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THERMAL AND ELECTRICAL STUDIES ON PORPHYRIN COMPOUNDS OF COBALT(II), COPPER(II) AND ZINC(II)

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ABSTRACT

Thermogravimetric and differential thermal analysis data are reported for 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine metal(II) complexes where the metal is cobalt, copper and zinc. Similar data are also reported for 5,10,15,20-tetrakis(4-methoxyphenyl)-21*H*,23*H*-porphine cobalt(II).

For the above compounds the electrical conductivities have been measured. There is evidence for space–charge limited conduction, and conductivities at room temperature under an applied field of 1×10^4 V m^{-1} are all within a factor of two either side of 2×10^{-8} Ω^{-1} m^{-1}. Activation energies for forming free carriers have been measured from the temperature dependence of the electrical conductivities.

INTRODUCTION

Metalloporphyrins are compounds widely occurring in nature and include chlorophyll and haem of the blood. At present the natural metalloporphyrins and their synthetic analogues have many industrial uses. The development of new semiconducting metalloporphyrins and especially the complexes of phthalocyanine is an important area of research [1–9]. This paper reports thermal analysis studies and electrical measurements for the metalloporphyrins given below.

The metalloporphyrins in which the ligand is the same enable us to study how conductivity varies with the spin state of the central metal ion—cobalt

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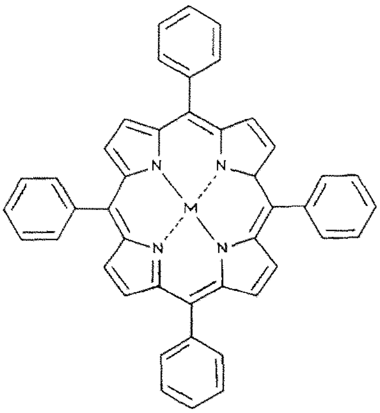
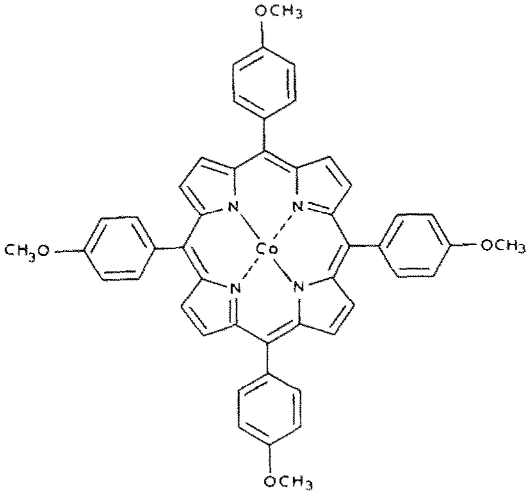


5,10,15,20-Tetraphenyl-21*H*, 23*H*-porphine metal(II)
(metal = cobalt, copper, zinc)



5,10,15,20-Tetrakis(4-methoxyphenyl)-21*H*, 23*H*-porphine cobalt(II)

(d^7), copper (d^9), zinc (d^{10}). The metalloporphyrins 5,10,15,20-tetrakis(4-methoxyphenyl)-21*H*,23*H*-porphine cobalt(II) and 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine cobalt(II) enable us to study the effect on the conductivity of attaching a different ligand to the same metal.

EXPERIMENTAL

The metalloporphyrins were obtained from the Aldrich Chemical Company.

The purity of the compounds was checked using the carbon, hydrogen and nitrogen analyses obtained from a Carlo Erba elemental analyser, with the following results.

5,10,15,20-tetraphenyl-21*H*,23*H*-porphine cobalt(II). Calc: %C 78.68, %H 4.20, %N 8.34. Found: %C 78.42, %H 3.91, %N 8.12.

5,10,15,20-tetraphenyl-21*H*,23*H*-porphine copper(II). Calc: %C 78.14, %H 4.17, %N 8.28. Found: %C 77.92, %H 3.66, %N 7.74.

5,10,15,20-tetraphenyl-21*H*,23*H*-porphine zinc(II). Calc: %C 77.93, %H 4.16, %N 8.26. Found: %C 77.14, %H 3.82, %N 7.51.

5,10,15,20-tetrakis(4-methoxyphenyl)-21*H*,23*H*-porphine cobalt(II). Calc: %C 72.81, %H 4.58, %N 7.07. Found: %C 72.66, %H 4.42, %N 6.82.

The thermal analysis measurements were performed using a Stanton–Redcroft model STA 781 thermobalance. Thermogravimetry (TG) and differential thermal analysis (DTA) curves were obtained at a heating rate of 6 °C min^{-1} in static air. In all cases the 20–1000 °C temperature range was studied.

The electrical conductivity at room temperature and the temperature dependence of the conductivity was measured for each compound. These measurements were made using discs of the compounds prepared by compressing powder under an applied force of 100 kN. The discs have a diameter of 13 mm and thicknesses in the range 0.64 mm to 1.42 mm. Conducting silver paint electrodes of diameter 4.9 mm were applied concentrically onto the flat faces of the discs. With a disc mounted on a copper heat sink which made contact with the lower electrode and a spring loaded wire in contact with the upper electrode, the d.c. characteristics of current (I) as a function of voltage (V) were obtained.

Measurements of I and V employed respectively a Keithley 610C electrometer and a digital voltmeter, the latter instrument connected so that the current which it drew did not pass through the electrometer. The voltage was increased in increments of 2 V from zero to 30 V, reduced to zero again in 2 V steps and then the experiment repeated with reversed polarity. For each applied voltage the current was measured, thus is follows that for any given voltage magnitude four readings of the current were obtained. These agreed to within 4% for any given disc indicating that the contacts were non-blocking to either sign of carrier. The disc thicknesses were all measured using a micrometer.

The temperature dependence of the conductivity was measured as follows: a previously calibrated copper-constantan thermocouple (formed from SWG 44 wires) was mounted on the upper face of each disc in turn. With the disc in an electrically heated oven and with a constant voltage of 10 V applied, the disc current was monitored as the temperature was raised from room temperature to approximately 350 K. During each measurement of disc current the oven heater current was momentarily switched off to avoid electrical pick-up problems. Further measurements were taken during cooling back to room temperature and these accurately reproduced the data during heating. This is expected since the TG measurements show that none of the compounds begins to decompose until much higher temperatures are reached than are used in the electrical work. The discs used for the elevated temperature electrical measurements were the same as those previously used for the room temperature measurements.

RESULTS AND DISCUSSION

The TG curves for the porphyrin compounds of cobalt, copper and zinc are shown in Fig. 1. The compounds undergo decomposition with loss of organic ligand and the formation of the metal oxide. The residue weights (Table 1) are in good agreement with the values required for the metallic oxides. The order of stability, based on the initial decomposition temperatures of the porphyrin compounds, can be listed as: Zn(TPP) > Cu(TPP) > Co(mTPP) > Co(TPP) where TPP is 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine and mTPP is 5,10,15,20-tetrakis(4-methoxyphenyl)-21*H*,23*H*-

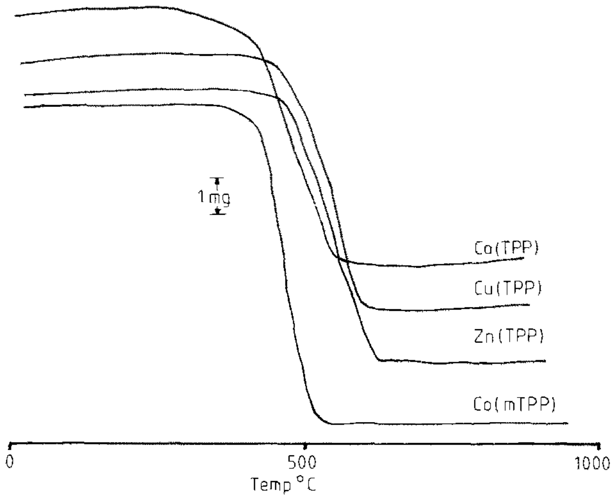


Fig. 1. Co(TPP): TG curve for 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine cobalt(II). Sample weight = 8.50 mg; Cu(TPP): TG curve for 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine copper(II). Sample weight = 8.38 mg; Zn(TTP): TG curve for 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine zinc(II). Sample weight = 9.20 mg; Co(mTPP): TG curve for 5,10,15,20-tetrakis(4-methoxyphenyl)-21*H*,23*H* cobalt(II). Sample weight = 10.50 mg.

TABLE 1

Decomposition processes of the porphyrin metal complexes

Processes	Temperature range (° C)	Thermal nature of transformation [a]	Residue weights (%)	
			Calc.	Found
Co(TPP) → Co_3O_4	280–530	EXO	11.94	11.76
Cu(TPP) → CuO	370–590	EXO	11.76	11.69
Zn(TPP) → ZnO	398–615	EXO	11.99	10.86
Co(mTPP) → Co_3O_4	340–525	EXO	10.13	11.42

[a] EXO = exothermic (obtained from DTA trace).

porphine. It is thus observed that, amongst the TPP complexes studied, the thermal stability becomes greater as the atomic number of the metal atom increases.

As explained in the experimental section, the current for any given applied voltage magnitude was measured four times for the room temperature characteristics. The mean of these four readings was plotted against applied voltage magnitude and, for all of the compounds, yielded curves which bent gently upwards showing non-ohmic behaviour. For Cu(TPP) the non-linearity was only barely detectable. The I versus V data were re-plotted using log–log axes and in all cases linear plots were obtained showing that $I \propto V^m$, where m is a constant characteristic of each compound. Examples of these plots for Co(mTPP) and Zn(TPP) are shown in Fig. 2. Accurate values of m were obtained by least-squares fitting of a linear relationship between $\log_{10} I$ and $\log_{10} V$; the corresponding results for m are listed in Table 2 and all lie in the range $1.06 < m < 1.21$. The symmetry of the I

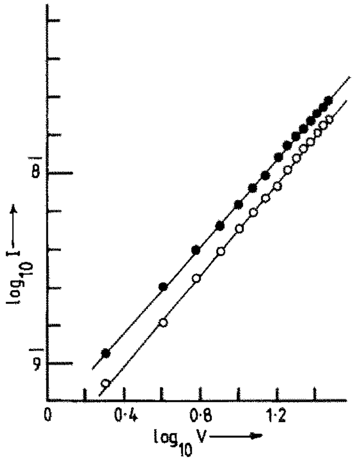


Fig. 2. Plots of $\log_{10} I$ versus $\log_{10} V$ at room temperature. ●, Co(mTPP); ○, Zn(TPP). I and V are in units of amp and volt respectively.

TABLE 2

Electrical properties of the porphyrin metal complexes

Complex	Electrical conductivity at a field of 1×10^4 V m^{-1} and room temperature (Ω^{-1} m^{-1})	ΔE [a] (eV)	m [b]
Co(TPP)	2.1×10^{-8} (23 °C)	1.37 ± 0.10	1.177 ± 0.013
Cu(TPP)	1.0×10^{-8} (18 °C)	1.78 ± 0.10	1.064 ± 0.010
Zn(TPP)	3.9×10^{-8} (20 °C)	1.71 ± 0.16	1.203 ± 0.010
Co(mTPP)	3.8×10^{-8} (17 °C)	1.43 ± 0.10	1.129 ± 0.007

[a] ΔE is the activation energy appearing in the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ where σ is the conductivity at absolute temperature T, k is Boltzmann's constant and σ_0 is a constant for a given material. The determinations are based on the gradients of the near-linear regions in the plots of Fig. 3 at high temperature.

[b] m is the exponent in the expression $I \propto V^m$ for room temperature data and determined from least-squares fitting of a linear relationship to $\log_{10}I$ versus $\log_{10}V$.

versus V characteristics on reversal of applied voltage, coupled with a value significantly greater than unity for the exponent m, is strong evidence for space–charge limited current (SCLC). Tredgold [10] has proposed a semi-empirical equation of the form $I = AV + BV^2$ (where A and B are constants for a given device) and such an equation has been given a theoretical basis [11,12] as an alternative to $I \propto V^m$. If the equation $I = AV + BV^2$ is a valid representation of the data, a plot of I/V against V would be linear. However, as exemplified in Fig. 3 for Co(mTPP) and Zn(TPP) using the same measurements as for Fig. 2, the plots are not straight so we conclude that the expression $I \propto V^m$ is a much superior description. The same

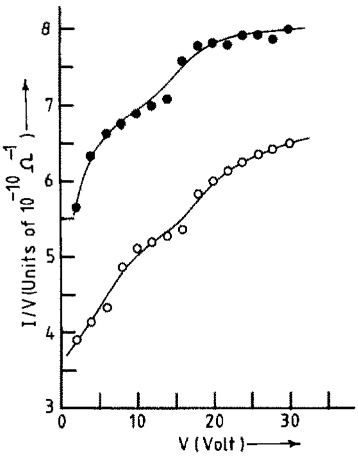


Fig. 3. Plots of I/V versus V at room temperature. ●, Co(mTPP); ○, Zn(TPP). The experimental data used is the same as that for Fig. 1.

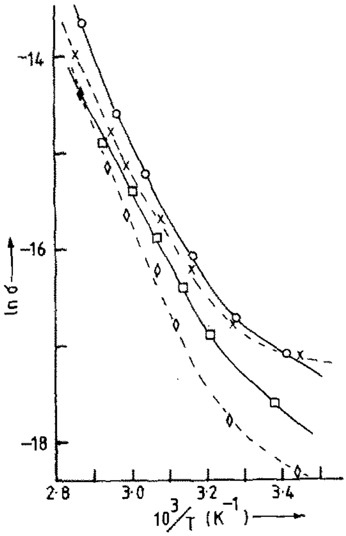


Fig. 4. Plots of $\ln \sigma$ versus $10^3/T$, where σ is the conductivity (in units of Ω^{-1} m^{-1}) as determined with 10 V applied and T is the absolute temperature. ○———○, Zn(TPP); ×----×, Co(mTPP); □———□, Co(TPP); ◇----◇, Cu(TPP); ◆, common to Co(TPP) and Cu(TPP).

conclusion is true for the other compounds studied and we have recently reported [13] similar results for another group of organometallic compounds that also yielded m values in the same range. Although an explanation is available [14] for $I \propto V^m$ with $m \geqslant 2$, involving SCLC associated with an exponential trap distribution, no corresponding theory appears to exist in the literature for the lower m values found here. It is suggested that SCLC through a suitable non-exponential trap distribution would explain the observed behaviour. The Joule heating rate was always less than 1 μW so heating as a cause of departure from Ohm's law is a rejected hypothesis. Since $m \neq 1$, it is not possible to specify a unique value for the conductivity; instead the conductivity corresponding to a mean field of 1×10^4 V m^{-1} has been evaluated and reported in Table 2. These room temperature conductivities all lie in the narrow range 1.0×10^{-8} Ω^{-1} m^{-1} to 3.9×10^{-8} Ω^{-1} m^{-1}. This shows that conductivity in the M(TPP) series is insensitive to the particular metal M and, as the conductivities for Co(TPP) and Co(mTPP) differ by less than a factor of two, the inclusion of the methoxy groups also has little effect on the conductivity.

The conductivities (σ), as measured with an applied voltage of 10 V across each disc, are plotted logarithmically against the reciprocal absolute temperature in Fig. 4. From the linear region at high temperature for each compound, the activation energy ΔE appearing in the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ has been determined and is listed in Table 2. Reference to this table shows there is no significant difference between the ΔE values obtained for Co(TPP) and Co(mTPP). This is consistent with the earlier conclusion that the methoxy groups are unimportant in the conduction mechanism.

As expected, the thermal decomposition studies have shown that the tetradentate porphyrin ring system has produced extremely stable compounds. It had also been anticipated, prior to undertaking the electrical measurements reported here, that the highly conjugated π electron system in the porphyrins would lead to large conductivities as judged by the standards of organometallic solids. However, this expectation has not been realised since the conductivities observed are smaller by a factor of several orders of magnitude than the highest values measured under identical conditions [15] for quinoxaline complexes and these latter compounds contain only two coupled π electron rings per molecule.

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