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Structural, thermal and electrical studies of some transition metal compounds of 2-methylpyrazine

J.R. Allan, A.D. Paton and K. Turvey

Department of Applied Chemical and Physical Sciences, Napier Polytechnic, Edinburgh (UK)

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Abstract

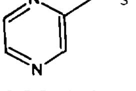
The preparation and some properties of complexes of 2-methylpyrazine with the chlorides of manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) are described. Magnetic measurements, and electronic and infrared studies indicate that the compounds have polymeric octahedral structures. The thermal behaviour of these compounds have been studied by thermogravimetry (TG) and differential thermal analysis (DTA).

Electrical measurements show that all compounds exhibit ohmic behaviour at room temperature with conductivities in the range 1.68×10^{-8} Ω^{-1} m^{-1} (for the cobalt compound) to 7.36×10^{-7} Ω^{-1} m^{-1} (for the copper compound). The temperature dependences of the conductivity have been determined for the compounds and used to measure the activation energies for conduction.

INTRODUCTION

This work is a continuation and extension of previously reported studies on substituted pyrazine compounds and the first-row transition elements [1–5]. In this present work we describe and discuss the structural properties and some electrical measurements of the complexes of 2-methylpyrazine with manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II).

In the ligand 2-methylpyrazine the two nitrogen atoms of the aromatic ring system are possible sites for coordination to metal ions.



2-Methylpyrazine (MeP)

Spectroscopic and magnetic studies of the complexes have been used to provide information about the type of coordination between the metal and ligand, and the metal ion stereochemical environment. Thermogravimetry (TG) and differential thermal analysis (DTA) were used to study the

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thermal stability of the compounds. The electrical properties of each complex were also studied.

EXPERIMENTAL

Preparation of the complexes

The complexes were prepared by drop-wise addition of 2-methylpyrazine (0.05 mol) to a boiling ethanolic solution (70 cm^3) of the metal chloride or bromide (0.025 mol). The resulting solution was heated for a further 15 min and then concentrated on a steam bath. The precipitated product was isolated by filtration, washed with a minimum of ethanol and air dried.

Apparatus and measurements

The metal concentration of the complexes were determined using a Perkin–Elmer 373 atomic absorption spectrophotometer. The carbon, hydrogen and nitrogen analyses were made using a Carlo Erba model 1106 elemental analyser.

Infrared absorption spectra were recorded on a Pye Unicam model SP3-300 spectrophotometer using KBr discs over the wavenumber range 4000–600 cm^{-1} and polyethylene discs over the range 600–200 cm^{-1}. Electronic spectra were recorded as solid diffuse reflectance spectra using a Beckman Acta MIV spectrophotometer.

Magnetic measurements were carried out at room temperature by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant. Diamagnetic corrections were applied to each magnetic moment using Pascal's constants [6].

The thermal analysis measurements were made on a Stanton Redcroft model STA 781 thermobalance. 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 in all cases.

Electrical conduction measurements were performed under d.c. conditions on discs of the compounds which were prepared by compressing a powdered samples of the complexes. These discs were 13 mm in diameter with thicknesses ranging from 0.52 to 0.72 mm. Electrodes 4.9 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 [1,7].

RESULTS AND DISCUSSION

Table 1 gives the analytical results for the complexes isolated from ethanolic solution. The experimental data agree with the given stoichiometry of $MLCl_2$ where M is the transition metal and L is 2-methylpyrazine.

TABLE 1

Analyses of the compounds

Compound	Colour	Theory (%)				Found (%)			
		Metal	Carbon	Nitrogen	Hydrogen	Metal	Carbon	Nitrogen	Hydrogen
$Mn(MeP)Cl_2$	White	24.98	27.28	12.73	2.73	25.16	27.56	12.72	2.72
$Co(MeP)Cl_2$	Purple	26.64	26.67	12.45	2.67	26.83	26.43	12.60	2.68
$Ni(MeP)Cl_2$	Yellow	26.24	26.82	12.52	2.68	26.43	26.60	12.68	2.55
$Cu(MeP)Cl_2$	Green	27.79	26.26	12.25	2.63	27.67	26.44	12.08	2.82
$Zn(MeP)Cl_2$	White	28.37	26.04	12.15	2.60	28.19	25.87	12.02	2.56

TABLE 2

Spectral and magnetic data for the compounds

Compound	Electronic spectra peak position	Infrared spectra (4000–200 cm^{-1}) [a]			Magnetic moment (BM)
		Ring vibrations	ν(M–X)	ν(M–N)	
MeP		1590(s) 1515(s)			
Mn(MeP)Cl_2	–	1595(s) 1520(s)	240(m)	425(m)	6.16
Co(MeP)Cl_2	6494 17094 19231	1596(s) 1518(s)	260(m)	428(m)	5.32
Ni(MeP)Cl_2	8065 17094 19231	1600(s) 1518(s)	250(m)	430(m)	3.15
Cu(MeP)Cl_2	14084	1600(s) 1518(s)	255(m)	435(m)	1.72
Zn(MeP)Cl_2	–	1615(s) 1518(s)	< 200	430(m)	–

[a] Key: s, sharp; m, medium.

The electronic spectra and the magnetic moments of the complexes are reported in Table 2. The position of the d–d bands for the cobalt, nickel and copper complexes indicate that the metal ion is in an octahedral environment [8,9]. The magnetic moments for the cobalt and nickel compounds provide further evidence of an octahedral environment for the metal atoms in these complexes. The magnetic moment for the copper compound is similar to the spin-only value. No information on the stereochemistry of the manganese and zinc compounds can be derived from the electronic spectra because no d–d transitions were observed. However, the magnetic moment of the manganese compound corresponds to five unpaired electrons associated with each metal ion, therefore suggesting either a tetrahedral or octahedral structure.

The wavenumbers of the infrared absorption bands and their assignments are given in Table 2 for the 2-methylpyrazine ligand and its complexes. The IR spectrum of 2-methylpyrazine is almost identical to those of its complexes in the region 4000–600 cm^{-1} except for the bands due to vibrations of the aromatic ring system, which are at higher frequencies in the complexes than in the uncomplexed 2-methylpyrazine ligand. This suggests that in each complex either one or both nitrogen atoms of the aromatic ring are coordinated to a metal atom [8,9].

Metal–halogen vibrations are observed for the complexes and are reported in Table 2. The assignment made for the ν(M–Cl) vibrations are consistent with those made for ν(M–Cl) vibrations in octahedral manganese, cobalt, nickel and copper complexes with bridging halogen atoms [8,9]. In the zinc complex no bands were observed above 200 cm^{-1} which could be assigned to the ν(Zn–Cl) vibration. This would suggest that the

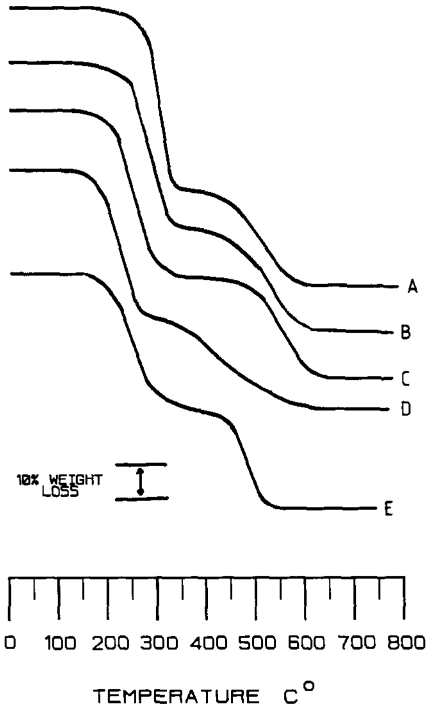

Fig. 1. Thermogravimetric (TG) curves for: (A) $Mn(MeP)Cl_2$ (mass 7.760 mg); (B) $Co(MeP)Cl_2$ (mass 6.938 mg); (C) $Ni(MeP)Cl_2$ (mass 12.212 mg); (D) $Cu(MeP)Cl_2$ (mass 7.768 mg); (E) $Zn(MeP)Cl_2$ (mass 13.862 mg). The TG curves are shifted in the vertical direction for clarity.

zinc ion is in an octahedral environment because tetrahedral compounds show strong absorption bands in the region 330–290 cm^{-1} [10].

No single crystals of the compounds were isolated from solution and hence, without X-ray analysis, no definite structures can be described. However, the information from the spectroscopic and magnetic data allows suggestions to be made for possible structures. It is thus postulated that the structure of the complexes is a planar arrangement of metal atoms bridged by halogens. The metal atoms in adjacent chains are linked by 2-methylpyrazine molecules which utilises both ring nitrogen atoms for coordination. Thus each metal atom has a coordination number of six, being surrounded by four planar chloride ions with a ring nitrogen atom from 2-methylpyrazine above and below the Cl–M–Cl plane [11].

The thermogravimetric (TG) and differential thermal analysis (DTA) traces for the complexes are shown in Fig. 1. The compounds initially undergo an endothermic reaction with loss of the organic ligand and subsequent formation of the metal chloride. The metal oxide is formed following an exothermic loss of the halogen. The experimental weight losses are shown in Table 3 and are in good agreement with the theoretical values.

TABLE 3

Thermal decomposition products

Starting material	decomposition temperature (° C)	Product	Weight loss (% of initial weight)	
			Calc.	Found
$Mn(MeP)Cl_2$	276	$MnCl_2$	42.79	42.50
	443	MnO_2	17.68	18.03
$Co(MeP)Cl_2$	253	$CoCl_2$	42.03	42.25
	442	Co_3O_4	22.13	22.18
$Ni(MeP)Cl_2$	243	$NiCl_2$	42.07	41.86
	481	NiO	24.54	24.29
$Cu(MeP)Cl_2$	216	$CuCl_2$	41.18	41.08
	355	CuO	24.02	24.49
$Zn(MeP)Cl_2$	238	$ZnCl_2$	40.85	40.48
	476	ZnO	23.78	23.93

The measured electrical properties of the compounds are summarised in Table 4. The room-temperature current (I) versus voltage (V) characteristics were obtained for each compound under conditions of rising and falling voltage in both polarities. The four currents measured were found to agree in absolute value within 15% and were usually closer than this, indicating that the electrodes were not rectifying. The current versus voltage relationship for each compound was found to exhibit ohmic behaviour throughout the voltage range investigated. The room temperature conductivity of each compound was determined from the gradient of the I–V characteristic. The range of observed conductivities is from 1.68×10^{-8} Ω^{-1} m^{-1} for $Co(MeP)Cl_2$ to 7.36×10^{-7} Ω^{-1} m^{-1} for $Cu(MeP)Cl_2$. The considerable range in conductivities for this group of compounds almost

TABLE 4

Electrical properties of the compounds

Compound	$10^8 \sigma$ [a] (Ω^{-1} m^{-1})	ΔE (eV) [b]	
		Heating	Cooling
$Mn(MeP)Cl_2$	2.56	0.76	1.09
$Co(MeP)Cl_2$	1.68	1.23	1.47
$Ni(MeP)Cl_2$	5.46	1.15	1.69
$Cu(MeP)Cl_2$	73.6	0.19	1.06
$Zn(MeP)Cl_2$	2.43	0.94	1.35

[a] Room temperature (21° C) conductivity.

[b] ΔE is the activation energy in the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$. Least-squares fitting of a line to a plot of ln σ against T^{-1} was used to determine ΔE. Separate results are given for heating and cooling cycles.

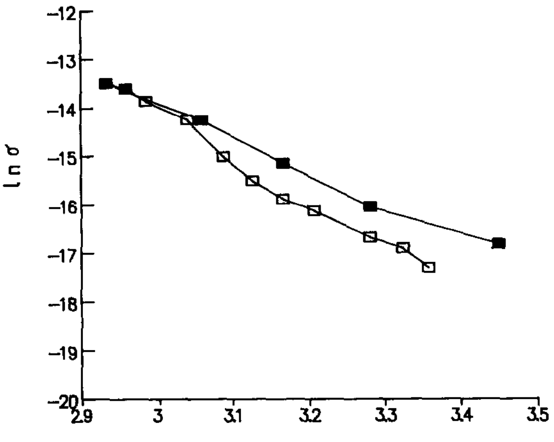

Fig. 2. Arrhenius plot in the form of ln σ versus $10^3/T$ (where σ = conductivity in units of Ω^{-1} m^{-1} and T is the absolute temperature) for a disc of Ni(MeP)Cl_2: ■, points obtained during heating; □, points obtained during cooling.

certainly reflects differing levels of impurities rather than any effect attributable to the metal ion present.

The temperature dependence of the conductivity (σ) for Ni(MeP)Cl_2 is shown in Fig. 2 as a plot of ln σ versus T^{-1} where T is the absolute temperature. Linearity of such plots would show the validity of the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ where ΔE can be considered as the activation energy for releasing free carriers. However, the current measured during

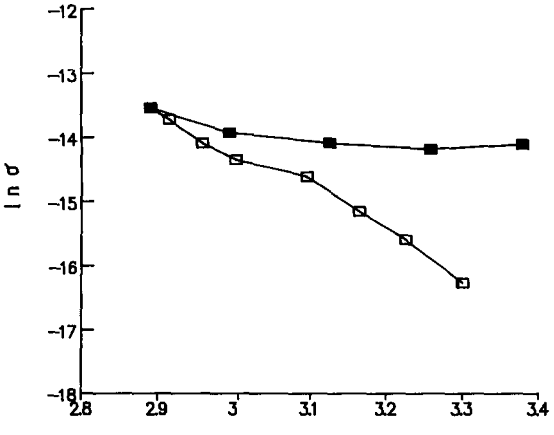

Fig. 3. Arrhenius plot in the form of ln σ versus $10^3/T$ (where σ = conductivity in units of Ω^{-1} m^{-1} and T is the absolute temperature) for a disc of Cu(MeP)Cl_2: ■, points obtained during heating; □, points obtained during cooling.

the cooling phase does not agree with that measured during the heating phase, even though the highest temperature reached was only 346 K which is significantly below the decomposition temperature found from the TG/DTA traces. The compounds Mn(MeP)Cl_2, Co(MeP)Cl_2 and Zn(MeP)Cl_2 exhibit similar temperature dependences of conductivity to that described for Ni(MeP)Cl_2. Values of ΔE, as calculated from the gradients of the best-fitting lines for both the heating and cooling cycles, are listed in Table 4 for each compound. Owing to the limited linearity of the temperature dependence plots and the disparity between the heating and cooling data, caution should be exercised in the interpretation of the tabulated ΔE values.

The temperature dependence of the conductivity for the most conductive of these compounds, Cu(MeP)Cl_2, is shown in Fig. 3 and is seen to exhibit negligible change in conductivity with temperature during heating. A possible explanation for this behaviour is that the species of impurity resulting in the room temperature conductivity is essentially fully ionised at 300 K and the intrinsic mechanism is not significantly activated until temperatures higher than those studied are reached.

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