Journal of Thermal Analysis, Vol. 45 (1995) 369-374

THERMAL AND STRUCTURAL STUDIES OF THE CHLORO COMPLEXES OF COBALT, NICKEL AND COPPER WITH 3-PHENYLPYRIDINE

B. R. Carson[1], *G. Kenessey*[2], *J. R. Allan*[1] *and G. Liptay*[2]

[1]Department of Applied Chemical and Physical Sciences, Napier University, Edinburgh, EH10 5DT, Scotland
[2]Thermoanalytical Research Group, Department of Inorganic Chemistry, Technical University of Budapest, H-1521, Hungary

(Received October 21, 1994)

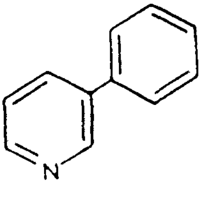
Abstract

The chloro complexes of cobalt, nickel and copper with 3-phenylpyridine were prepared in ethanolic solution from which solid compounds were isolated. The cobalt and copper complexes have stoichiometry M_2LCl_4 while the nickel complex has stoichiometry $NiLCl_2$. The suggested structure for the cobalt and copper complexes is tetrahedral, while for the nickel complex it is octahedral. Thermal analysis studies show that the cobalt and copper complexes form intermediate complexes before their metal oxides are produced. The nickel complex also forms an intermediate complex and then nickel chloride before the nickel oxide is obtained.

Keywords: chloro complexes, structural studies

Introduction

The compound 3-phenylpyridine has one donor site for forming bonds with metal ions: the nitrogen atom of the aromatic ring.



3-phenylpyridine ($C_{11}H_9N$)

In this paper we report studies of the chloro complexes of cobalt, nickel and copper with 3-phenylpyridine. Spectral and magnetic measurements have been used to characterise each metal complex and to interpret the type of coordina-

0368–4466/95/ $ 4.00

John Wiley & Sons, Limited
Chichester

tion which takes place with the metal ion. The thermal decomposition studies of the complexes are also reported.

Experimental

Preparation of complexes

The metal(II) halides (0.05 mol) were dissolved in a minimum of boiling ethanol. To the boiling ethanol solution were added 0.1 mol of 3-phenylpyridine with stirring. The resulting solution was heated for a few minutes and then concentrated on a steam bath. The precipitated product was then isolated by filtration, washed with a minimum of ethanol and air dried.

Apparatus and measurement

The concentration of the metal ion was determined using a Perkin Elmer 373 atomic absorption spectrometer. The carbon, hydrogen and nitrogen analyses were made using a Carlo Erba elemental analyser. The IR spectra were recorded using KBr discs over the range 4000–600 cm^{-1} and polyethylene discs over the range 600–200 cm^{-1} on a Perkin Elmer IR spectrophotometer. The electronic spectra were recorded as solid diffuse reflectance spectra Beckmann Acta MIV spectrophotometer. Measurements of magnetic moments were made using the Gouy method with $Hg[Co(SCN)_4]$ as calibrant. The thermal analysis measurements were made on a Stanton Redcroft thermobalance model 1500. Thermogravimetry (TG) and differential thermal analysis (DTA) traces were obtained at a heating rate of 6 deg·min^{-1} in static air. The 20–800°C temperature range was studied in all cases. Sample weights of 8 to 10 mg were used.

Results and discussion

The analytical results for the complexes are given in Table 1. The elemental analysis agree with the formulae proposed for the complexes which are also given in Table 1.

Table 1 Analyses of complexes

Complex		Metal	Carbon	Nitrogen	Hydrogen
$Co_2(C_{11}H_9N)Cl_4$	Theory (%)	28.4	31.8	3.4	2.2
	Found (%)	28.1	31.4	3.1	2.0
$Ni(C_{11}H_9N)Cl_2$	Theory (%)	20.6	46.4	4.9	3.2
	Found (%)	20.3	46.1	4.6	3.0
$Cu_2(C_{11}H_9N)Cl_4$	Theory (%)	30.0	31.2	3.3	2.1
	Found (%)	29.5	30.9	3.0	2.0

The bands observed in the electronic spectra of the complexes along with their magnetic moments are listed in Table 2. In the cobalt complex the position and intensity of the bands are characteristic of the cobalt atoms in a tetrahedral environment [1]. The magnetic moment lies in the range 4.2–4.8 BM and is in accord with the previous conclusion about the environment of the cobalt atoms in this complex [1]. The nickel complex has a magnetic moment in the range 2.8–3.4 BM which is indicative of the nickel atoms in an octahedral environment [1]. The electronic spectrum is typical of a compound with an octahedral structure [1]. The position and intensity of the narrow band in the electronic spectrum of the copper complex would suggest that it has a distorted tetrahedral structure [2]. The magnetic moment of 1.90 BM would support this suggestion [3].

Table 2 Electronic spectra and magnetic moments

Complex	Colour	Band position/cm^{-1}	*d-d* transition	μ (B.M.)
$Co_2(C_{11}H_9N)Cl_4$	Blue	4347	$^4A_2\ (F) \rightarrow {}^4T_2\ (F)$	4.41
		6494	$^4A_2\ (F) \rightarrow {}^4T_1\ (F)$	
		19949	$^4A_2\ (F) \rightarrow {}^4T_2\ (P)$	
$Ni(C_{11}H_9N)Cl_2$	Green	7692	$^3A_{2g}\ (F) \rightarrow {}^3T_{2g}\ (F)$	3.23
		14084	$^3A_{2g}\ (F) \rightarrow {}^3T_{1g}\ (F)$	
		23809	$^3A_{2g}\ (F) \rightarrow {}^3T_{1g}\ (F)$	
$Cu_2(C_{11}H_9N)Cl_4$	Green	12658	$^2B_2 \rightarrow {}^2A_1$	1.90

Table 3 Infrared spectroscopy (4000–200 cm^{-1})

Complex	Ring vibrations			$\nu_{(M-X)}$		$\nu_{(M-N)}$
$C_{11}H_9N$	1586(s)	1475(s)	1411(s)	–		–
$Co_2(C_{11}H_9N)Cl_4$	1607(s)	1477(s)	1419(s)	338(s)	290(s)	256(m)
$Ni(C_{11}H_9N)Cl_2$	1615(s)	1479(s)	1415(s)	222(w)		260(m)
$Cu_2(C_{11}H_9N)Cl_4$	1606(s)	1477(s)	1415(s)	303(s)	286(s)	258(m)

s strong; m medium; w weak

In Table 3 the main bands in the infrared spectra are listed together with their descriptions and assignments. The infrared spectrum of 3-phenylpyridine is very similar to that of its complexes in the range 4000–600 cm^{-1} except that the bands due to the ring vibrations of the pyridine are shifted to higher wavenumbers on complexation. This suggests that the nitrogen atom of the pyridine ring is coordinated to a metal atom [1]. Further evidence for the proposed tetrahedral environment for the cobalt and copper complexes is obtained from the ν(M–Cl) vibrations [1, 4]. The ν(Ni–Cl) band for the nickel complex agrees with the suggestion of an octahedral structure for this compound [1].

The complexes were isolated from the ethanolic solution as powders and not as single crystals and this meant that no complete structure determination was possible. However, spectral and magnetic data enable us to postulate structures. The cobalt and copper complexes are dimeric and have tetrahedral structures. It is suggested that each metal atom is bonded to two bridging chlorine atoms. The tetra-coordinate environment for each metal atom is obtained by one of the metal atoms being attached to two terminal chlorine atoms and the other metal atom

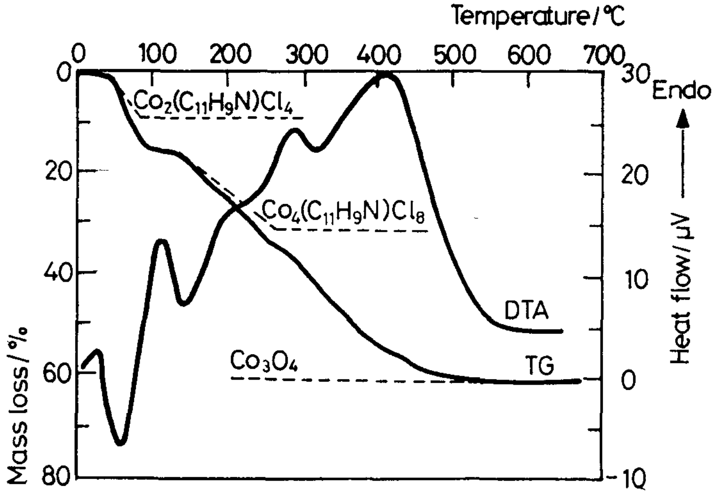


Fig. 1 TG and DTA trace for $Co_2(C_{11}H_9N)Cl_4$

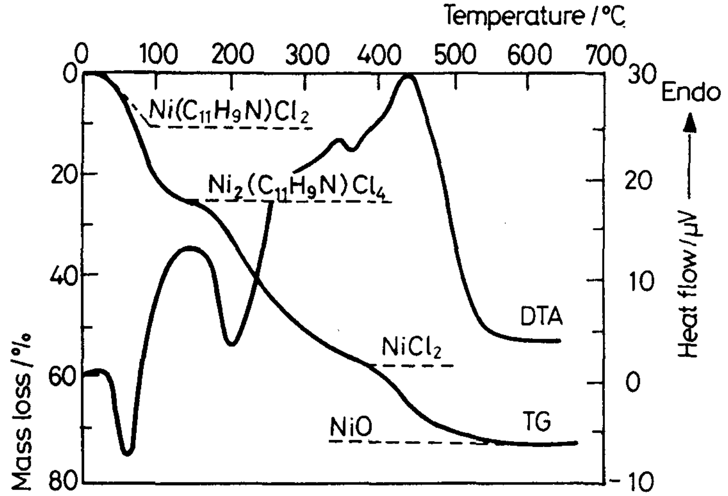


Fig. 2 TG and DTA trace for $Ni(C_{11}H_9N)Cl_2$

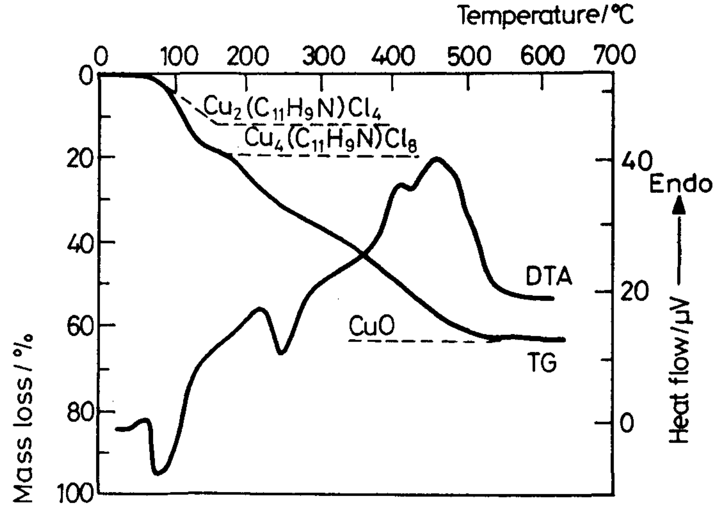


Fig. 3 TG and DTA trace for $Cu_2(C_{11}H_9N)Cl_4$

being attached to a terminal chlorine atom and to a nitrogen atom of the aromatic ring of the 3-phenylpyridine. The nickel complex has two chains of nickel atoms bonded to chlorine atoms, with the 3-phenylpyridine molecules above and below the plane of the meta lhalogen chain, to give a polymeric structure.

In previous work on methyl pyridines (5, 6, 7) it was reported that when the methyl group is in the 2-position the steric effect is dominant whereas in the 3-position steric and electronic effects are involved. In the 4-position only the electronic effect is significant. This is clearly shown by the coordination numbers of the compounds reported. When the electron releasing methyl group is replaced by an electron withdrawing chloro group this, along with the steric effect, is a further factor in reducing the coordination number of the metal [8, 9]. In the present work a phenyl group is in the 3-position of the pyridine. The phenyl group does not have the electron releasing properties of the methyl groups so that here the steric effect is the dominant one and would account for the proposed structures. The TG and DTA traces for the cobalt, nickel and copper complexes of 3-phenylpyridine are given in Figs 1–3. The thermal decomposition scheme for the metal complexes is:

$$Co_2(C_{11}H_9N)Cl_4 \xrightarrow{\text{Endo}} Co_4(C_{11}H_9N)Cl_8 \xrightarrow{\text{Endo/Exo}} Co_3O_4$$

$$Ni\ (C_{11}H_9N)Cl_2 \xrightarrow{\text{Endo}} Ni_2(C_{11}H_9N)Cl_4 \xrightarrow{\text{Endo}} NiCl_2 \xrightarrow{\text{Exo}} NiO$$

$$Cu_2(C_{11}H_9N)Cl_4 \xrightarrow{\text{Endo}} Cu_4(C_{11}H_9N)Cl_8 \xrightarrow{\text{Endo/Exo}} CuO$$

The observed weight losses for these processes compare favourably with the theoretical values given in Table 4.

Table 4 Thermal decomposition products

Starting material	Decomposition temperature/°C	Product	Weight loss/%	
			Calc.	Found
$Co_2(C_{11}H_9N)Cl_4$	36 (endo)	$Co_4(C_{11}H_9N)Cl_8$	18.7	18.6
	124 (endo/exo)	Co_3O_4	42.6	42.5
$Ni(C_{11}H_9N)Cl_2$	28 (endo)	$Ni_2(C_{11}H_9N)Cl_4$	27.2	27.2
	172 (endo)	$NiCl_2$	27.2	26.8
	368 (exo)	NiO	19.3	19.0
$Cu_2(C_{11}H_9N)Cl_4$	76 (endo)	$Cu_4(C_{11}H_9N)Cl_8$	18.3	18.2
	176 (endo/exo)	CuO	44.2	44.1

endo – endothermic; exo – exothermic

References

1 J. R. Allan and G. M. Baillie, J. Thermal Anal., 14 (1978) 291.
2 A. B. P. Lever, Inorganic Spectroscopy (2nd Edition), Elsevier 1984, p. 569, 570.
3 B. N. Figgis and J. Lewis, Progress in Inorganic Chemistry, 6 (1964) 37.
4 J. R. Allan, A. D. Paton and K. Turvey, Thermochim. Acta, 196 (1992) 391.
5 J. Kansikas, M. Leskelä, G. Kenessey, P.-E. Werner and G. Liptay, Acta Chem. Scand., 48 (1994) 951.
6 G. Kenessey, L. Párkányi, P.-E. Werner, G. M. Keserü, T. Wadsten, L. Bihátsi and G. Liptay, Struct. Chem., 5 (1994) 123.
7 G. Liptay, G. Kenessey, L. Bihátsi, T., Wadsten and J. Mink, J. Thermal Anal., 38 (1992) 899.
8 L. Hiltunen, L. Niinistö, G. Kenessey and G. Liptay, Acta Chem. Scand., 48 (1994) 456.
9 G. M. Keserü, Z. Hajnal, G. Kenessey and G. Liptay, J. Mol. Struct. (Theochem.), 306 (1994) 289.

Zusammenfassung — In einer ethylalkoholischen Lösung wurden die Chlorokomplexe von Kobalt, Nickel und Kupfer mit 3-Phenylpyridin hergestellt und dann als Feststoffe isoliert. Die Kobalt- und Kupferkomplexe haben die Stöchiometrie M_2LCl_4, der Nickelkomplex dagegen die Stöchiometrie $NiLCl_2$. Dies deutet auf eine tetraedrische Struktur der Kobalt- und Kupferkomplexe sowie auf eine oktaedrische Struktur des Nickelkomplexes hin. Thermoanalytische Untersuchungen zeigen, daß die Kupfer- und Kobaltkomplexe intermediäre Komplexe bilden, bevor ihre Metalloxide entstehen. Der Nickelkomplex bildet vor der Bildung des Metalloxides erst einen intermediären Komplex und anschließend Nickelchlorid.