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Preparation, structural characterisation, thermal and electrical studies of cobalt chloride and zinc chloride compounds of poly(2-vinylpyridine)

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Abstract

The reaction of poly(2-vinylpyridine) with cobalt chloride and zinc chloride produced compounds of stoichiometry $[Co(2\text{-}Vpy)_{2.5}(H_2O)Cl_2]_n$ and $[Zn(2\text{-}Vpy)_{2.5}Cl_2]_n$. In the cobalt compound, the cobalt ion was found to exist in both octahedral and tetrahedral environments, while in the zinc compound the zinc ion was observed to be in a tetrahedral environment. Poly(2-vinylpyridine) and its metal polymers have been further characterised by gel permeation chromatography, differential thermal analysis and thermogravimetry. The room temperature electrical conductivities of these polymers lie in the range 6.07×10^{-8}–$1.12 \times 10^{-7}\ \Omega^{-1}\ m^{-1}$ and they show ohmic conductivity.

INTRODUCTION

At present, a considerable research effort in both the academic and industrial sectors is being directed towards the preparation of metal-containing polymers and the discovery of their properties. These new materials could well have potential applications as semi-conductors and catalysts. In this paper we report the preparation of the metal–polymer systems formed by the reaction of cobalt(II) chloride and zinc(II) chloride with poly(2-vinylpyridine). In each of the metal–polymer systems, spectral and magnetic studies have been used to determine the environment of the cobalt ion, while spectral studies alone were used to determine the environment of the zinc ion. We also report thermal analyses, and gel permeation chromatography and electrical conductivity studies in order to demonstrate the stability, molecular weight and potential semi-conductor properties of the compounds.

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EXPERIMENTAL

Syntheses

Preparation of poly(2-vinylpyridine), (2-Vpy)$_n$

Benzoyl peroxide (0.1 g) was dissolved in 10 g 2-vinylpyridine (2-Vpy). This mixture was placed in a sealed glass bottle under nitrogen and put into an oven set at 60°C. After 4 h, the bottle was removed and dimethylformamide was added to the mixture in the bottle. This was then left aside for 24 h. A mixture of ethanol and ether (1:10) was then added and the mustard-coloured precipitate obtained was filtered and then dried in a vacuum oven.

Preparation of the complex formed between poly(2-vinylpyridine) and cobalt chloride

Poly(2-vinylpyridine) (3 g) was dissolved in dimethylformamide (20 cm^3) and an excess of a hot ethanolic solution of $CoCl_2 \cdot 6H_2O$ was added. The blue compound which precipitated was filtered, washed thoroughly with warm ethanol and then dried in a vacuum oven at 60°C.

Preparation of the complex formed between poly(2-vinylpyridine) and zinc chloride

Poly(2-vinylpyridine) (3 g) was dissolved in dimethylformamide (20 cm^3) and excess of a hot ethanolic solution of $ZnCl_2 \cdot 2H_2O$ was added. The pale brown compound which precipitated was filtered, washed thoroughly with warm ethanol and then dried in a vacuum oven at 60°C.

Apparatus and measurements

The concentrations of metal ions were determined using a Perkin-Elmer 373 atomic absorption spectrophotometer; carbon, hydrogen and nitrogen analyses were obtained on a Carlo Erba elemental analyser; the chloride ion was determined gravimetrically [1]. Infrared spectra were obtained using KBr discs (4000–600 cm^{-1}) and polythene discs (600–200 cm^{-1}) on a Perkin–Elmer infrared spectrophotometer Model 598.

The electronic spectrum for the cobalt compound was obtained as a diffuse reflectance spectrum on a Beckmann Acta MIV spectrophotometer.

The magnetic moment for the cobalt compound was obtained on a magnetic balance using the Gouy method and the calibrant $Hg[Co(SCN)_4]$. The thermal analysis measurements were carried out on a Stanton Redcroft Model STA 1500 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.

Molecular weight distributions were determined using a Waters gel permeation chromatograph (GPC). All measurements for the polymers were performed in dimethylformamide at a flow rate of 1 ml min^{-1}. A polyethylene glycol/polyethylene oxide calibration was employed, and therefore the weight-average molecular weights $\bar{M}_w$ and the number-average molecular weights ($\bar{M}_n$) quoted are polyethylene glycol/polyethylene oxide equivalent molecular masses. All sample solutions were injected into the instrument at a concentration of 2 mg ml^{-1}.

Electrical measurements were carried out on discs prepared by compressing each powdered sample in a hydraulic press. The current versus voltage characteristics at room temperature were obtained using an electrometer to register current and a digital voltmeter for the voltage. Readings of current were obtained for a series of voltages. The thickness of each disc, which was needed for calculating the conductivity, was obtained using a micrometer.

RESULTS AND DISCUSSION

The analytical results for the metal and chloride ions, and for carbon, nitrogen and hydrogen are listed in Table 1 and are in agreement with the given formulae. The wavenumbers of the IR absorption bands for 2-Vpy, $[\text{2-Vpy}]_n$, and for the metal polymers are given in Table 2. The absence of the C=C vibration in the IR spectrum of $[\text{2-Vpy}]_n$ and in the metal polymer samples indicates that polymerisation of the 2-Vpy is complete. The IR spectrum of $[\text{2-Vpy}]_n$ is similar to that of the metal polymers in the 4000–600 cm^{-1} region, except the bands due to the ring vibrations which move to higher wavenumber on complex formation. This suggests that the nitrogen atom of the aromatic ring is coordinated to a metal ion [2].

In the cobalt polymer, a band was observed at 338 cm^{-1} and this has been assigned to the $Co–OH_2$ vibration. Also in this region, 600–200 cm^{-1}, bands due to the ν(M–Cl) and ν(M–N) vibrations have been assigned. For the cobalt polymer, bands are observed at 302 and 256 cm^{-1} for the Co–Cl vibration. On the basis of known wavenumbers of Co–Cl vibrations for

TABLE 1

Analyses in % of compounds

Compound		M	C	N	H	Cl
$[\text{2-Vpy}]_n$	Calc.	–	79.96	13.32	6.71	–
	Found	–	79.75	13.16	6.59	–
$[\text{Co(2-Vpy)}_{2.5}(\text{H}_2\text{O})\text{Cl}_2]_n$	Calc.	14.35	51.17	8.53	4.79	17.26
	Found	14.06	50.82	8.48	4.44	16.73
$[\text{Zn(2-Vpy)}_{2.5}\text{Cl}_2]_n$	Calc.	16.38	52.66	8.77	4.41	17.76
	Found	16.05	52.17	8.49	4.02	17.40

TABLE 2

Infrared spectra (4000–200 cm^{-1})

Compound	ν(C=C)	Ring vibrations		ν(M–Cl)	ν(M–OH_2)	ν(M–N)
[2-Vpy]	1632(*w*)	1589(s)	1435(s)	–	–	–
$[2\text{-Vpy}]_n$	–	1590(s)	1433(s)	–	–	–
$[Co(2\text{-Vpy})_{2.5}(H_2O)Cl_2]_n$	–	1608(s)	1439(s)	302(s) 256(m)	338(s)	280(m)
$[Zn(2\text{-Vpy})_{2.5}Cl_2]_n$	–	1609(s)	1441(s)	326(s) 300(s)	–	278(m)

Key: s, strong; m, medium.

cobalt in different environments, the bands observed in the present investigation are due to tetrahedrally (302 cm^{-1}) and octahedrally (256 cm^{-1}) coordinated cobalt atoms [3]. The bands at 326 cm^{-1} and 300 cm^{-1} in the zinc polymer are due to tetrahedrally coordinated zinc atoms [4]. The electronic spectrum of the cobalt polymer, Table 3, shows bands at 14 084 and 18 691 cm^{-1} which are characteristic both in position and shape of cobalt in a tetrahedral environment [3]. However the bands are only about half as intense as expected for a cobalt compound in a tetrahedral environment. Furthermore, the other band (6250 cm^{-1}) which is reported would normally be observed in compounds where the cobalt atom is in an octahedral environment. These spectral data support the conclusions obtained from the far-IR spectrum of the cobalt polymer that the cobalt atoms are present in both octahedral and tetrahedral environments. For cobalt atoms in such environments, the magnetic moments are in the ranges 5.0 ± 0.2 and 4.5 ± 0.3 [3]. Hence, the assumption of equal numbers of cobalt atoms on the two coordinated types, the mean magnetic moment would be 4.75 ± 0.25 BM. The observed magnetic moment is 4.56 BM.

The metal polymers were isolated as powders. Therefore no crystal structures could be obtained, but structural data from IR and magnetic analyses, together with the molecular formulae from elemental analyses,

TABLE 3

Electronic spectrum and magnetic moment

Compound	Band position/cm^{-1}	μ/BM
$[Co(2\text{-Vpy})_{2.5}(H_2O)Cl_2]_n$	6250 14084 18691	4.56

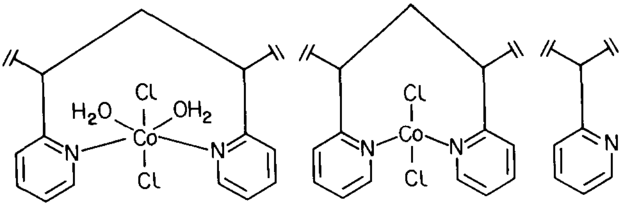

Fig. 1. Proposed structure for $[Co(2\text{-}Vpy)_{2.5}(H_2O)Cl_2]_n$.

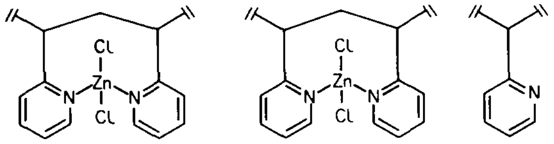

Fig. 2. Proposed structure for $[Zn(2\text{-}Vpy)_{2.5}Cl_2]_n$.

lead to the conclusion that each polymer chain contains three basic building blocks.

The blocks which occur in random order in the cobalt polymer are illustrated in Fig. 1, the average repeating structural formula being $[Co(2\text{-}Vpy)_{2.5}(H_2O)Cl_2]_n$. For the zinc polymer the blocks occurring in random order are illustrated in Fig. 2, the average repeating structural formula being $[Zn(2\text{-}Vpy)_{2.5}Cl_2]_n$.

The TG and DTA traces for poly(2-vinylpyridine) and the metal polymers formed between poly(2-vinylpyridine) and cobalt chloride and zinc chloride are shown in Figs. 3–5. The TG traces for poly(2-vinylpyridine), Fig. 3, shows that the compound begins to decompose at 96°C and finishes its decomposition at 632°C. The DTA trace shows that exothermic peaks are associated with the decomposition processes. The TG and DTA traces for the metal polymers, Figs. 4 and 5, show that they

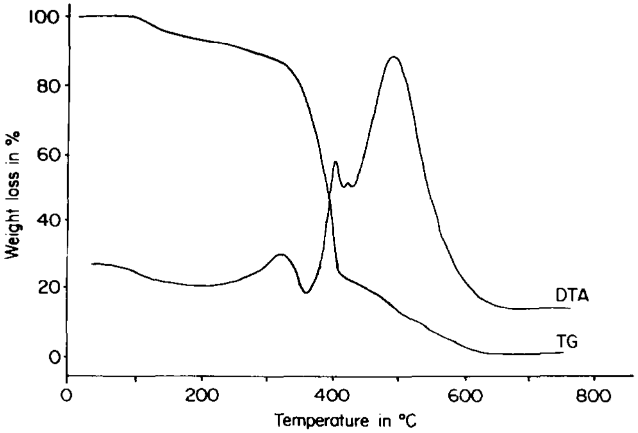

Fig. 3. TG and DTA trace for $[2\text{-}Vpy]_n$. Sample weight = 8.58 mg.

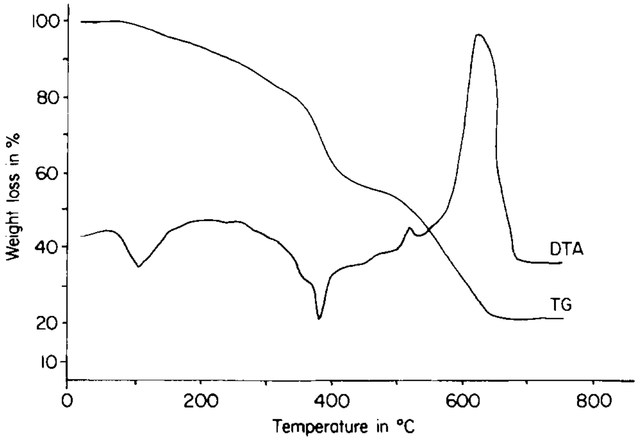

Fig. 4. TG and DTA trace for $[Co(2\text{-}Vpy)_{2.5}(H_2O)Cl_2]_n$. Sample weight = 9.4 mg.

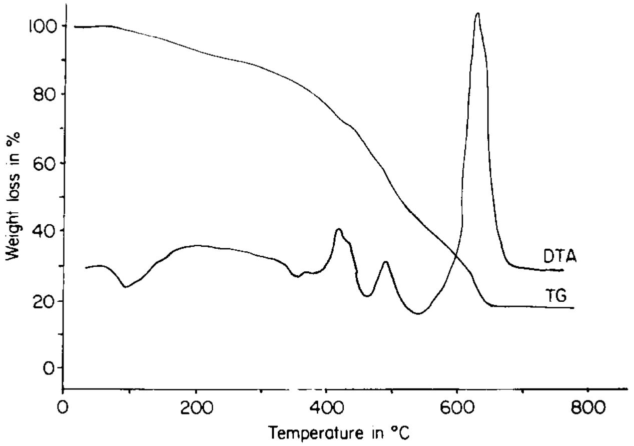

Fig. 5. TG and DTA trace for $[Zn(2\text{-}Vpy)_{2.5}Cl_2]_n$. Sample weight = 11.38 mg.

undergo endothermic reactions to give metal oxides. The observed weight loss for each decomposition process compares favourably with the theoretical values, see Table 4.,

TABLE 4

Thermal analysis data

Starting material	Decomp. temp./°C	Resulting compound	Weight loss/%	
			Calc.	Found
$[Co(2\text{-}Vpy)_{2.5}(H_2O)Cl_2]_n$	74 (Endo/Exo)	Co_3O_4	80.43	79.58
$[Zn(2\text{-}Vpy)_{2.5}Cl_2]_n$	60 (Endo/Exo)	ZnO	79.62	78.90

Key: Endo, endothermic; Exo, exothermic (from the DTA trace).

TABLE 5

Results of molecular weight determinations and electrical conductivity measurements for the polymer systems

Material	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	Conductivity at 21°C/Ω^{-1} m^{-1}
[2-Vpy]	38100	16600	2.3	2.65×10^{-8}
$[Co(2\text{-}Vpy)_{2.5}(H_2O)Cl_2]_n$	39400	17000	2.1	1.12×10^{-7}
$[Zn(2\text{-}Vpy)_{2.5}Cl_2]_n$	39100	19200	2.3	6.07×10^{-8}

Key: $\bar{M}_w$ is the weight-average molecular weight; $\bar{M}_n$ is the number-average molecular weight.

The molecular weight averages $\bar{M}_w$ and $\bar{M}_n$ for the materials are listed in Table 5 together with the polydispersity ratio ($\bar{M}_w/\bar{M}_n$). The molecular weight distribution is wide for all materials (as shown by $\bar{M}_w/\bar{M}_n \gg 1$). Table 5 also contains the measured room-temperature electrical conductivity σ of each polymer system. The room-temperature current I versus voltage V characteristics were obtained under conditions of rising and falling voltage in both polarities. The $I-V$ relationship for all the polymers was found to be linear through the voltage range studied, indicating that the electrical conduction was ohmic. The electrical conductivities reported in Table 5 are calculated from the gradients of the $I-V$ plots, assuming that the current flow is perpendicular to the electrodes. The higher electrical conductivity of the polymer $[Co(2\text{-}Vyp)_{2.5}(H_2O)Cl_2]_n$ compared to the conductivities of the polymers $[2\text{-}Vpy]_n$ and $[Zn(2\text{-}Vpy)_{2.5}Cl_2]_n$ could be due to the incorporation of water molecules in its structure.

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