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PREPARATION, CHARACTERIZATION, THERMAL AND ELECTRICAL STUDIES OF POLY(4-VINYLPYRIDINE) AND ITS COBALT(II) BROMIDE COMPLEX

J.R. ALLAN, B.R. CARSON and K. TURVEY

Department of Applied Chemical and Physical Sciences, Napier Polytechnic, Edinburgh (U.K.)

J. BIRNIE and D.L. GERRARD

British Petroleum Research Centre, Sunbury, Middlesex (U.K.)

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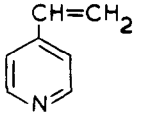
ABSTRACT

A polymer–metal complex was prepared by complexing cobalt bromide with poly(4-vinylpyridine) in aqueous ethanol. Analysis of the complex shows that its formula is $[Co(Vpy)_2Br_2 \cdot H_2O]_n$, where (Vpy) represents a molecule of 4-vinylpyridine. From spectral and magnetic data, the environment of the cobalt atom is found to be tetrahedral. The metal polymer has been further characterized using gel permeation chromatography, differential thermal analysis and thermogravimetry. The electrical conductivity and its temperature dependence were obtained for the cobalt bromide complex and for poly(4-vinylpyridine). From this work and comparison with earlier work on cobalt chloride complexes of poly(4-vinylpyridine), it is concluded that the metal and halogen atoms play only minor roles in the electrical properties.

INTRODUCTION

The compound 4-vinylpyridine has two ways in which it can bond to a metal atom: via the nitrogen atom of the aromatic ring and via the potentially reactive vinyl group which is attached to the ring system.



4-vinylpyridine (Vpy).

The coordination compounds formed between transition metal halides and 4-vinylpyridine are well documented [1–3]. Metal–polymer systems produced from dichlorobis(vinylpyridine)cobalt(II) and the reaction of poly(vinylpyridine) with cobalt(II) chloride have been previously reported

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by us [4]. This paper describes the preparation, analysis and some spectral, magnetic and electrical properties of the metal–polymer system produced by the reaction of poly(vinylpyridine) with cobalt(II) bromide.

EXPERIMENTAL

Preparation of the compounds

Preparation of poly(4-vinylpyridine)

4-Vinylpyridine (6 g) and benzoyl peroxide (0.1 g) were heated under nitrogen at 70 °C for 1 hour. The red precipitate of poly(4-vinylpyridine) was filtered and oven-dried at 60 °C for 24 hours.

Preparation of dibromo-bis(4-vinylpyridine)cobalt(II)

The monomer complex was prepared by mixing stoichiometric amounts of 4-vinylpyridine and a solution of the hydrated cobalt bromide in boiling ethanol. The crystals which formed were filtered under suction, washed with ethanol, and dried in a vacuum oven at 60 °C for 24 hours.

Preparation of the poly(4-vinylpyridine) complex of cobalt bromide

Poly(4-vinylpyridine) (6 g), prepared as described above, was dissolved at 70 °C in dimethylformamide. To this solution was added a solution of hydrated cobalt bromide (10 g) in ethanol (50 cm^3). The mixture was refluxed for three days; then the precipitate was filtered, washed with boiling ethanol, and dried under vacuum at 60 °C for 24 hours.

Apparatus and measurements

The concentration of cobalt ion was determined using a Perkin–Elmer 373 atomic absorption spectrophotometer; the carbon, nitrogen and hydrogen were analysed using a Carlo Erba elemental analyser; the bromide ions were analysed using a gravimetric method [5].

IR spectra were obtained using KBr discs (4000–600 cm^{-1} range) and polyethylene discs (600–200 cm^{-1} range) on a Perkin–Elmer IR spectrophotometer, Model 598. For the metal polymer, electronic spectra were obtained on a Beckman Acta MIV spectrophotometer and its magnetic moment was determined by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant.

Thermal analysis measurements were carried out on a Stanton Redcroft 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 for poly(4-vinylpyridine) and its metal polymer were determined using a Waters 150C gel permeation chromatography instrument. For the polymers, the measurements were performed in dimethylformamide/0.1 M LiCl solution at a concentration of 1 mg ml^{-1} and at a flow rate of 1 ml min^{-1}.

Electrical conduction in the poly(4-vinylpyridine) and the polymerized cobalt bromide complex of 4-vinylpyridine was studied using samples in the form of discs of compacted powder and provided with electrodes of conductive silver paint. The details of the method have been previously described [4]. In addition, the temperature dependence of the electrical conductivity in these materials was also obtained, again using the method previously described [4].

RESULTS AND DISCUSSION

The compounds which have been prepared are listed in Table 1. The elemental analyses agree with the given formulae for the compounds.

The bands in the electronic spectrum of $[Co(Vpy)_2Br_2 \cdot H_2O]_n$ are listed in Table 2. Bands are observed at 7246, 15231 and 16051 cm^{-1} which suggests that in this compound the cobalt atoms are in a tetrahedral environment [6]. The magnetic moment reported in Table 2 for this compound lies between 4.2 and 4.8 B.M., agreeing with the suggested tetrahedral arrangement of ligands around the cobalt atom [6]. Table 2 also lists the main IR bands of Vpy, PVpy and $[Co(Vpy)_2Br_2 \cdot H_2O]_n$. The strong, broad absorption band in the region 3580–3000 cm^{-1} for the metal polymer has been assigned to the ν(O–C) vibration of water and indicates the presence of water of crystallisation [7]. The band at 1620 cm^{-1} in Vpy has been assigned to the ν(C=C) vibration. The absence of this band in PVpy and $[Co(Vpy)_2Br_2 \cdot H_2O]_n$ indicates the high degree of polymerization in these compounds. The bands attributable to the aromatic ring vibrations move to higher wavenumbers following complexation. This suggests that the nitrogen atoms of the aromatic rings are coordinated to the cobalt atom [7]. The wavenumbers of the bands due to ν(Co–N) and ν(Co–Br) are listed in Table 2. The cobalt–bromine mode is in the region 280–250 cm^{-1} and is

TABLE 1

Analyses of compounds

Compound		M	C	N	H	Br
PVpy	Calc. (%)	–	79.96	13.32	6.71	–
	Found (%)	–	79.90	13.20	6.70	–
$Co(Vpy)_2Br_2$	Calc. (%)	13.73	39.19	6.53	3.28	37.23
	Found (%)	13.62	39.19	6.41	3.09	36.97
$[Co(Vpy)_2Br_2 \cdot H_2O]_n$	Calc. (%)	13.18	37.61	6.26	3.16	35.75
	Found (%)	12.90	38.21	6.97	3.64	35.37

TABLE 2

Magnetic moment and IR and electronic spectra

Compound	Magnetic moment (B.M.)	Electronic spectrum (cm^{-1})	IR spectra (cm^{-1})				
			ν_{O-H}	$\nu_{C=C}$	Ring vibrations	ν_{Co-Br}	ν_{Co-N}
Vpy	–	–	–	1620(w)	1594(s) 1408(s)	–	–
PVpy	–	–	–	–	1598(s) 1414(s)	–	–
$Co(Vpy)_2Br_2$	4.32	7246 15231 16051	3580– 3000(br, s)	–	1608(s) 1422(s)	266(m)	233(m)

br, broad; s, strong; m, medium; w, weak.

again indicative of a cobalt atom in a tetrahedral environment [6]. A possible structure for the polymer–metal complex $[Co(Vpy)_2Br_2 \cdot H_2O]_n$ is shown in Fig. 1.

Table 3 lists the molecular weight averages, $\overline{M}_w$ and $\overline{M}_n$, together with the polydispersity ratio ($\overline{M}_w/\overline{M}_n$) for PVpy and $[Co(Vpy)_2Br_2 \cdot H_2O]_n$. The molecular weight distribution is wide for both materials (as shown by $\overline{M}_w/\overline{M}_n \gg 1$) with $[Co(Vpy)_2Br_2 \cdot H_2O]_n$ having the wider relative distribution.

Attempts to prepare $[Co(Vpy)_xBr_2]_n$ by polymerization of the momomer $Co(Vpy)_2Br_2$ proved unsuccessful, whereas in an earlier study [4], differing only in the halogen being chlorine instead of bromine, the corresponding polymerization was achieved. It is therefore suggested that the larger effective diameter of bromine compared with chlorine inhibits polymerization of an initially formed monomer.

The TG and DTA traces for PVpy are shown in Fig. 2. The pyrolytic decomposition starts at 32°C and finishes at 644°C with total elimination of the sample. The DTA trace shows a glass transition at 103°C followed by exothermic peaks for the decomposition process. The TG and DTA trace,

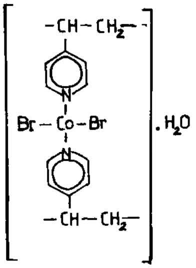

Fig. 1. Possible structure for a unit of $Co(Vpy)_2Br_2 \cdot H_2O$ in its polymer.

TABLE 3

Results of molecular weight determinations

Material [a]	$\overline{M}_w$ [b]	$\overline{M}_n$ [c]	$\overline{M}_w/\overline{M}_n$
PVpy	7800	30600	2.54
$[Co(Vpy)_2Br_2 \cdot H_2O]_n$	41600	12700	3.27

[a] PVpy, poly(vinylpyridine); VPy, vinyl pyridine.

[b] $\overline{M}_w$ is the weight-average molecular weight, i.e. $\overline{M}_w = \Sigma(n_i M_i^2)/\Sigma(n_i M_i)$.

[c] $\overline{M}_n$ is the number-average molecular weight, i.e. $\overline{M}_n = \Sigma(n_i M_i)/\Sigma n_i$.

Fig. 3, for the metal–polymer $[Co(Vpy)_2Br_2 \cdot H_2O]_n$ shows that it undergoes an endothermic reaction at 40° C with loss of water molecules. The dehydration process takes place in one step. The observed weight loss for this process compares favourably with the theoretical value, see Table 4. Exothermic decomposition of the anhydrous metal–polymer follows immediately after the dehydration process and the residual weight is in good agreement with the value required for Co_3O_4 (Table 4).

The results of the electrical measurements, which were performed only for PVpy and $[Co(Vpy)_2Br_2 \cdot H_2O]_n$ are summarized in Table 5. A plot of the current (I) versus voltage (V) for a disc of $[Co(Vpy)_2Br_2 \cdot H_2O]_n$ at room temperature is shown in Fig. 4; the corresponding plot for Vpy (which is not presented) is similar. Reference to the figure shows that after measurements of the current as a function of voltage in the initial applied polarity had been obtained, larger currents were then obtained at corresponding voltages under reversed polarity. The same behaviour was also noted in our earlier work [4] on cobalt chloride complexes of vinylpyridine and suggests that in Vpy itself, and in both its cobalt chloride and cobalt bromide complexes, the initial applied field direction produces a change which may be either a permanent distortion in the molecules or the formation of a barrier at one contact. From Table 5 for Vpy and $[Co(Vpy)_2Br_2 \cdot H_2O]_n$, and from earlier work on the cobalt chloride complexes [4], it is seen that under increasing

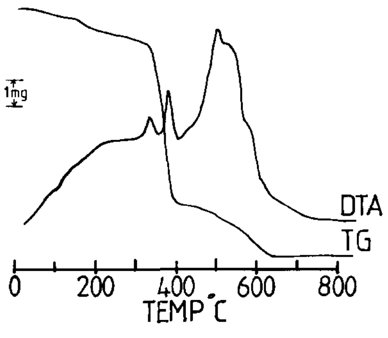

Fig. 2. TG/DTA trace for PVpy. Sample weight = 9.75 mg.

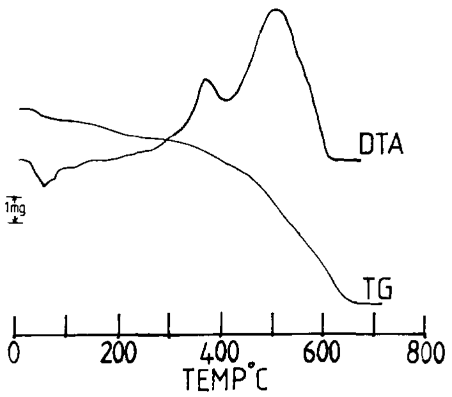

Fig. 3. TG/DTA trace for $[Co(Vpy)_2Br_2 \cdot H_2O]_n$. Sample weight = 9.30 mg.

voltage the current increases more rapidly than predicted by Ohm's law, as the exponent m in the empirical expression $|I| \propto |V|^m$ exceeds unity. In all cases $1.14 < m < 1.44$; therefore, the departure from Ohm's law ($m = 1$) is not great. Almost certainly, the excess value of m over unity is due to space-charge limitation of current (SCLC) although the theory [8–10] for this type of conduction is better formulated for $m > 2$ rather than for the observed case of $1 < m < 2$. One model [11] for SCLC predicts an equation of the form $|I| = a|V| + b|V|^2$ in which a and b are constants; but this fits the measured data much less satisfactorily than the expression $|I| \propto |V|^m$.

Because $m \neq 1$, a unique conductivity cannot be assigned. Instead, in Table 5, conductivities are reported corresponding to a mean applied field of 1×10^4 V m^{-1}; this field is arbitrarily chosen but is close to the mid-range of the applied fields. From the data in Table 5, in conjunction with data from the earlier work [4] for cobalt chloride complexes of vinylpyridine, it is found that the room temperature conductivities at a field of 1×10^4 V m^{-1} all lie in the narrow range 3.7×10^{-8}–1.3×10^{-7} Ω^{-1} m^{-1} suggesting that the type of halogen is unimportant in controlling conductivity. The conductivity is lowest for PVpy, showing that the incorporation of the metal raises conductivity, but has only a weak effect.

TABLE 4

Thermal analysis data

Starting material	Decomposition temperature (°C)	Resulting compound	% Weight loss [a]	
			Calc.	Found
$[Co(Vpy)_2Br_2 \cdot H_2O]_n$	40 (endo)	$[Co(Vpy)_2Br_2]_n$	4.02	4.30
	72 (exo)	Co_3O_4	83.24	82.79

[a] The loss in weight is expressed as a percentage of the weight of the original $[Co(Vpy)_2Br_2 \cdot H_2O]_n$.

TABLE 5

Electrical properties

Compound	m [a]		Conductivity at 21° C (Ω^{-1} m^{-1}) [b]		ΔE (eV) [c]		
	Initial polarity	Reversed polarity	Initial polarity	Reversed polarity	Heating	Cooling	Combined heating and cooling cycle
PVpy	1.26 ± 0.07	1.38 ± 0.02	$(3.7 \pm 1.3) \times 10^{-8}$	$(4.2 \pm 0.5) \times 10^{-8}$	1.24 ± 0.07	1.61 ± 0.04	1.45 ± 0.07
$[Co(Vpy)_2Br_2H_2O]_n$	1.14 ± 0.01	1.14 ± 0.01	$(7.5 \pm 0.5) \times 10^{-8}$	$(9.1 \pm 0.5) \times 10^{-8}$	1.36 ± 0.14	1.73 ± 0.07	1.59 ± 0.09

[a] m is the exponent in the empirical expression $|I| \propto |V|^m$ for the room temperature (21° C) current (I) versus voltage (V) characteristics for a disc of the compound. The value of m is found from the gradient of the least-squares-fitted line to a plot of $\ln |I|$ versus $\ln |V|$.

[b] The conductivity is quoted for a mean field across the disc of 1×10^4 V m^{-1}.

[c] ΔE is the energy term in the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$, where σ is the conductivity at absolute temperature T. For the separate cases of heating, cooling and the combined heating and cooling cycle, ΔE is obtained from the gradient of the least-squares-fitted line to a plot of $\ln \sigma$ versus T^{-1}.

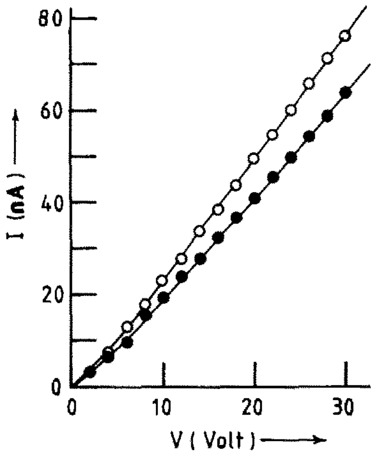

Fig. 4. Plot of current, *I*, versus voltage, *V*, for a disc of $[Co(Vpy)_2Br_2 \cdot H_2O]_n$ at a temperature of 21° C. Points for initial polarity (●); points for reversed polarity (○). In each polarity good reproducibility was obtained for increasing and decreasing magnitude of the applied voltage.

The temperature dependence of electrical conductivity (σ) for PVpy is shown in Fig. 5 in the form of an Arrhenius plot. A graph of similar shape was also obtained for $[Co(Vpy)_2Br_2 \cdot H_2O]_n$ but is not shown. The activation energy, ΔE, in the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ was obtained from the

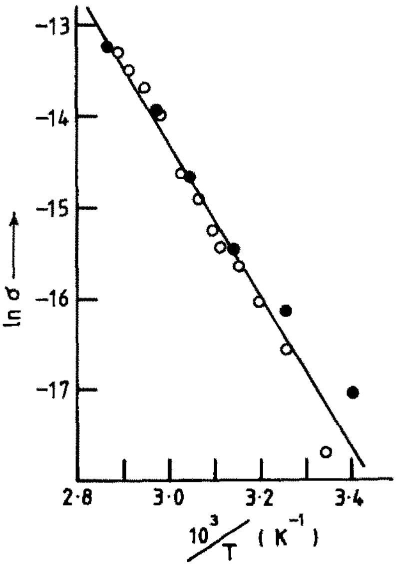

Fig. 5. Plot of ln σ versus $10^3\ T^{-1}$ for PVpy where σ is the conductivity in units of $\Omega^{-1}\ m^{-1}$ and is determined from the current flowing under an applied voltage of 10 V across a disc of thickness 0.94 mm and *T* is the absolute temperature. Points for heating (●); points for cooling (○). The line is least-squares-fitted to the total of the heating and cooling points.

gradient of the least-squares-fitted line in the Arrhenius plot and is listed, for both materials, in Table 5. Because of the poor reproducibility during heating and cooling, separate values of ΔE are given for the cases of rising temperature, falling temperature and the combined heating and cooling cycle. Part of the cause of this poor reproducibility is the low thermal decomposition temperatures of the materials, as found in the TG/DTA measurements. The values of ΔE are in a similar range to those found [4] for cobalt chloride complexes of vinylpyridine. On the basis of a so-called compensation law [12–14] connecting σ_0 and ΔE, it was tentatively concluded [4] that conduction in the cobalt chloride complexes is controlled by quantum-mechanical tunnelling [15] between intermolecular barriers. By analogy, considering the similarity of the electrical data in the present work and in the earlier work [4], it is suggested that the same conduction mechanism operates in Vpy and $[Co(Vpy)_2Br_2 \cdot H_2O]_n$.

REFERENCES

1 N.H. Agnew and L.F. Larkworthy, J. Chem. Soc., (1965) 4669.
2 N.H. Agnew, R.J. Collin and L.F. Larkworthy, J. Chem. Soc., Dalton Trans., (1974) 272.
3 R.J. Collin and L.F. Larkworthy, J. Inorg. Nucl. Chem., 37 (1975) 334.
4 J.R. Allan, B.R. Carson, A.D. Paton, K. Turvey, J. Birnie and D.L. Gerrard, Plastics and Rubber Processing and Applications (in press).
5 A.I. Vogel, Quantitative Inorganic Analysis, Longman, London, 1964, p. 266.
6 J.R. Allan and G.M. Baillie, J. Therm. Anal., 14 (1978) 291.
7 J.R. Allan, N.D. Baird and A.L. Kassyk, J. Therm. Anal., 16 (1979) 79.
8 F. Gutmann and L.E. Lyons, Organic Semiconductors, Wiley, New York, 1967, pp. 558–631.
9 H. Meier, Organic Semiconductors, Verlag-Chemie, Weinheim, 1974, pp. 288–300.
10 M.A. Lampert, Phys. Rev., 103 (1956) 1648.
11 S.M. Sze, Physics of Semiconductor Devices, Wiley-Interscience, New York, 1969, pp. 417–421.
12 A. Many, E. Harnik and J. Gerlich, J. Chem. Phys., 23 (1955) 1733.
13 M.E. Green, J. Chem. Phys., 51 (1969) 3279.
14 G. Kemeny and B. Rosenberg, J. Chem. Phys., 52 (1970) 4151.
15 F. Gutmann and L.E. Lyons, Organic Semiconductors, Wiley, New York, 1967, pp. 425–438.