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Preparation, structural characterisation, thermal and electrical studies of some first row transition metal complexes of 2,3-bis(2-pyridyl)pyrazine

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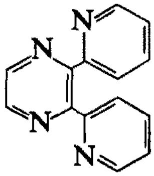
Abstract

The chloro compounds of cobalt, nickel and copper with 2,3-bis(2-pyridyl)pyrazine have been prepared in ethanolic solution. The thermal behaviour of these compounds, and of the compound 2,3-bis(2-pyridyl)pyrazine, has been studied by thermogravimetry and differential thermal analysis. Thermal decomposition studies on the complexes show that intermediate compounds are produced before the metal oxides are formed. Electrical measurements show that all of the compounds exhibit ohmic behaviour at room temperature. The small differences in the electrical conductivity observed for each of the metal complexes indicates that the coordinated metal ion plays no part in the conduction process.

INTRODUCTION

In this work we describe and discuss thermal and electrical studies of 2,3-bis(2-pyridyl)pyrazine, together with the chloro complexes formed by 2,3-bis(2-pyridyl)pyrazine and the transition metals cobalt, nickel and copper.



2,3-Bis(2-pyridyl)pyrazine ($C_{14}H_{10}N_4$).

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Spectral and magnetic studies have been used to characterise each metal complex and to interpret the type of coordination which takes place to the metal ion.

EXPERIMENTAL

Preparation of the complexes

The compound 2,3-bis(2-pyridyl)pyrazine (0.01 mol) was dissolved in 250 cm^3 of boiling ethanol. The metal halide (0.01 mol) was dissolved in 50 cm^3 of warm ethanol. The solutions were mixed and the resultant solution refluxed for 2 h. The volume of the solution was then reduced until the complexes precipitated. The complexes were filtered, washed with warm ethanol and dried in a desiccator over calcium chloride.

APPARATUS AND MEASUREMENTS

The concentration of the metal ion was obtained using a Perkin-Elmer 373 atomic absorption spectrophotometer, and the carbon, hydrogen and nitrogen analyses were carried out using a Carlo Erba elemental analyser.

The IR spectra were obtained using KBr discs (4000–200 cm^{-1}) and polyethylene discs (600–200 cm^{-1}) on a Perkin-Elmer model 598 IR spectrophotometer.

Electronic diffuse reflectance spectra were recorded with a Beckmann Acta MIV spectrophotometer.

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 thermogravimetry (TG) and differential thermal analysis (DTA) traces were obtained at a heating rate of 6°C min^{-1} in static air. The 20–800°C temperature range was studied.

Electrical conduction measurements were performed under d.c. conditions on discs of the compounds which were prepared by compressing powdered samples of the complexes. These discs were 13 mm in diameter with thicknesses of approximately 1 mm. Electrodes 5.9 mm in diameter were formed on the flat surfaces of the discs by applying a silver based conductive paint. Details of the methods used for the electrical measurements have been previously described [1, 2].

RESULTS AND DISCUSSION

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

TABLE 1

Analyses (%) of metal complexes

Compound	Colour		M	C	N	H
$Co(C_{14}H_{10}N_4)Cl_2$	Brown	Theory	16.18	46.18	15.38	2.76
		Found	15.73	45.49	15.01	2.66
$Ni(C_{14}H_{10}N_4)Cl_2$	Black	Theory	16.13	46.21	15.39	2.77
		Found	15.66	45.92	15.17	2.41
$Cu(C_{14}H_{10}N_4)Cl_2$	Green	Theory	17.23	45.60	15.19	2.73
		Found	16.98	45.27	14.88	2.35

The molecular magnetic moments and the bands in the electronic spectra of the complexes are listed in Table 2. The position of the bands in the cobalt and nickel compounds would suggest that the metal ions are in an octahedral environment [3]. The values obtained for the magnetic moments support this suggestion [3]. In the copper compound a broad band is observed between 10 000 and 15 000 cm^{-1}, indicating that the copper ions are in an octahedral environment [3]. The magnetic moment for this compound is lower than the spin only value, indicating a strong copper–copper magnetic interaction. The wavenumbers of the IR absorption bands for 2,3-bis(2-pyridyl)pyrazine and for its chloro complexes isolated from ethanolic solution are given in Table 3, together with the descriptions and assignments. The IR spectrum of 2,3-bis(2-pyridyl)-pyrazine is very similar to that of its complexes in the region 4000–600 cm^{-1}, except that the bands due to the aromatic ring vibrations are shifted to higher wavenumbers on formation of the complexes. This would suggest that the nitrogen atoms of the aromatic ring are coordinated to a metal ion [3]. The ν(M–Cl) bands observed for the complexes show that

TABLE 2

Electronic spectra and magnetic moments

Compound	Band position (cm^{-1})	d–d Transition	μ (BM)
$Co(C_{14}H_{10}N_4)Cl_2$	8403	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	4.86
	14706	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	
	23641	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	
$Ni(C_{14}H_{10}N_4)Cl_2$	10410	$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	3.07
	18182	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	
	24691(sh)	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	
$Cu(C_{14}H_{10}N_4)Cl_2$	12658	$^2E_g(D) \rightarrow {}^2T_{2g}(D)$	1.54

Key: sh, shoulder.

TABLE 3

IR spectra (4000–200 cm^{-1})

Compound	Ring vibrations	ν(M–N)	ν(M–X)
$C_{14}H_{10}N_4$	1585(s), 1560(s), 1390(s)	–	–
$Co(C_{14}H_{10}N_4)Cl_2$	1600(s), 1570(s), 1400(s)	420(m)	236(m)
$Ni(C_{14}H_{10}N_4)Cl_2$	1602(s), 1568(s), 1414(s)	422(s)	245(m)
$Cu(C_{14}H_{10}N_4)Cl_2$	1594(s), 1570(s), 1398(s)	434(m)	266(m)

Key: s, strong; m, medium.

cobalt, nickel and copper ions are in a six-coordinate environment [3]. The ν(M–N) bands are also listed for the complexes.

No single crystals of the compounds were isolated from ethanolic solution and without X-ray analysis no definite structures can be described. However, the spectroscopic and magnetic data enable possible structures to be predicted. The ligand 2,3-bis(2-pyridyl)pyrazine has four coordinating nitrogen atoms and the stereochemistry of the ligand is such that the nitrogen atoms coordinate in pairs with the metal ions in the complexes, thus linking together adjacent ligand molecules. We thus suggest a planar arrangement for every four nitrogen atoms. The six-coordinate environment for each metal atom is completed by a bonding chlorine atom on either side of the plane.

The TG and DTA traces for 2,3-bis(2-pyridyl)pyrazine and its chloro complexes with cobalt, nickel and copper are shown in Figs. 1–4. The TG and DTA trace for 2,3-bis(2-pyridyl)pyrazine (Fig. 1) shows that the compound is thermally stable in the temperature range 20–172°C. Its pyrolytic decomposition starts at 172°C and finishes at 538°C with the total elimination of the sample. The DTA trace shows an endothermic peak at 168°C corresponding to fusion. Endothermic and exothermic peaks are

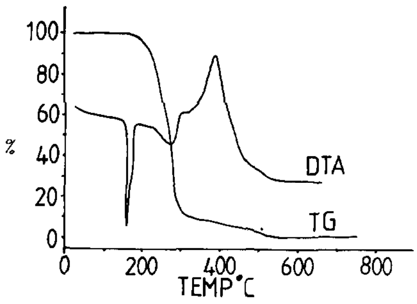

Fig. 1. TG and DTA traces for 2,3-bis(2-pyridyl)pyrazine. Sample weight = 8.17 mg.

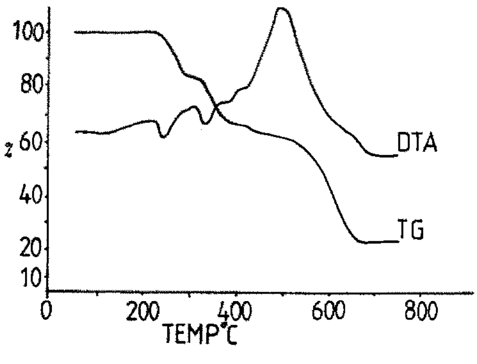

Fig. 2. TG and DTA traces for $Co(C_{14}H_{10}N_4)Cl_2$. Sample weight = 4.84 mg.

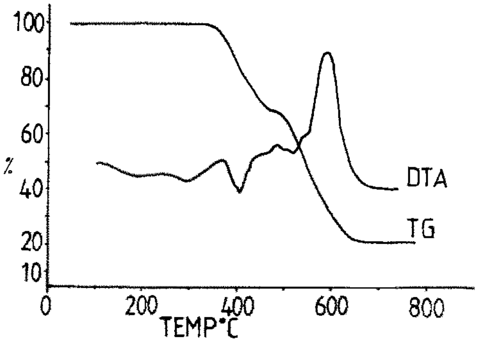

Fig. 3. TG and DTA traces for $Ni(C_{14}H_{10}N_4)Cl_2$. Sample weight = 7.65 mg.

produced on decomposition of the compound. The TG and DTA traces for the complexes are shown in Figs. 2–4. The results of the TG and DTA analysis are given in Table 4. The temperatures quoted are for the maximum rate of decomposition under the conditions used. The complexes decompose with endothermic reactions to give intermediate compounds and then finally by exothermic reactions to give the metal oxide.

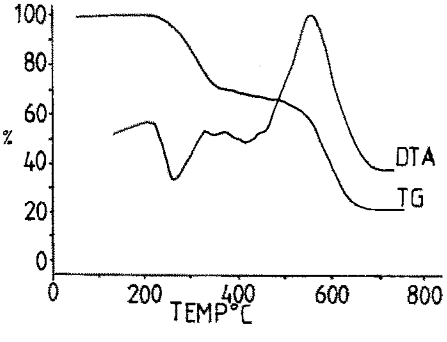

Fig. 4. TG and DTA traces for $Cu(C_{14}H_{10}N_4)Cl_2$. Sample weight = 7.70 mg.

TABLE 4

Thermal decomposition processes of metal complexes

Starting material	Decomp. temp. (°C)	Product	Weight loss (%)	
			Calc.	Found
$Co(C_{14}H_{10}N_4)Cl_2$	236(endo)	$Co_4(C_{14}H_{10}N_4)_3Cl_8$	16.1	16.3
	298(endo)	$Co_2(C_{14}H_{10}N_4)Cl_4$	32.2	33.0
	390(exo)	Co_3O_4	78.0	78.2
$Ni(C_{14}H_{10}N_4)Cl_2$	328(endo)	$Ni_2(C_{14}H_{10}N_4)Cl_4$	32.2	31.6
	478(exo)	NiO	79.5	79.0
$Cu(C_{14}H_{10}N_4)Cl_2$	218(endo)	$Cu_2(C_{14}H_{10}N_4)Cl_4$	31.8	31.4
	371(endo)	CuO	78.4	78.6

Key: endo, endothermic; exo, exothermic (obtained from DTA trace).

TABLE 5

Room temperature electrical conductivities

Compound	σ (Ω^{-1} m^{-1})
$C_{14}H_{10}N_4$	7.05×10^{-8}
$Co(C_{14}H_{10}N_4)Cl_2$	5.24×10^{-8}
$Ni(C_{14}H_{10}N_4)Cl_2$	4.35×10^{-8}
$Cu(C_{14}H_{10}N_4)Cl_2$	3.51×10^{-8}

The decomposition schemes are

$$Co(C_{14}H_{10}N_4)Cl_2 \xrightarrow{\text{endo}} Co_4(C_{14}H_{10}N_4)_3Cl_8 \xrightarrow{\text{endo}} Co_2(C_{14}H_{10}N_4)Cl_4 \xrightarrow{\text{exo}} Co_3O_4$$

$$Ni(C_{14}H_{10}N_4)Cl_2 \xrightarrow{\text{endo}} Ni_2(C_{14}H_{10}N_4)Cl_4 \xrightarrow{\text{exo}} NiO$$

$$Cu(C_{14}H_{10}N_4)Cl_2 \xrightarrow{\text{endo}} Cu_2(C_{14}H_{10}N_4)Cl_4 \xrightarrow{\text{exo}} CuO$$

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

The measured room temperature electrical conductivity σ of each compound and the uncomplexed ligand are given in Table 5. The room temperature current (I) versus voltage (V) characteristics were obtained under conditions of rising and falling voltage in both polarities. There was no evidence of any blocking behaviour at the contacts because the four currents measured were found to agree within a maximum of 15%. The I–V relationships for all of the compounds were found to be linear throughout the voltage range investigated, indicating ohmic electrical conduction. The electrical conductivity for each compound was determined from the gradient of the *I–V* characteristic.

The limited range in electrical conductivity observed for the metal complexes suggests that the coordinated metal ion plays no part in the process of conduction. Comparison of the electrical conductivities of the metal complexes with that of the free ligand shows that the uncomplexed ligand exhibits the highest conductivity. Thus, from these studies it would appear that complexing 2,3-bis(2-pyridyl)pyrazine with metal ions produces an apparent reduction in the observed electrical conductivity. Such a phenomenon has been observed in studies of transition metal complexes of 4,7-phenanthroline [4]. It was postulated in ref. 4 that the electrical conduction pathway was predominantly via suitable orbitals belonging to ligand molecules in close proximity to one another. On coordination, the incorporation of a metal ion destroyed or hindered this conduction path by increasing the intermolecular distance between ligand molecules. It is suggested that a similar effect is operating in the present compounds studied.

REFERENCES

1 J.R. Allan, H.J. Bowley, D.L. Gerrard, A.D. Paton and K. Turvey. Thermochim. Acta 122 (1987) 403.
2 J.R. Allan, A.D. Paton and K. Turvey. Thermochim. Acta, 164 (1990) 177.
3 J.R. Allan, N.D. Baird and A.L. Kassyk. J. Therm. Anal., 16 (1979) 79.
4 J.R. Allan, B. McCloy and A.D. Paton. Thermochim. Acta, 214 (1993) 211.