

## **STRUCTURAL, THERMAL AND ELECTRICAL STUDIES OF PYRAZINE-2-CARBOXYLIC ACID 5,10,15,20-TETRAKIS- (4-METHOXYPHENYL)-21H,23H-PORPHINE COBALT(III)**

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### **ABSTRACT**

The preparation and some properties of the compound produced by the reaction of pyrazine-2-carboxylic acid 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. Thermogravimetric and differential thermal analysis data are reported for the compound. Electrical measurements show that the compound has very nearly ohmic behaviour, and the conductivity ( $\sigma$ ) varies with temperature ( $T$ ) in accord with the equation  $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ .

### **INTRODUCTION**

The coordination chemistry of the metalloporphyrins is of growing interest because of the unique nature of the coordination of the porphyrin ligand and the metal ion. The porphyrin ligand can act as a bi-, tri-, tetra-, and hexadentate ligand, while the metal ion can be found in a 4-, 5-, 6- or 8-coordinate environment [1–3]. The biological significance of porphyrin compounds such as haemoglobin, vitamin B<sub>12</sub> and cytochrome and the development of new semiconducting metalloporphyrins are important areas of current research [4–7].

This paper reports the compound formed between 5,10,15,20-tetrakis(4-methoxyphenyl)-21H,23H-porphine cobalt(II) and pyrazine-2-carboxylic acid. Spectral and magnetic studies have been used to interpret the type of coordination to the metal ion. The thermal decomposition and electrical conductivity have been studied.

## EXPERIMENTAL

*Preparation of the complex*

An amount of 1.25 mmol (1.0 g) of 5,10,15,20-tetrakis(4-methoxyphenyl)-21*H*,23*H*-porphine cobalt(II) was dissolved in 70 ml of pyridine, and 2.5 mmol (0.31 g) of pyrazine-2-carboxylic acid was added to the pyridine solution. The solution was constantly stirred and left to react for 3 days. The pyridine solution was then poured into 300 ml of water, whereupon an opaque brown solution was formed. The water-pyridine mixture was left until all the pyridine had naturally evaporated (several days). At this point the solution was clear and pale green-yellow in colour and fine purple crystals were present.

The crystals were isolated by filtering. After washing with water the crystals were dried over silica gel.

*Measurements*

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

IR absorption spectra were recorded using KBr discs over the wavenumber range 4000–400  $\text{cm}^{-1}$  on a Pye Unicam, SP3-300 spectrophotometer. Thermal analysis measurements were made on a Stanton Redcroft model STA 781 thermobalance. The thermogravimetry (TG) and differential thermal analysis (DTA) traces were obtained at a heating rate of 6  $^{\circ}\text{C min}^{-1}$ . The 20–600  $^{\circ}\text{C}$  temperature range was studied.

The electrical conductivity of the compound at room temperature (15  $^{\circ}\text{C}$ ) and the temperature dependence of the electrical conductivity were investigated. The experimental method for these determinations has been previously described [8] and uses the material in the form of a disc of compressed powder. Electrodes formed from conductive silver paint were applied to the flat faces of the disc. The dimensions used are as follows: disc diameter 13 mm, disc thickness 0.89 mm, and electrode diameter 4.9 mm.

## RESULTS AND DISCUSSION

As may be seen from Table 1, the experimental results for the elemental analyses of the complex agree with the formula  $\text{CoPor}(\text{Pzca}')(\text{Pzca}'')$  where CoPor, Pzca' and Pzca'' respectively represent 5,10,15,20-tetrakis(4-meth-

TABLE 1

Elemental analyses of the complex

	Calculated (wt.%)	Found (wt.%)
Co	5.67	5.32
C	66.92	66.57
N	10.77	10.46
H	4.23	4.10

oxyphenyl)-21*H*,23*H*-porphine cobalt(III), pyrazine-2-carboxylic acid and pyrazine-2-carboxylate. Additional evidence for the suggested formula is presented later. The complex is diamagnetic, showing that cobalt is present as  $\text{Co}^{3+}$  as opposed to  $\text{Co}^{2+}$ ; the latter would lead to a strong paramagnetic moment. The reflectance spectrum for the complex exhibits bands centred at 16086, 18018 and 24390  $\text{cm}^{-1}$  and resembles that normally found [9] for the  $\text{Co}^{3+}$  ion in an octahedral environment. From X-ray evidence, which is to be reported more fully [10], the structure of the complex is as shown in Fig. 1, and partial refinement of this structure yields bond lengths within the CoPor molecule that are similar to those for corresponding bonds in other

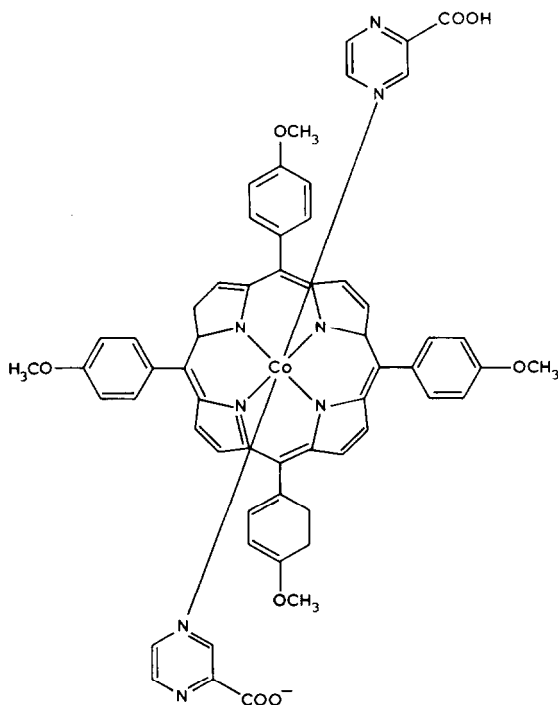
Fig. 1. Proposed structure (not to scale) for  $\text{CoPor}(\text{Pzca}')(\text{Pzca}'')$ .

TABLE 2

Infrared absorption spectra

CoPor		CoPor(Pzca')(Pzca'')		Increase in absorbance due to Pzca' and Pzca'' (%)
Band wave-number <sup>a</sup> (cm <sup>-1</sup> )	Absorbance <sup>b</sup>	Band wave-number <sup>a</sup> (cm <sup>-1</sup> )	Absorbance <sup>b</sup>	
3947	0.52	3945	0.52	0
2927	0.45	2935	0.47	6
2830	0.42	2835	0.45	6
1603	0.39	1604	0.59	51
1570	0.22	1571	0.36	61 <sup>c</sup>
1501	0.50	1502	0.60	20
1001	0.53	1004	0.59	11

<sup>a</sup> Bands common to both spectra.<sup>b</sup> Normalised absorbance to same porphyrin content in CoPor and CoPor(Pzca')(Pzca'') samples.<sup>c</sup> For comparison, the value for a pyrazine ring acting as a bridging ligand between the CoPor molecules is 1% (ref. 13).

cobalt porphyrins. The Pzca' and Pzca'' molecules are at opposite ends of an axis that passes perpendicularly through the approximate plane formed by the CoPor molecule. The bond lengths from the cobalt atom to the nearest nitrogen atom of the Pzca' and Pzca'' molecules are  $1.966 \pm 0.009$  Å and  $1.990 \pm 0.008$  Å [10], although doubt remains concerning which length to identify with each bond. As may be seen from the quoted uncertainties in these bond lengths, there appears to be a just-significant difference between them which is consistent with the small difference between Pzca' and Pzca''. The mean of the Co–N bond lengths is similar to that reported [11–15] for the compound [(Pip)<sub>2</sub>Co(TPP)]NO<sub>3</sub>, where Pip and TPP respectively represent the piperidine and tetraphenylporphyrin molecules. Because in [(Pip)<sub>2</sub>Co(TPP)]NO<sub>3</sub> the cobalt atom is in a +3 oxidation state [11–13], some additional support is obtained for the suggestion that cobalt has this same oxidation state in CoPor(Pzca') and CoPor(Pzca'').

Relative absorbance values corresponding to strong absorption bands in the IR and normalised to the same CoPor content are listed in Table 2 for both CoPor itself and CoPor(Pzca')(Pzca''). For a given wavenumber, the difference between these normalised relative absorbance values is evidently due to the combined absorption of the Pzca' and Pzca'' molecules. Collman et al. [14] showed that absorption in the region of 1570 cm<sup>-1</sup> (corresponding to a pyrazine vibration) is strongly influenced by whether the pyrazine molecule acts as a terminal ligand or forms a bridge between metalloporphyrin molecules. In the latter case the pyrazine molecules contribute, at 1570 cm<sup>-1</sup>, only 1% of the total absorbance of the complex [14]. In contrast we find (see Table 2) a 61% increase of absorbance at 1570 cm<sup>-1</sup> due to the

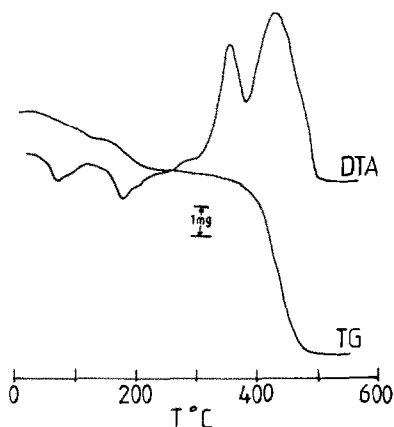


Fig. 2. TG/DTA curves for  $\text{CoPor}(\text{Pzca}')(\text{Pzca}'')$ . The initial sample mass was 8.79 mg.

presence of  $\text{Pzca}'$  and  $\text{Pzca}''$ , leading us to assert that these are terminal ligands.

A band at  $1720\text{ cm}^{-1}$  attributed to the  $\nu(\text{COO})$  vibration is observed in pyrazine-2-carboxylic acid but not in the complex  $\text{CoPor}(\text{Pzca}')(\text{Pzca}'')$ . However, broad bands occur in the ranges  $1680\text{--}1640\text{ cm}^{-1}$  and  $3310\text{--}3120\text{ cm}^{-1}$ , which we suggest are due to  $\nu(\text{COO}^-)$  and  $\nu(\text{COOH})$  vibrations respectively.

The TG/DTA trace for the complex is shown in Fig. 2 and the thermal decomposition data are summarised in Table 3. In a pair of successive endothermic reactions, first one and then the other axial ligand are lost, although the order of the loss of  $\text{Pzca}'$  and  $\text{Pzca}''$  was not identified. At higher temperature, the remaining cobalt porphyrin undergoes exothermic decomposition, leaving a residue of  $\text{Co}_3\text{O}_4$ .

TABLE 3

Thermal decomposition products

Starting material	Decomposition temperature ( $^{\circ}\text{C}$ )	Product	Weight loss (% of initial weight)	
			Calc.	Found
$\text{CoPor}(\text{Pzca}')(\text{Pzca}'')$	49 (ENDO)	$\text{CoPor}(\text{Pzca}')$ or $\text{CoPor}(\text{Pzca}'')$	11.9	11.4
	138 (ENDO)	$\text{CoPor}(\text{Pzca}'')$ or $\text{CoPor}(\text{Pzca}')$	11.9	11.6
	264 (EXO)	$\text{Co}_3\text{O}_4$	70.5	69.5

$\text{CoPor}$ , 5,10,15,20-tetrakis(4-methoxyphenyl)-21*H*,23*H*-porphine cobalt(III);  $\text{Pzca}'$ , pyrazine-2-carboxylic acid;  $\text{Pzca}''$ , pyrazine-2-carboxylate.

ENDO, endothermic, EXO, exothermic.

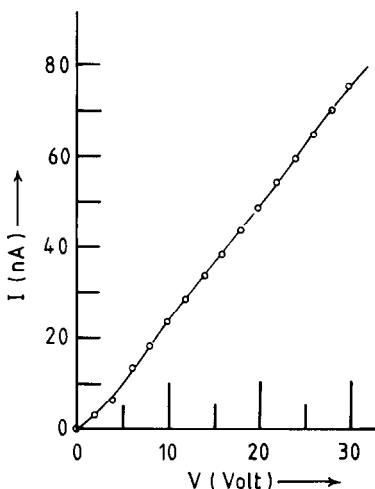


Fig. 3. Current ( $I$ ) against voltage ( $V$ ) plot for a disc of  $\text{CoPor}(\text{Pzca}')(\text{Pzca}'')$  at room temperature.

The room temperature current versus voltage characteristic for a disc of the  $\text{CoPor}(\text{Pzca}')(\text{Pzca}'')$  compound having conductive silver paint electrodes is shown in Fig. 3. Each experimental point in the figure represents the mean of the current magnitude obtained at a given voltage for conditions of increasing and decreasing voltage in both polarities. Any asymmetry in the characteristic due to reversing the polarity is less than 3%, and this suggests that the electrodes are not significantly blocking to either electrons or holes. No evidence is found for any hysteresis in the characteristic, although this effect has been observed [15,16] in similar measurements made for certain other metallo-organic compounds. The slight curvature in the current–voltage graph in the vicinity of the origin (see Fig. 3) may be a consequence of space charge limitation of current [17]. The gradient of the linear part of the graph leads to a room temperature conductivity of  $1.2 \times 10^{-7} \Omega^{-1} \text{ m}^{-1}$ . As previously noted,  $\text{CoPor}(\text{Pzca}')(\text{Pzca}'')$  has pyrazine-2-carboxylic acid and pyrazine-2-carboxylate as terminal ligands, and it is predicted that in a structure consisting of successive cobalt porphyrin molecules bridged by pyrazine rings the conductivity would be much larger because of the existence of a longer intramolecular conducting pathway. This prediction is under investigation in the authors' laboratories.

An Arrhenius plot, in the form of a graph of  $\ln \sigma$  against  $10^3/T$  (where  $\sigma$  = conductivity and  $T$  = absolute temperature) is shown in Fig. 4 for the same disc of  $\text{CoPor}(\text{Pzca}')(\text{Pzca}'')$  as used to obtain Fig. 3. The data for the Arrhenius plot were obtained with application of 10 V across the disc, and this is within the ohmic region of the  $I$ – $V$  characteristic. Although the highest temperature reached in obtaining the data for the Arrhenius plot exceeds that for onset of decomposition as found from TG/DTA, neverthe-

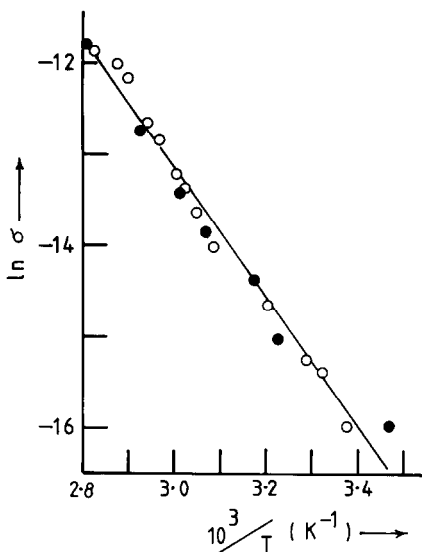


Fig. 4. Plot of  $\ln \sigma$  against  $10^3/T$  for a disc of CoPor(Pzca')(Pzca'') ( $\sigma$  = electrical conductivity, expressed in units of  $\Omega^{-1} \text{ m}^{-1}$  and  $T$  = absolute temperature). Points for rising temperature ( $\bullet$ ); points for falling temperature ( $\circ$ ). The line is fitted by least-squares linear regression.

less the heating and cooling data fit to the same line. From the gradient of this line, the activation energy  $\Delta E$  in the equation  $\sigma = \sigma_0 \exp(-\Delta E/2kT)$  is  $1.22 \pm 0.04$  eV. A possible interpretation for  $\Delta E$  is that it is the energy gap between valence and conduction bands [18], in which case, because of the linearity of the plot throughout the investigated temperature range, the measured room temperature conductivity is that due to intrinsic activation rather than to activation involving donors or acceptors. However, an equation of the form  $\sigma = \sigma_0 \exp(-\Delta E/2kT)$  is derivable [19,20] for hopping conduction, as well as for the band model, and in these circumstances  $\Delta E/2$  represents an activation energy for hopping.

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