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Preparation, structural characterisation, thermal and electrical studies of a novel polymer produced from dichlorobis(2-vinylpyridine)cobalt(II)

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Abstract

A metal polymer has been prepared from dichlorobis(2-vinylpyridine)cobalt(II). Spectral and magnetic studies have shown that the cobalt atoms are in a tetrahedral environment in the polymer system. The metal polymer has been further characterised using differential thermal analysis and thermogravimetry. The room temperature electrical conductivity for the polymer is $5.51 \times 10^{-5}\ \Omega^{-1}\ \mathrm{m}^{-1}$ and ohmic behaviour is observed.

INTRODUCTION

The incorporation of metals into polymers is not only of interest academically but also industrially. The development of these materials as new semi-conducting and conducting polymers is due to their potential applications as sensors and rectifiers where low density materials with thermal and chemical stability are required. In this paper we discuss the preparation and some properties of the metal polymer system produced when the monomeric compound dichloro(2-vinylpyridine)cobalt(II) undergoes polymerisation. Magnetic, electronic and infrared studies have been used to obtain information about the environment of the cobalt ion in this polymer. We also report thermal analysis and electrical studies.

EXPERIMENTAL

Preparation of the compounds

Preparation of dichlorobis(2-vinylpyridine)cobalt(II)

The monomer complex was prepared by mixing stoichiometric amounts of 2-vinylpyridine and a solution of the hydrated cobalt chloride in boiling ethanol. The precipitate which formed was filtered under suction, washed with ethanol, and dried in a vacuum oven at 60°C for 24 h.

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Preparation of the metal polymer from dichlorobis(2-vinylpyridine)cobalt(II)

Dichlorobis(2-vinylpyridine)cobalt(II) (1.0 g) and benzoyl peroxide (0.1 g) were dissolved in dimethylformamide (20 cm^3) and heated under nitrogen for 24 h at 70°C. The resulting precipitate was filtered under suction, washed with boiling ethanol, and dried under vacuum for 24 h at 60°C.

Apparatus and measurements

The concentration of cobalt ion was determined using a Perkin-Elmer 373 atomic absorption spectrophotometer; carbon, hydrogen and nitrogen analyses were carried out on a Carlo Erba elemental analyser; 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 measured 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.

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

RESULTS AND DISCUSSION

The experimental results from the analyses of metal ion, carbon, nitrogen, hydrogen and chloride ion content of the cobalt polymer are given in Table 1. The results give an empirical formula of $Co(2\text{-}Vpy)_{0.75}Cl_2(H_2O)_{0.5}$ for the metal polymer.

TABLE 1

Elemental analysis (in %) of polymer prepared from dichlorobis(2-vinylpyridine)cobalt(II)

	M	C	N	H	Cl
Theory	35.25	25.88	4.61	2.78	31.14
Found	34.81	25.69	3.94	2.61	30.41

The electronic spectrum of the metal polymer shows bands at 4993, 15 748 and 19 047 cm^{-1}. The position and intensity of these bands is indicative of the cobalt ion being in a tetrahedral environment [2] and they correspond to the d–d transitions $^4A_2(F) \rightarrow {}^4T_2(F)$; $^4A_2(F) \rightarrow {}^4T_1(F)$ and $^4A_2(F) \rightarrow {}^4T_1(P)$. The magnetic moment of the metal polymer is 4.42 BM and is in the expected range of 4.2–4.8 BM for compounds where the cobalt ion is in a tetrahedral environment [2]. The main bands in the IR spectrum of the metal polymer and the IR spectrum of 2-vinylpyridine are similar in the region 4000–600 cm^{-1} except that the bands assigned to the ring vibrations which appear at 1589 and 1435 cm^{-1} in 2-vinylpyridine and 1609 and 1447 cm^{-1} in the metal polymer. This shows that the nitrogen atom of the aromatic ring is coordinated to the cobalt atom in the polymer [2]. A sharp band at 3549 cm^{-1} has been attributed to the presence of coordinated water molecules. A band at 1632 cm^{-1} due to the C=C vibration is observed in the IR spectrum of 2-vinylpyridine. There is no trace of this band in the IR spectrum of the metal polymer and this indicates that the polymerisation reaction involving dichlorobis (2-vinylpyridine)cobalt(II) has reached completion. In the region 600–200 cm^{-1} bands due to Co–Cl and Co–N vibrations are observed. The bands at 304 and 265 cm^{-1} due to the Co–Cl vibrations show the presence of terminal and bridging halogens while the band at 282 cm^{-1} indicates the Co–N vibration. A shoulder on one of the Co–Cl bands at 348 cm^{-1} is considered to be due to the Co–OH$_2$ vibration.

The fact that the metal polymer was isolated as a powder and not as single crystals means that no complete structure determination could be made. However the information obtained from the magnetic moment, electronic and IR spectra enable us to predict that the cobalt ion is in a tetrahedral environment. It is postulated that the metal polymer is made up of a dimeric structure whereby cobalt atoms are bonded to terminal and bridging chlorines, a nitrogen atom in the pyridine ring and a water molecule. The elemental analyses indicate that there is one pyridine moiety not bonded to cobalt for every two complexed pyridine rings (see Fig. 1).

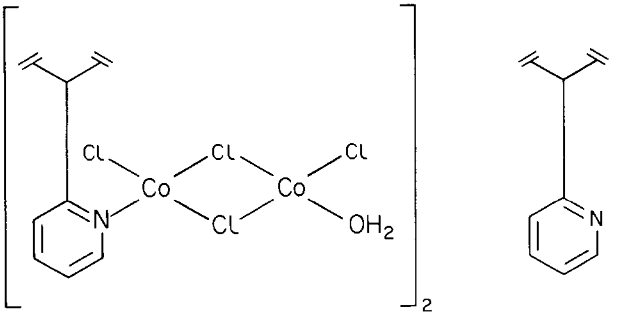

Fig. 1. Proposed structural units in the polymer chain of $Co(2\text{-}Vpy)_{0.75}Cl_2(H_2O)_{0.5}$.

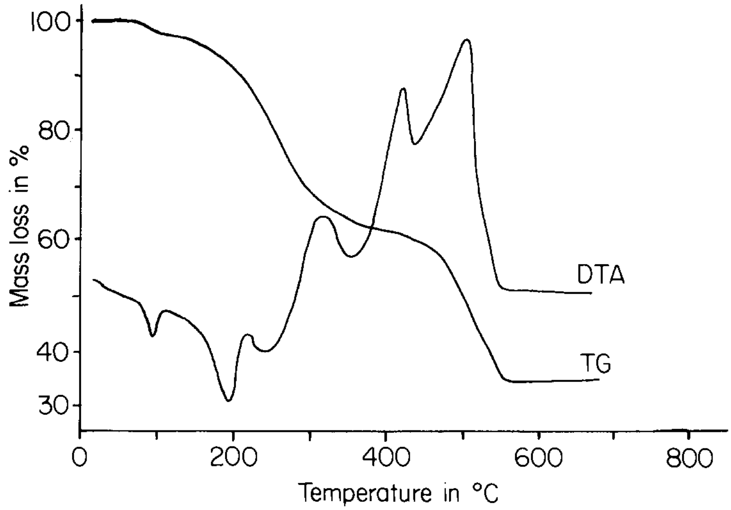

Fig. 2. TG and DTA traces for $Co(2\text{-}Vpy)_{0.75}Cl_2(H_2O)_{0.5}$.

The TG and DTA traces for the metal polymer are shown in Fig. 2. The DTA trace shows that the metal polymer undergoes an endothermic reaction and this is accompanied by a mass loss in the TG trace which corresponds to loss of the water. A further endothermic reaction is observed in the DTA trace which corresponds on the TG trace to a mass loss due to the organic ligand. The final mass loss on the TG trace which is accompanied by exothermic effects on the DTA trace results in the formation of Co_3O_4.

In the electrical studies the room temperature current (I) versus voltage (V) characteristics were obtained under conditions of rising and falling voltages in both polarities. The I–V relationship for the compound was found to be linear throughout the studied range ($0 < V < 120$), indicating ohmic behaviour. The measured room temperature electrical conductivity σ, derived from the gradient of the I–V plot was found to be $5.51 \times 10^{-5}\ \Omega^{-1}\ m^{-1}$. This value is similar to that obtained for the compound $Si(acac)_3CoCl_3$ where dimeric cobalt atoms were also found to exist and the cobalt atoms were in a tetrahedral environment [3].

REFERENCES

1 A.I. Vogel, Quantitative Inorganic Analysis, Longmans, London, 1964, p. 266.
2 J.R. Allan and G.M. Baillie, J. Therm. Anal., 14 (1978) 291.
3 J.R. Allan, D.L. Gerrard, S. Hoey, A.D. Paton and K. Turvey, Thermochim. Acta, 146 (1989) 317.