Thermal, spectral and magnetic studies of cobalt(II), copper(II) and zinc(II) complexes of 5,6-benzoquinoline and 6-methoxyquinoline

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Abstract

The chloro complexes of cobalt, copper and zinc with 5,6-benzoquinoline and 6-methoxyquinoline have been prepared. The stereochemical configuration of the complexes were deduced using spectral and magnetic data. The decomposition of each complex was studied by thermogravimetry and differential thermal analysis.

INTRODUCTION

In this paper, the structural characterisation and thermal studies of the chloro compounds of cobalt, copper and zinc with 5,6-benzoquinoline and 6-methoxyquinoline are described and discussed. The molecule of 5,6-benzoquinoline has one donor site: the nitrogen atom of the aromatic ring system for bonding to metal ions.
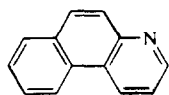
5,6-benzoquinoline ($C_{13}H_9N$)

The molecule of 6-methoxyquinoline has two donor sites: the oxygen atom of the methoxy group and the nitrogen atom of the aromatic ring system for bonding to metal ions.
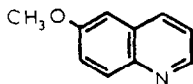
6-methoxyquinoline ($C_{10}H_9NO$)

Spectral and magnetic studies were used to characterise 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 using thermogravimetry and differential thermal analysis.

EXPERIMENTAL

Preparation of the 5,6-benzoquinoline complexes

The chloro complexes of cobalt, copper and zinc with 5,6-benzoquinoline were prepared by adding 25 cm^3 of 5,6-benzoquinoline (0.02 mol in ethanol) to 25 cm^3 of a warm solution of the hydrated metal halide (0.01 mol in ethanol). The complexes which precipitated on cooling were filtered, purified by repeated washing with boiling ethanol and air dried.

Preparation of the 6-methoxyquinoline complexes

The chloro complexes of cobalt, copper and zinc with 6-methoxyquinoline were prepared by adding an excess of 6-methoxyquinoline to 25 cm^3 of a warm solution of the hydrated metal halide (0.01 mol in ethanol). The complexes which precipitated on cooling were filtered, washed with a solution of ethanol: 6-methoxyquinoline and air dried.

Apparatus

The concentration of the metal ion was obtained using a Perkin–Elmer 373 atomic absorption spectrophotometer and the carbon, hydrogen and nitrogen analyses were made 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 spectrophotometer Model 598.

The electronic spectra were obtained on a Beckman 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 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. Intermediate compounds were isolated from the starting materials by heating them at a fixed temperature on the thermobalance until a constant weight was obtained.

RESULTS AND DISCUSSION

The complexes prepared are listed in Table 1. The analytical results agree with the stoichiometry of the complexes.

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TABLE 1

Analyses of the compounds

Compound	Colour	Theory (%)				Found (%)			
		Metal	Carbon	Nitrogen	Hydrogen	Metal	Carbon	Nitrogen	Hydrogen
$Co(C_{13}H_9N)_2Cl_2$	Blue	11.82	63.95	5.73	3.74	12.36	63.86	5.49	3.56
$Co(C_{13}H_9N)Cl_2$ [a]	Blue	19.06	50.52	4.53	2.93	18.86	50.13	4.04	2.64
$Cu(C_{13}H_9N)_2Cl_2$	Green	12.89	63.35	5.68	3.68	12.27	63.02	5.66	3.49
$Zn(C_{13}H_9N)_2Cl_2$	White	13.21	63.12	5.66	3.66	13.02	63.04	5.57	3.36
$Zn_3(C_{13}H_9N)_4Cl_6$ [a]	White	17.42	55.48	4.97	3.22	16.86	54.67	4.03	2.73
$Co(C_{10}H_9NO)_2Cl_2$	Blue	13.14	53.59	6.25	4.04	13.31	53.16	6.05	3.91
$Co(C_{10}H_9NO)Cl_2$ [a]	Blue	20.38	41.55	4.84	3.13	20.16	41.29	4.47	2.87
$Co_3(C_{10}H_9NO)_2Cl_6$ [a]	Blue	24.97	33.93	3.95	2.56	24.19	33.27	3.54	1.83
$Cu(C_{10}H_9NO)_2Cl_2$	Green	14.03	53.04	6.18	4.06	13.91	52.67	6.14	3.86
$Zn(C_{10}H_9NO)_2Cl_2$	White	14.37	52.83	6.16	5.28	14.21	52.55	5.86	3.77
$Zn(C_{10}H_9NO)Cl_2$ [a]	White	22.12	40.65	4.74	3.07	21.71	39.87	4.18	2.51

[a] Thermal decomposition products.

TABLE 2

Electronic spectra and magnetic moments

Compound	Band position (cm^{-1})	μ (BM)
Co(C$_{13}$H$_9$N)$_2$Cl$_2$	8850	4.24
	16129	
	21186	
Cu(C$_{13}$H$_9$N)$_2$Cl$_2$	16260	1.97
	19801	
Co(C$_{10}$H$_9$NO)$_2$Cl$_2$	9000	4.33
	15748	
	19531	
Cu(C$_{10}$H$_9$NO)$_2$Cl$_2$	16666	1.90
	19305	

The electronic spectra and magnetic measurements are listed in Table 2 for the cobalt and copper complexes. The position of the bands in the electronic spectra and the magnetic moments of the cobalt complexes would suggest that the cobalt atoms are in a tetrahedral environment [1]. The copper complexes have bands of equal intensity above 15000 cm^{-1} and no bands below 10000 cm^{-1}. This would indicate a square-planar environment for the copper atoms in each of these complexes [2]. The magnetic moment for each of the copper complexes is greater than the spin-only value of 1.73 BM, indicating no magnetic spin–spin interaction.

Table 3 lists the main bands in the IR spectra of 5,6-benzoquinoline and 6-methoxyquinoline and their complexes. The IR spectra of 5,6-benzoquinoline and 6-methoxyquinoline are almost identical to that of their complexes in the 4000–600 cm^{-1} region, except for the bands due to the aromatic ring vibrations which move to higher wave numbers on complexation. This would suggest that bonding is taking place between the metal atoms and the nitrogen atom in each of the aromatic rings [3]. The fact that

TABLE 3

Infrared spectra (40000–200 cm^{-1}) [a]

Compound	Ring vibrations	ν(C–O)	ν(M–Cl)	ν(M–N)
C$_{13}$H$_9$N	1578(s) 1502(s)	–	–	–
Co(C$_{13}$H$_9$N)$_2$Cl$_2$	1592(s) 1504(s)	–	340(s) 320(s)	240(m)
Cu(C$_{13}$H$_9$N)$_2$Cl$_2$	1581(s) 1505(s)	–	322(s)	262(m)
Zn(C$_{13}$H$_9$N)$_2$Cl$_2$	1582(s) 1507(s)	–	320(s) 312(s)	238(m)
C$_{10}$H$_9$NO	1575(s) 1502(s)	1230(s)	–	–
Co(C$_{10}$H$_9$NO)$_2$Cl$_2$	1593(s) 1512(s)	1229(s)	332(s) 308(s)	242(m)
Cu(C$_{10}$H$_9$NO)$_2$Cl$_2$	1592(s) 1511(s)	1230(s)	326(s)	260(m)
Zn(C$_{10}$H$_9$NO)$_2$Cl$_2$	1592(s) 1510(s)	1229(s)	320(s) 300(s)	240(m)

[a] s, strong; m, medium.

TABLE 4

Thermal decomposition products

Starting material	Decomposition temperature ($^\circ$C)	Resulting compound	Weight loss	
			Calc.	Found
$Co(C_{13}H_9N)_2Cl_2$	210 (endo)	$Co(C_{13}H_9N)Cl_2$	36.7	36.2
	312 (exo)	Co_3O_4	84.6	84.2
$Cu(C_{13}H_9N)_2Cl_2$	188 (endo/exo)	CuO	83.9	83.6
$Zn(C_{13}H_9N)_2Cl_2$	212 (endo)	$Zn_3(C_{13}H_9N)_4Cl_6$	24.1	24.0
	304 (exo)	ZnO	83.6	83.2
$Co(C_{10}H_9NO)_2Cl_2$	198 (endo)	$Co(C_{10}H_9NO)Cl_2$	35.5	35.2
	392 (endo)	$Co_3(C_{10}H_9NO)_2Cl_6$	47.3	47.1
	567 (exo)	Co_3O_4	82.1	82.2
$Cu(C_{10}H_9NO)_2Cl_2$	108 (endo/exo)	CuO	83.9	83.6
$Zn(C_{10}H_9NO)_2Cl_2$	206 (endo)	$Zn(C_{10}H_9NO)Cl_2$	35.0	34.8
	396 (exo)	ZnO	82.1	82.0

little or no change is observed for the ν(C–O) vibration in the 6-methoxyquinoline on complexation would suggest that the oxygen atom of the methoxy group is not bonded to the metal atoms [4].

Metal–chloride and metal–nitrogen bands are assigned for the complexes and are reported in Table 3. The ν(Zn–Cl) vibrations show that the zinc atoms are in a tetrahedral environment [5].

The fact that no single crystals were obtained on precipitation of the complexes from ethanolic solution means that no complete structure determination can be made. However, the spectroscopic and magnetic data enables us to predict the environment of the metal ion in the complexes. In the cobalt and zinc complexes the metal atoms are in a tetrahedral environment with each metal atom bonded to two chloride ions and to two molecules of the organic ligand through the nitrogen atom of the aromatic ring. In each of the copper complexes the copper atoms are in a square-planar environment with the copper atom bonded to two chloride ions and to two molecules of the organic ligand through the nitrogen atom in the aromatic ring system.

The thermal decomposition data are given in Table 4 and the TG and DTA curves are shown in Figs. 1–6. The dark blue compound $Co(C_{13}H_9N)_2Cl_2$ undergoes an endothermic reaction with the loss of one molecule of 5,6-benzoquinoline to give $Co(C_{13}H_9N)Cl_2$. An exothermic reaction takes place when the remaining molecule of 5,6-benzoquinoline plus the chlorine is lost and the compound Co_3O_4 is formed.

The green compound $Cu(C_{13}H_9N)_2Cl_2$ undergoes an endothermic reaction followed by an exothermic reaction with the loss of two molecules of 5,6-benzoquinoline and chlorine to give CuO. The white compound $Zn(C_{13}H_9N)_2Cl_2$ undergoes an endothermic reaction with the loss of
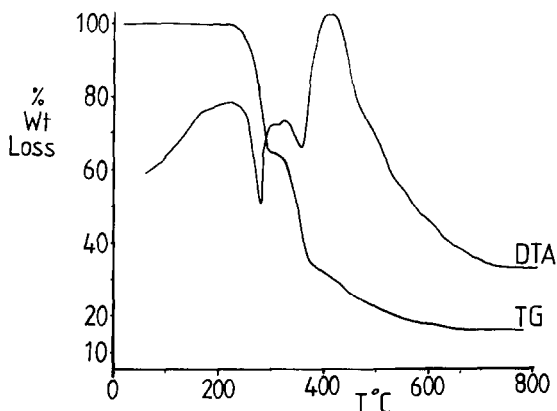
Fig. 1. TG and DTA trace for $Co(C_{13}H_9N)_2Cl_2$, sample weight = 8.36 mg.

two-thirds of a molecule of 5,6-benzoquinoline to give $Zn_3(C_{13}H_9N)_4Cl_6$ followed by an exothermic reaction with the loss of the remaining 5,6-benzoquinoline and chlorine to give ZnO. The dark blue compound $Co(C_{10}H_9NO)_2Cl_2$ undergoes an endothermic reaction with the loss of one molecule of 6-methoxyquinoline to give $Co(C_{10}H_9NO)Cl_2$. A further endothermic reaction then takes place and one-third of a molecule of 6-methoxyquinoline is lost to give the compound $Co_3(C_{10}H_9NO)_2Cl_6$. An exothermic reaction then takes place when the remaining 6-methoxyquinoline plus the chlorine is lost and the compound Co_3O_4 is formed. The green compound $Cu(C_{10}H_9NO)_2Cl_2$ undergoes an endothermic reaction followed by an exothermic reaction with the loss of two molecules of 6-methoxyquinoline and chlorine to give CuO. The white compound $Zn(C_{10}H_9NO)_2Cl_2$ undergoes an endothermic reaction to give
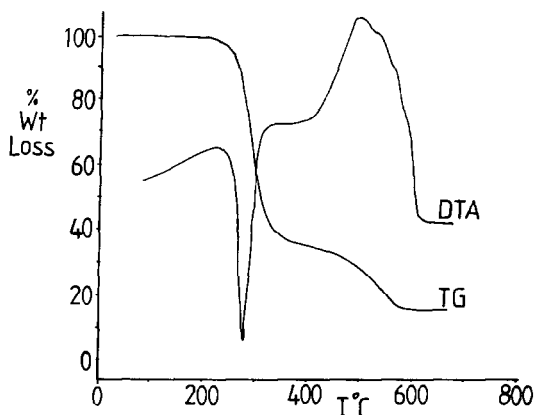
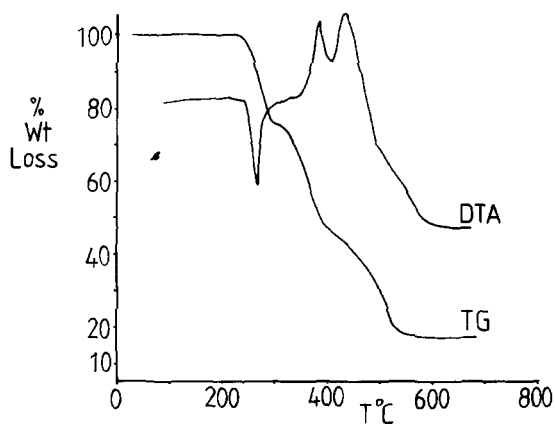Fig. 2. TG and DTA trace for $Cu(C_{13}H_9N)_2Cl_2$, sample weight = 7.49 mg.

Fig. 3. TG and DTA trace for $Zn(C_{13}H_9N)_2Cl_2$, sample weight = 7.84 mg.
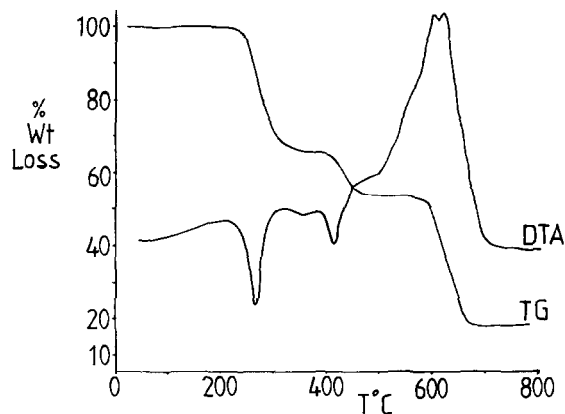
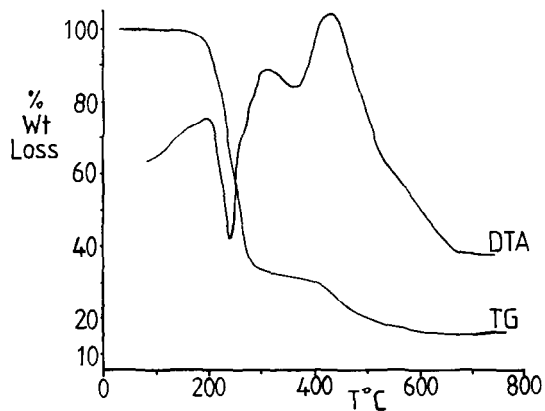Fig. 4. TG and DTA trace for $Co(C_{10}H_9NO)_2Cl_2$, sample weight = 10.31 mg.

Fig. 5. TG and DTA trace for $Cu(C_{10}H_9NO)_2Cl_2$, sample weight = 3.18 mg.

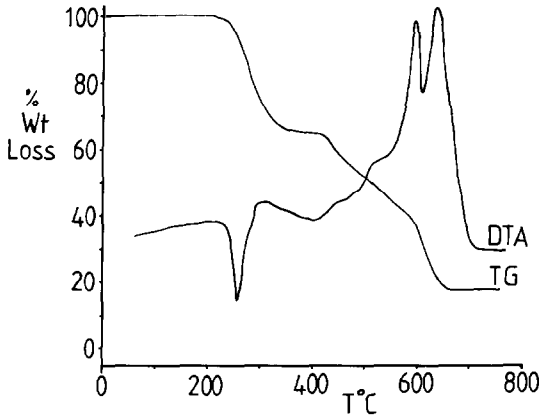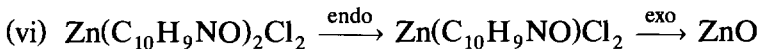Fig. 6. TG and DTA trace for $Zn(C_{10}H_9NO)_2Cl_2$, sample weight $= 11.97$ mg.

$Zn(C_{10}H_9NO)Cl_2$ followed by an exothermic reaction with the loss of the remaining molecule of 6-methoxyquinoline and chlorine to give ZnO.

In summary, the decomposition schemes are:

(i) $Co(C_{13}H_9N)_2Cl_2 \xrightarrow{\text{endo}} Co(C_{13}H_9N)Cl_2 \xrightarrow{\text{exo}} Co_3O_4$

(ii) $Cu(C_{13}H_9N)_2Cl_2 \xrightarrow{\text{endo/exo}} CuO$

(iii) $Zn(C_{13}H_9N)_2Cl_2 \xrightarrow{\text{endo}} Zn_3(C_{13}H_9N)_4Cl_6 \xrightarrow{\text{exo}} ZnO$

(iv) $Co(C_{10}H_9NO)_2Cl_2 \xrightarrow{\text{endo}} Co(C_{10}H_9NO)Cl_2 \xrightarrow{\text{endo}}$
       $Co_3(C_{10}H_9NO)_2Cl_6 \xrightarrow{\text{exo}} Co_3O_4$

(v) $Cu(C_{10}H_9NO)_2Cl_2 \xrightarrow{\text{endo/exo}} CuO$

(vi) $Zn(C_{10}H_9NO)_2Cl_2 \xrightarrow{\text{endo}} Zn(C_{10}H_9NO)Cl_2 \xrightarrow{\text{exo}} ZnO$
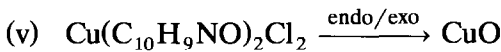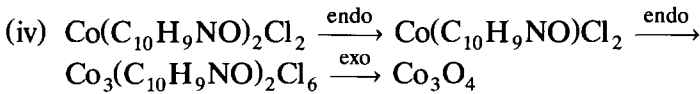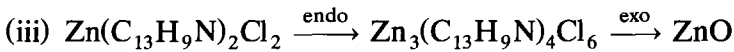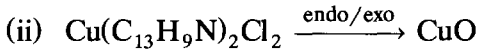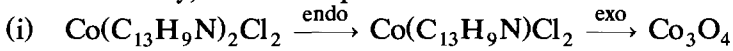
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