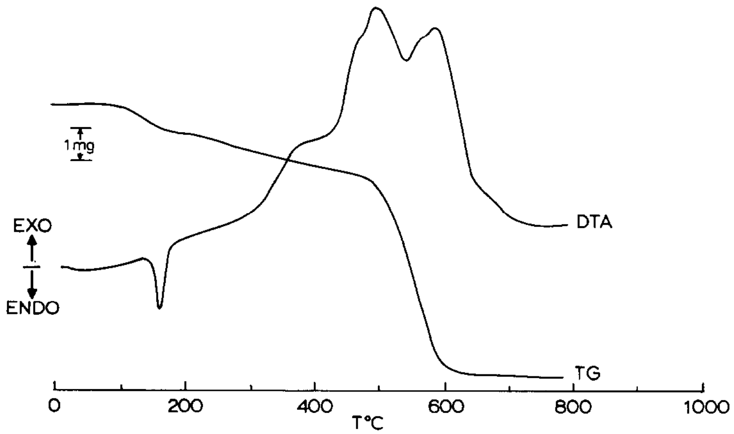

Fig. 4. TG and DTA trace for $Cu(C_{10}H_{10}N_2)_2Cl_2 \cdot 2.5H_2O$. Sample weight = 9.73 mg.

640 °C with the total elimination of the sample. The DTA trace of 4-aminoquinaldine (Fig. 1) displays an endothermic peak at 168 °C corresponding to fusion. The value for the fusion enthalpy calculated from the area of this effect is 6.1 kJ mol^{-1}. The ligand, 4-aminoquinaldine, decomposed immediately producing an exothermic peak at 460 °C. The TG and DTA traces for the complexes formed between 4-aminoquinaldine and the chlorides of cobalt, nickel and copper are given in Figs. 2–4. The TG and DTA traces for the complexes are similar. The dehydration of the complexes takes place in one step. The observed weight losses for these processes compare favourably with the theoretical values in Table 4. The expected endothermic peak for the dehydration processes associated with these compounds was observed in the DTA traces. The dehydration enthalpies have been calculated and are given in Table 4. Decomposition of the anhydrous complexes follows immediately after the dehydration process and the residual weights are in good agreement with the values required for the metallic oxides (Table 5). In the DTA traces these decomposition processes

TABLE 4

Dehydration processes of the 4-aminoquinaldine metal compounds

Process	Peak temperature (° C)	Thermal nature of transformation	Weight loss (%)		Enthalpy (kJ mol^{-1})
			Calc.	Found.	
$Co(C_{10}H_{10}N_2)_2Cl_2 \cdot 2H_2O \rightarrow Co(C_{10}H_{10}N_2)_2Cl_2$	180	Endo	7.47	7.97	18.5
$Ni(C_{10}H_{10}N_2)_2Cl_2 \cdot 1.5H_2O \rightarrow Ni(C_{10}H_{10}N_2)_2Cl_2$	142	Endo	5.70	5.93	10.9
$Cu(C_{10}H_{10}N_2)_2Cl_2 \cdot 2.5H_2O \rightarrow Cu(C_{10}H_{10}N_2)_2Cl_2$	160	Endo	9.07	9.55	18.1

TABLE 5

Decomposition processes of 4-aminoquinaldine and the metal compounds

Process	Temperature range (°C)	Thermal nature of transformation	Residue (%)	
			Calc.	Found
$C_{10}H_{10}N_2 \rightarrow$ pyrolitic process	170–640	Exo	–	–
$Co(C_{10}H_{10}N_2)_2Cl_2 \rightarrow Co_3O_4$	214–720	Exo	16.67	16.66
$Ni(C_{10}H_{10}N_2)_2Cl_2 \rightarrow NiO$	160–750	Exo	15.79	15.93
$Cu(C_{10}H_{10}N_2)_2Cl_2 \rightarrow CuO$	175–685	Exo	16.03	15.41

correspond to exothermic effects for the complexes and these have been indicated in Table 5.

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