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THERMAL, SPECTRAL AND MAGNETIC STUDIES OF SOME FIRST ROW TRANSITION METAL COMPLEXES OF 2-(*p*-TOLYL) PYRIDINE

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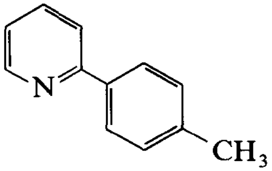
ABSTRACT

Some chloro complexes of cobalt, nickel and copper with 2-(*p*-tolyl) pyridine have been prepared. The stereochemical configurations of the complexes were deduced using spectral and magnetic properties. The decomposition of the complexes was studied by thermogravimetry and differential thermal analysis.

INTRODUCTION

The compound 2-(*p*-tolyl) pyridine has one donor site for forming bonds with metal ions: the nitrogen atom of the aromatic ring system.



2-(*p*-tolyl) pyridine

Information concerning the stereochemistry of the 2-(*p*-tolyl) pyridine metal complexes has been obtained from spectral and magnetic studies. A study of the thermal stability of the 2-(*p*-tolyl) pyridine metal complexes has been carried out.

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TABLE 1

Analyses of complexes

Compound	Theory				Found				Method of preparation
	Metal	Carbon	Nitrogen	Hydrogen	Metal	Carbon	Nitrogen	Hydrogen	
$Co(C_{12}H_{11}N)_2Cl_2$	12.58	61.55	5.98	4.74	12.77	61.23	5.76	4.62	A
$Co_2(C_{12}H_{11}N)_3Cl_4$	15.36	56.34	5.48	4.34	15.01	55.82	4.91	4.02	B
$Co_2(C_{12}H_{11}N)Cl_4$	27.48	33.60	3.27	2.59	26.66	32.98	2.97	2.84	B
$Ni(C_{12}H_{11}N)_2Cl_2$	12.54	61.58	5.99	4.75	12.45	61.41	5.41	4.42	A
$Ni_2(C_{12}H_{11}N)_3Cl_4$	15.31	56.38	5.48	4.35	16.02	56.11	5.71	4.88	B
$Ni(C_{12}H_{11}N)Cl_2$	19.64	48.23	4.69	3.72	19.51	48.63	4.31	3.19	B
$Cu(C_{12}H_{11}N)_2Cl_2$	13.44	60.95	5.92	4.69	13.62	60.51	5.63	4.74	A
$Cu_2(C_{12}H_{11}N)_3Cl_4$	16.37	55.67	5.41	4.29	16.46	55.31	5.69	4.15	B
$Cu_2(C_{12}H_{11}N)Cl_4$	29.01	32.89	3.19	2.54	28.82	32.67	2.86	2.73	B

EXPERIMENTAL

Preparation of the complexes

(a) The metal halide (1 g) was dissolved in warm ethanol (50 cm^3); 2-(*p*-tolyl) pyridine (5 cm^3) was then added to the warm solution with stirring. On cooling, the compound which precipitated from the ethanolic solution was filtered, washed with an ethanol : 2-(*p*-tolyl) pyridine solution, and dried in an oven at 60 ° C.

(b) A complex prepared by method (a) was heated on a thermal balance in static air at a fixed temperature until constant weight was obtained. The fixed temperature was chosen between the initial temperature T_i and the final temperature T_f for that stage of the reaction.

Analysis

The complexes prepared are listed in Table 1. The concentration of the metal ion was obtained on a Perkin–Elmer 373 atomic absorption spectrophotometer and the carbon, hydrogen and nitrogen analysis was obtained 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.

TABLE 2

Thermal decomposition products

Starting material	Decomposition temperature (° C)	% Mass loss		Resulting compound
		Calc.	Obs.	
$Co(C_{12}H_{11}N)_2Cl_2$	142 (endo)	18.06	18.21	$Co_2(C_{12}H_{11}N)_3Cl_4$
	250 (endo)	54.21	55.26	$Co_2(C_{12}H_{11}N)Cl_4$
	348 (exo)	82.86	82.63	Co_3O_4
$Ni(C_{12}H_{11}N)_2Cl_2$	145 (endo)	18.08	18.26	$Ni_2(C_{12}H_{11}N)_3Cl_4$
	212 (endo)	36.16	36.34	$Ni(C_{12}H_{11}N)Cl_2$
	308 (exo)	84.04	83.65	NiO
$Cu(C_{12}H_{11}N)_2Cl_2$	148 (endo)	17.89	16.65	$Cu_2(C_{12}H_{11}N)_3Cl_4$
	252 (endo)	53.68	54.80	$Cu_2(C_{12}H_{11}N)Cl_4$
	358 (exo)	83.18	86.54	CuO

Thermal analysis studies, Table 2, were carried out on a Stanton Redcroft model STA 781 thermobalance. The thermogravimetry (TG) and differential thermal analysis (DTA) were obtained at a heating rate of 10 °C min^{-1} in static air and over a temperature range of 20–1 000 °C.

RESULTS AND DISCUSSION

Table 1 lists the compounds isolated from ethanolic solution and those obtained on the thermal balance at a fixed temperature. The elemental analyses agree with the given formulae for the complexes. The position of the bands in the electronic spectra and the values for Dq of the cobalt and nickel complexes of 2-(*p*-tolyl) pyridine isolated from ethanolic solution, see Table 3, clearly indicate a four-coordinate environment for the cobalt atom and a six-coordinate environment for the nickel atom [1]. The values reported for the Racah parameter B and the nephelauxetic ratio β are indicative of a certain degree of ionic character in the metal–ligand bond [2]. The magnetic moment for the cobalt complex lies in the expected range of 4.2–4.8 B.M. for a tetrahedral complex [3] while the magnetic moment of the nickel complex lies in the expected range of 3.2–3.8 B.M. for an octahedral complex [4]. The copper complex isolated from ethanolic solution has two bands in its electronic spectra between 15 000 and 20 000 cm^{-1} and a magnetic moment of 1.80 B.M.

Table 4 reports the main bands in the infrared spectra of 2-(*p*-tolyl) pyridine and its complexes isolated from ethanolic solution. The IR spectrum of the 2-(*p*-tolyl) pyridine is almost identical to that of its complexes in the region 4000–625 cm^{-1} except for the bands due to the ring vibrations of the aromatic ring which move to higher wavenumbers in the complexes. This would suggest that coordination is taking place between the metal and the nitrogen atom in the aromatic ring [4]. Metal–chloride and metal–nitrogen bands are assigned for the complexes and are reported in Table 4.

TABLE 3

Electronic spectra (cm^{-1}) and magnetic moments

Compound	Peak position (cm^{-1})	Dq	B	β	μ (B.M.)
$Co(C_{12}H_{11}N)_2Cl_2$	7462 18621	405	927	0.95	4.31
$Ni(C_{12}H_{11}N)_2Cl_2$	8064 13888 23923	806	908	0.87	3.77
$Cu(C_{12}H_{11}N)_2Cl_2$	16260 19260				1.80

TABLE 4

Infrared spectra (4000–200 cm^{-1})

Compound	Ring vibrations		ν_{M-X}	ν_{M-N}
$C_{12}H_{11}N$	1609(S)	1458(S)	–	–
$Co(C_{12}H_{11}N)_2Cl_2$	1613(S)	1460(S)	300(S)	242(S)
$Ni(C_{12}H_{11}N)_2Cl_2$	1612(S)	1465(S)	256(M)	238(W)
$Cu(C_{12}H_{11}N)_2Cl_2$	1614(S)	1460(S)	298(S)	240(W)

S = strong; M = medium; W = weak.

The assignment of the ν(M–Cl) vibrations for the cobalt and nickel complexes agrees with the suggestions of tetrahedral and octahedral structures, respectively, for these complexes [3,4]. The band at 298 cm^{-1} in the copper complex which has been assigned to the ν(Cu–Cl) vibration, is indicative of the copper atom in a tetragonal 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 enable us to predict that in the cobalt complex, the cobalt atom is in a tetrahedral environment with the cobalt atom bonded to halogens and the nitrogen atom of the aromatic ring of the 2-(*p*-tolyl) pyridine. In the nickel complex the nickel atom is in an octahedral environment. The poor solubility of this complex in both polar and non-polar solvents suggests a polymeric structure [4]. The complex is considered to consist of a chain of nickel atoms bonded to halogens with 2-(*p*-tolyl) pyridine molecules above and below the plane of the nickel–halogen chain. It is further suggested that the 2-(*p*-tolyl) pyridine molecules are bonded to the nickel atom through the lone pair of electrons on the nitrogen atom of the aromatic ring. The

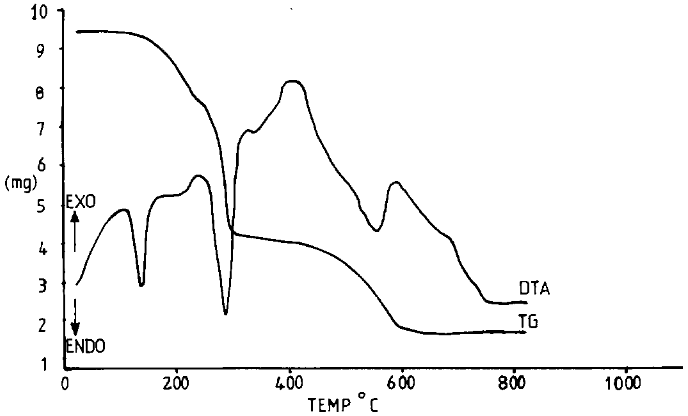

Fig. 1. TG/DTA curves for $Co(C_{12}H_{11}N)_2Cl_2$, sample weight = 9.50 mg.

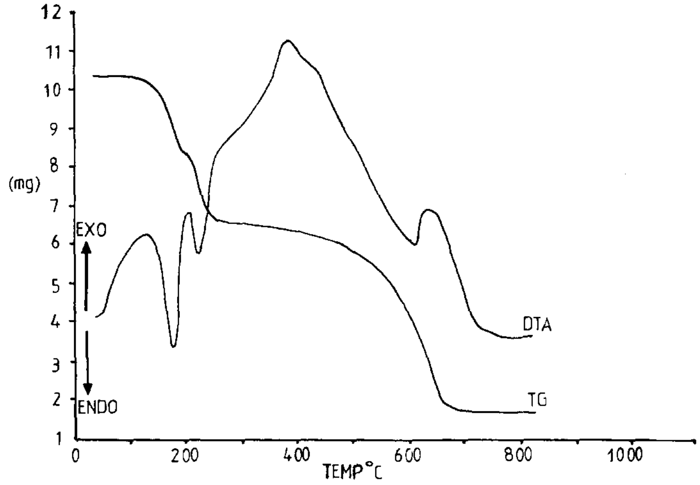

Fig. 2. TG/DTA curves for $Ni(C_{12}H_{11}N)_2Cl_2$, sample weight = 10.40 mg.

tetragonal structure for the copper complex is obtained by considering the complex to have a planar arrangement of ligands with the apical positions being free so that the copper might coordinate to halogens of further $Cu(C_{12}H_{11}N)_2Cl_2$ groups [6].

The results of the thermogravimetric studies are given in Figs. 1–3 and Table 2. Thermal decomposition studies show that the cobalt complex undergoes an endothermic reaction at 142 ° C with loss of half a molecule of 2-(*p*-tolyl) pyridine, followed by another endothermic reaction at 250 ° C with loss of a further one molecule of 2-(*p*-tolyl) pyridine and, finally, an exothermic reaction at 348 ° C results in the loss of the remaining half molecule of 2-(*p*-tolyl) pyridine and the chlorine to give Co_3O_4. The nickel

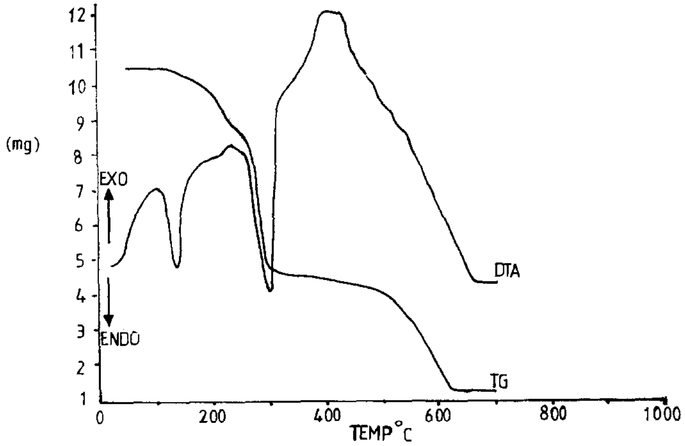

Fig. 3. TG/DTA curves for $Cu(C_{12}H_{11}N)_2Cl_2$, sample weight = 10.50 mg.

compound undergoes two endothermic reactions at 145 and 212° C followed by an exothermic reaction at 308° C with a loss of half a molecule of 2-(*p*-tolyl) pyridine, a further half molecule of 2-(*p*-tolyl) pyridine, and then the remaining molecule of 2-(*p*-tolyl) pyridine and chlorine to give NiO. The copper compound undergoes two endothermic reactions at 148 and 252° C followed by an exothermic reaction at 358° C, with loss of one half of a molecule of 2-(*p*-tolyl) pyridine, one molecule of 2-(*p*-tolyl) pyridine, and finally half a molecule of 2-(*p*-tolyl) pyridine plus the chlorine to give CuO.

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