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Thermal and electrical studies of dibromotetrakis(4-vinylpyridine)cobalt(II)

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Abstract

Thermal analysis studies show that the compound dibromotetrakis(4-vinylpyridine)cobalt(II) decomposes to give the thermal decomposition products dibromobis(4-vinylpyridine)cobalt(II) and dibromo(4-vinylpyridine)cobalt(II). Electronic spectra have been used to determine the coordination about the cobalt atom in each of the thermal decomposition products. Some preliminary results on the electrical conductivity and its temperature dependence are presented for dibromotetrakis(4-vinylpyridine)cobalt(II).

INTRODUCTION

The stoichiometry and stereochemistry of the compound dibromotetrakis-(4-vinylpyridine)cobalt(II) has been reported in the literature [1]. Recently, the present authors reported [2] on the preparation, structure and electrical properties of the related compound, dichlorobis(4-vinylpyridine)cobalt(II), and of a product formed from its polymerisation. We have also described [3] the preparation, structure, thermal decomposition and electrical conductivity of a polymerised complex of cobalt bromide with 4-vinylpyridine. The purpose of the present work is two-fold: firstly, to study the thermal decomposition of dibromotetrakis(4-vinylpyridine)cobalt(II) and to deduce from the electronic spectra and elemental analyses the nature and possible environment of the cobalt atom in the thermal decomposition products; and secondly, to obtain electrical conductivity data for dibromotetrakis(4-vinylpyridine)cobalt(II).

EXPERIMENTAL

Preparation of complexes

(A) The complex was prepared by dissolving cobalt bromide in boiling ethanol and adding an excess of 4-vinylpyridine dissolved in ethanol. The complex which precipitated out of solution was washed with warm ethanol containing some 4-vinylpyridine and then air-dried.

(B) These complexes were obtained by heating the complex prepared by method (A). The heating was performed on a thermobalance at a fixed temperature until a constant weight was obtained.

Apparatus and measurements

The concentration of metal ion was determined using a Perkin–Elmer 373 atomic absorption spectrophotometer. The carbon, hydrogen and nitrogen analyses were made using a Carlo Erba elemental analyser. The electronic spectra were recorded as solid diffuse reflectance spectra using a Beckman Acta MIV spectrophotometer. The thermal analysis measurements were made on a Stanton Redcroft Model 1500 thermobalance. Thermogravimetry (TG) and differential thermal analysis (DTA) curves were obtained at a heating rate of 6 °C min^{-1} in static air. The 20–800 °C temperature range was studied. Electrical conduction at room temperature and the temperature-dependence of the electrical conductivity were investigated for the complex prepared by method (A) only. The measurements were obtained for a disc of the complex formed by compressing the powder to form an aggregate. This disc had a thickness of 1.0 mm, a diameter of 13.0 mm and was provided with a conductive silver paint electrode of diameter 4.9 mm on each of the flat faces. Current (I) was measured as a function of applied voltage (V) at room temperature and I was also measured as a function of temperature for a fixed applied voltage of 10 V across the electrodes. Details of the procedure were as previously described [2].

RESULTS AND DISCUSSION

The reaction in ethanolic solution of cobalt bromide and 4-vinylpyridine produced a purple complex, the elemental analyses of which are reported in Table 1. From these elemental analyses, the complex is identified as dibromotetrakis(4-vinylpyridine)cobalt(II), i.e. $Co(C_7H_7N)_4Br_2$. Using this compound as starting material, the TG and DTA traces shown in Fig. 1 were obtained. The TG trace shows that during heating there are three

TABLE 1

Analyses of starting compound

Compound		Analyses (wt.%)			
		Metal	Carbon	Nitrogen	Hydrogen
$Co(C_7H_7N)_4Br_2$	Theory	9.21	52.60	8.76	4.41
	Found	8.74	52.49	8.63	4.39

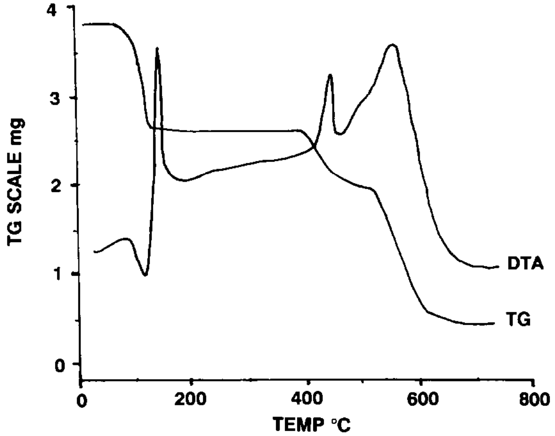

Fig. 1. Thermogravimetric (TG) and differential thermal analysis (DTA) traces obtained for a sample of dibromotetrakis(4-vinylpyridine)cobalt(II) heated in air.

successive products which, from elemental analyses, are identified as $Co(C_7H_7N)_2Br_2$, $Co(C_7H_7N)Br_2$ and Co_3O_4. Table 2 summarises the decomposition temperatures (read from the TG trace), the colours of the initial and intermediate complexes and the elemental analyses of each product. The DTA trace in Fig. 1 shows that the reaction $Co(C_7H_7N)_4Br_2 \rightarrow Co(C_7H_7N)_2Br_2$ involves an endothermic stage followed by an exothermic stage. Also from the DTA trace, it is found that the reactions $Co(C_7H_7N)_2Br_2 \rightarrow Co(C_7H_7N)Br_2$ and $Co(C_7H_7N)Br_2 \rightarrow Co_3O_4$ are both exothermic.

Agnew et al. [1] have suggested that the environment of the cobalt ion in dibromotetrakis(4-vinylpyridine)cobalt(II) is octahedral, on the basis of their spectral and magnetic measurements. In the present work, the environment of the cobalt ion for this complex was not studied although it was for $Co(C_7H_7N)_2Br_2$ and $Co(C_7H_7N)Br_2$. The electronic spectrum for $Co(C_7H_7N)_2Br_2$ exhibits strong bands at 16050 and 5180 cm^{-1} whilst $Co(C_7H_7N)Br_2$ has bands at 20100, 14060 and 8600 cm^{-1}; the positions of these bands indicate [4] tetrahedral and octahedral environments of the cobalt ion in $Co(C_7H_7N)_2Br_2$ and $Co(C_7H_7N)Br_2$ respectively.

The room-temperature measurements of current (I) as a function of applied voltage (V) for the disc of $Co(C_7H_7N)_4Br_2$ show, from the linearity of the double-logarithmic plot of I against V (which is not reproduced as a figure), that the relationship between I and V is of the form $I \propto V^m$. The value of m as found by least-squares fitting of the line is 1.18 ± 0.01 and this result is the same for both polarities. The small excess of m over the Ohm's law value of unity is attributed to partial space-charge-limitation of current; similar values of m were found in earlier work for dichlorobis(4-vinylpyridine)cobalt(II) [2] and for a polymerised complex of cobalt bromide with 4-vinylpyridine [3]. The room-temperature conductivity for the monomer

TABLE 2

Thermal decomposition data

Starting material			Decomposition		Product			Analyses (wt.%)				
Formula	Colour	Co^{2+} environment [a]	Temperature (°C)	Nature [b]	Formula	Colour	Co^{2+} environment [a]		Co	C	N	H
$Co(C_7H_7N)_4Br_2$	Purple	Octa [c]										
			68	Endo	$Co(C_7H_7N)_2Br_2$	Blue	Tetra	Theory	13.73	39.19	6.53	3.28
				Exo				Found	13.68	39.07	6.41	3.34
			380	Exo	$Co(C_7H_7N)Br_2$	Blue	Octa	Theory	18.19	25.95	4.32	2.17
								Found	17.36	25.42	3.79	1.96
			500	Exo	Co_3O_4			Theory	73.42	–	–	–
								Found	72.66	–	–	–

[a] Octa = octahedral; Tetra = tetrahedral.

[b] Endo = endothermic; Exo = exothermic.

[c] Structure proposed by Agnew et al. [1].

$Co(C_7H_7N)_4Br_2$ forming the subject of the present paper is 7.5×10^{-8} Ω^{-1} m^{-1} as determined for a mean applied field of 1×10^4 V m^{-1}. From measurements of the conductivity (σ) as a function of absolute temperature (T), the activation energy (ΔE) in the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ was determined from the gradient of the least-squares-fitted line to a plot of ln σ against T^{-1}. For rising temperature over the range 300–351 K, the result for ΔE is 1.00 ± 0.15 eV. During cooling back to 300 K, the corresponding result for ΔE is 1.37 ± 0.07 eV. The poor agreement between these values of ΔE is explained by reference to the TG/DTA data which show that the maximum temperature attained during the electrical measurements is a few degrees higher than that for the onset of decomposition; the value for ΔE obtained for the heating phase is therefore considered more reliable than that for cooling.

From the present work on $Co(C_7H_7N)_4Br_2$, the earlier work already referred to [2,3] on related complexes and other earlier work [5] on monomer and polymer complexes of zinc chloride with 4-vinylpyridine, it is found that there is correlation between the pre-exponential factor (σ_0) and the activation energy (ΔE) in the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$. This correlation is in the form of a linear relationship between ln σ_0 and ΔE, i.e. $\ln \sigma_0 = \alpha\Delta E + \beta$, where α and β are constants [6]. The observed correlation is predicted by a model [7,8] in which conduction is by electron-tunnelling through successive barriers along a molecular pathway in bulk material, although an alternative model [9] that would also explain the correlation is based on tunnelling at the interface between an injecting electrode and the organic semiconductor.

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