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# STRUCTURAL, THERMAL AND ELECTRICAL STUDIES OF PYRAZINE-BRIDGED 5,10,15,20-TETRAKIS-(4-METHOXYPHENYL)-21H,23H-PORPHINE COBALT(II)

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## ABSTRACT

The preparation and some properties of the compound produced by the reaction of pyrazines with 5,10,15,20-tetrakis(4-methoxyphenyl)-21H,23H-porphine cobalt(II) are reported. Spectral and magnetic studies show that the compound has an octahedral structure involving pyrazine bridges between successive cobalt porphyrin layers. Thermogravimetric and differential analysis data are reported for the compound.

The electrical conductivity and its temperature dependence are compared with earlier results for the same cobalt porphyrin group in a structure without bridging. The electrical properties are similar in both respects, leading us to postulate that most carrier transfer takes place within the cobalt porphyrin layers rather than through the bridges between these layers.

## INTRODUCTION

Because of the chemical versatility of the metalloporphyrins, the preparation of a large selection of electrically conductive materials is possible. The metalloporphyrins can form a stacking system with intermediate bridging ligands [1-4] and it appears probable that these bridges would provide a conduction pathway. This paper reports on the compound formed between 5,10,15,20-tetrakis(4-methoxyphenyl)-21H,23H-porphine cobalt(II) and pyrazine. Spectral and magnetic studies of the complex were used to interpret the type of coordination to the metal ion. The results of thermal analyses and electrical studies on the complex are also reported.

## EXPERIMENTAL

### *Preparation of the complex*

A mixture of 0.2 g ($5.0 \times 10^{-4}$ mol) of 5,10,15,20-tetrakis(4-methoxyphenyl)-21H,23H-porphine cobalt(II) and 2.0 g ($2.5 \times 10^{-2}$ mol) of pyrazine were thoroughly ground together. The mixture was then fused in a sealed vessel for 24 hours at a temperature of 70 ° C. The excess unreacted pyrazine was then removed by sublimation under vacuum whilst the mixture was heated. After sublimation small purple needle-like crystals remained.

### *Measurements*

The metal ion concentration was determined by atomic absorption spectrophotometry (Perkin–Elmer 373 spectrophotometer) and the carbon, hydrogen and nitrogen contents were analysed using a Carlo Erba elemental analyser. The electronic spectrum was measured on a Beckmann Acta MIV spectrophotometer as solid diffuse reflectance spectra. Magnetic moments were measured by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant.

Infrared absorption spectra were recorded using KBr discs over the 4000–400 $cm^{-1}$ wavenumber range on a Pye Unicam SP3-300 spectrophotometer.

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 $min^{-1}$. The 20–600 ° C temperature range was studied.

The current–voltage characteristics at room temperature and the temperature dependence of the electrical conductivity for the complex were obtained by compressing the prepared powder into a disc of diameter 13 mm and thickness 0.86 mm; a conductive silver paint electrode of diameter 4.9 mm was applied to each of its flat faces. Details of the disc preparation and the method of obtaining the electrical data have been previously described [5].

## RESULTS AND DISCUSSION

The compound prepared has the stoichiometry CoPorPyz where CoPor and Pyz represent 5,10,15,20-tetrakis(4-methoxyphenyl)-21H,23H-porphine cobalt(III) and pyrazine respectively. Table 1 shows that the analytical

TABLE 1

Elemental analyses of the complex

| | Calculated (wt.%) | Found (wt.%) |
|---|---|---|
| Co | 6.76 | 6.42 |
| C | 71.57 | 70.71 |
| N | 9.63 | 9.56 |
| H | 4.59 | 4.59 |

results for the compound are in good agreement with the given formula. Additional evidence supporting the suggested formula is presented later. The compound is diamagnetic, showing that cobalt is present as $Co^{3+}$ as opposed to $Co^{2+}$ as compounds of the latter would exhibit strong paramagnetism. The reflectance spectrum of the complex has bands centred at 17 857 and 20 920 $cm^{-1}$ and resembles that normally found for the $Co^{3+}$ ion in an octahedral environment [6].

Pavlović et al. [7] showed that cobalt(II) porphyrins are oxidised to cobalt(III) by oxygen in the presence of nitrogen ligands. We suggest that a similar mechanism occurred in our reaction system.

Table 2 lists the relative absorbance values of the strong IR absorption bands, normalised to the same CoPor content, for both CoPor and CoPorPyz. For a given wavenumber, the difference between these normalised relative absorbance values is evidently due to the absorption of the Pyz molecules. Collman et al. [2] have shown that absorption in the 1570 $cm^{-1}$ region (corresponding to a pyrazine vibration) is strongly influenced by whether the pyrazine molecule acts as a terminal ligand or forms a bridge between the metalloporphyrin molecules. In the former case there is a strong contribution to the absorption at 1570 $cm^{-1}$ whilst in the latter case the absorption is small or negligible. In this study, only a 1% increase in the absorbance at 1570 $cm^{-1}$ due to the presence of Pyz was found (see Table 2), which suggests that these are bridging pyrazines. In contrast, in the compound CoPorPzca′Pzca″ (where CoPor is as already defined and Pzca′ and Pzca″ represent pyrazine-2-carboxylic acid and pyrazine-2-carboxylate, respectively), we observed a 61% increase in the absorbance at 1570 $cm^{-1}$ due to the presence of Pzca′ and Pzca″, which led to the conclusion that they are

TABLE 2

IR absorption spectra

| CoPor | | CoPorPyz | | % Increase in Absorbance due to Pyz |
|---|---|---|---|---|
| Band wavenumber [a] ($cm^{-1}$) | Absorbance [b] | Band wavenumber [a] ($cm^{-1}$) | Absorbance [b] | |
| 3947 | 0.52 | 3955 | 0.52 | 0 |
| 2927 | 0.45 | 2932 | 0.45 | 0 |
| 2830 | 0.42 | 2832 | 0.43 | 1 |
| 1603 | 0.39 | 1602 | 0.38 | −5 |
| 1570 | 0.22 | 1571 | 0.23 | 1 [c] |
| 1501 | 0.50 | 1501 | 0.51 | 3 |
| 1001 | 0.53 | 994 | 0.65 | 22 |

[a] Bands common to both spectra.

[b] Absorbance normalised to the same porphyrin content in CoPor and CoPorPyz samples.

[c] For comparison, the value for a pyrazine ring acting as a terminal ligand on CoPor molecules is 61% [8].

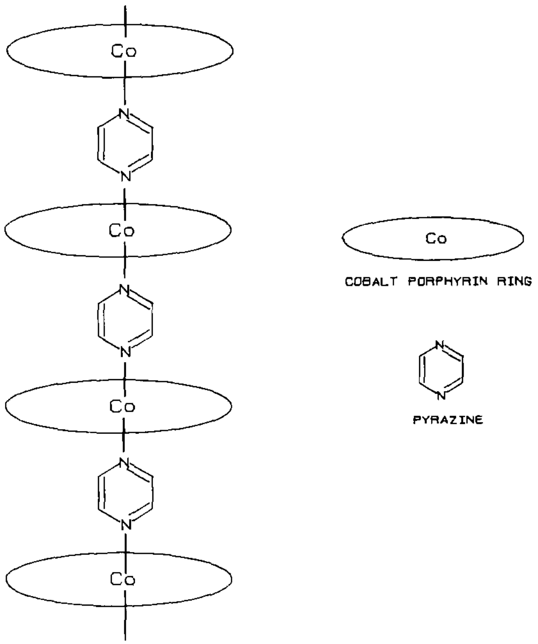

Fig. 1. Proposed structure (not to scale) for CoPorPyz in which CoPor layers are stacked parallel to each other and bridged by intermediate pyrazine rings.

terminal ligands [8]. The proposed structure for the complex CoPorPyz is shown in Fig. 1.

The TG–DTA trace for the CoPorPyz complex is shown in Fig. 2 and the thermal decomposition data are summarised in Table 3. During heating the

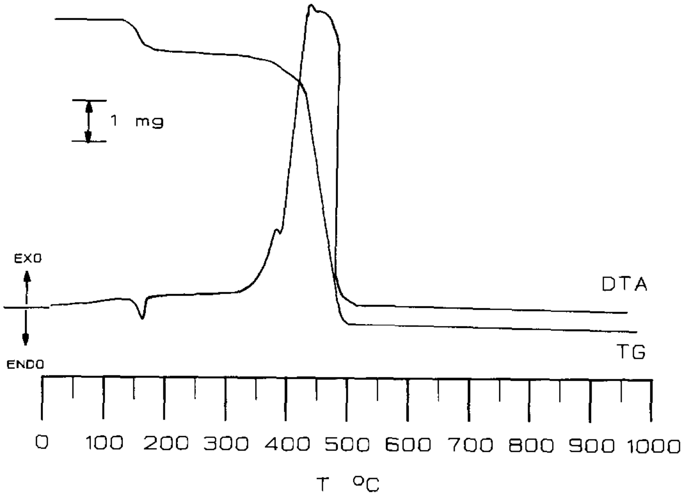

Fig. 2. Thermogravimetric (TG) and differential thermal analysis (DTA) curves for the CoPorPyz complex.

TABLE 3

Thermal decomposition products

| Starting material | Decomposition temperature (°C) | Product | Weight loss (% of initial weight) | |
|---|---|---|---|---|
| | | | Calc. | Found |
| CoPorPyz | 180 (Endo) | CoPor | 9.19 | 9.18 |
| | 430 (Exo) | $Co_3O_4$ | 81.61 | 81.26 |

Endo : endothermic; Exo : exothermic

complex initially undergoes an endothermic loss of the pyrazine molecules. At higher temperatures, the remaining cobalt porphyrin decomposes exothermically leaving a residue of $Co_3O_4$.

The room-temperature current ($I$)–voltage ($V$) characteristic for the disc of the complex, shown in Fig. 3, is linear except for a slight curvature in the range 0–3 $V$. The ordinate for each plotted point is the mean current magnitude from the following four measurements: increasing voltage, decreasing voltage in the same polarity, increasing voltage for reversed polarity and decreasing voltage in this reversed polarity. The reversed polarity data closely replicate those in the original polarity and there is no evidence of hysteresis. From the linear region of the graph (Fig. 3) and the known disc thickness and electrode diameter, an electrical conductivity at room temperature of $1.0 \times 10^{-7}$ $\Omega^{-1}$ $m^{-1}$ can be deduced. It had been anticipated that the presence of Pyz bridging molecules between successive CoPor molecules would greatly enhance the conductivity by providing a conducting pathway through the stacked structure. However, this expectation was not supported

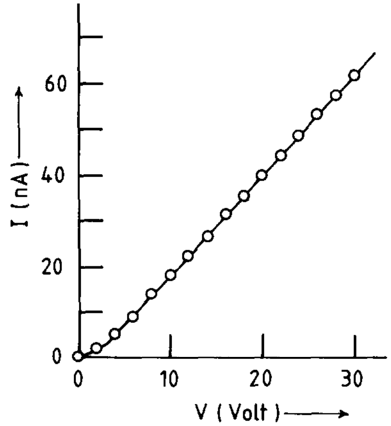

Fig. 3. Current ($I$) as a function of voltage ($V$) for a disc of CoPorPyz at room temperature (19 °C). The disc thickness is 0.86 mm, its diameter is 13 mm and the electrode on each face of the disc has a diameter of 4.9 mm.

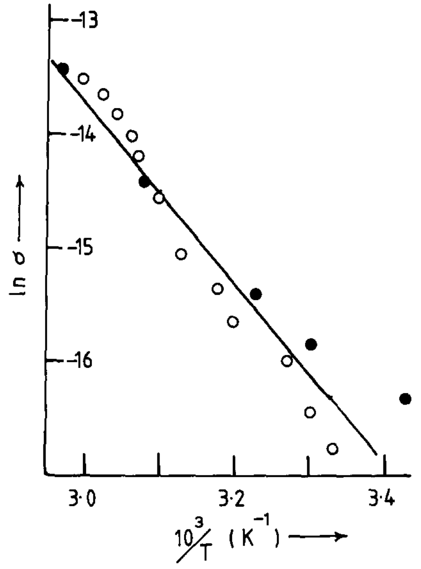

Fig. 4. Arrhenius plot (in the form of ln $\sigma$ versus $10^3/T$ where $\sigma$ is the conductivity ($\Omega^{-1}m^{-1}$) and $T$ is the absolute temperature) for the same disc of CoPorPyz as was used to obtain Fig. 3: points obtained during heating, ●; points obtained during cooling, ○.

by the measurements: the conductivity quoted above is indistinguishable (when allowance is made for an estimated error of ±10%) from the result of $1.2 \times 10^{-7}\ \Omega^{-1}\ m^{-1}$ which we found [8] at room temperature for CoPorPzca′Pzca″ using an identical measuring technique. The simplest explanation for these conductivity results is that in both CoPorPzca′Pzca″ and CoPorPyz, almost all carrier transfer takes place in the near-planar CoPor layers; thus, in view of the postulated negligible conduction perpendicular to these layers, the presence or absence of the bridges would not affect the conductivity of the aggregated powders. The room temperature $I$–$V$ characteristic obtained for CoPorPzca′Pzca″ [8] are similar to those in Fig. 3, showing curvature in the 0–3 V range and no hysteresis. This provides further, though admittedly weak, support for the suggestion that conduction is confined mainly to within the CoPor layers. To check this hypothesis, large single crystals of both CoPorPyz and CoPorPzca′Pzca″ could be used to measure the conductivities parallel and perpendicular to the CoPor layers: however, we did not succeed in growing large enough crystals.

Figure 4 shows the temperature dependence of the electrical conductivity ($\sigma$) of the CoPorPyz disc in the form of an Arrhenius plot. From the gradient of the least-squares fitted line through all the points in this plot (those obtained during heating and cooling) the activation energy ($\Delta E$) in the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ is deduced to be $1.36 \pm 0.10$ eV. According to the above hypothesis that conduction in both the pyrazine-bridged compound CoPorPyz and the non-bridged compound CoPorPzca′Pzca″ is limited to the CoPor layers, it would be expected that the $\Delta E$ value for both compounds is the same. This expectation is nearly upheld, as can be seen by comparing the above quoted $\Delta E$ for CoPorPyz with the result of $\Delta E = 1.22 \pm 0.04$ eV found for CoPorPzca′Pzca″ [8]. Reference to Fig. 4 shows there is no evidence for flattening of the plot at the lower end of the temperature range, indicating that if the band model is appropriate then conduction is due to electron activation from the valence to conduction bands (rather than activation from donor or acceptor impurities) [9]; the same conclusion was also reached for CoPorPzca′Pzca″ [8], thereby allowing meaningful comparison of $\Delta E$ values. If the band model is not valid, then the linearity of the Arrenhius plots suggests that conduction may take place by hopping of carriers [10,11], but again, if the same mechanism is appropriate for both compounds, the $\Delta E$ values are expected to agree. Inspection of Fig. 4 shows that if a smooth curve is imagined to be drawn through first the points of the heating phase and then the points of the cooling phase (as opposed to simply drawing in the best straight line through all points), the curve generated is of the same shape as that found for CoPorPzca′Pzca″ [8]. This is consistent with the suggestion that the provision of pyrazine bridges between layers of CoPor in CoPorPyz does not affect its conductivity, although the deviation between heating and cooling data for CoPorPzca′Pzca″ is less than for CoPorPyz.

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