

Electrical Conductivity in Complexes of 'Crowned'-Phthalocyanines with Metal Salts

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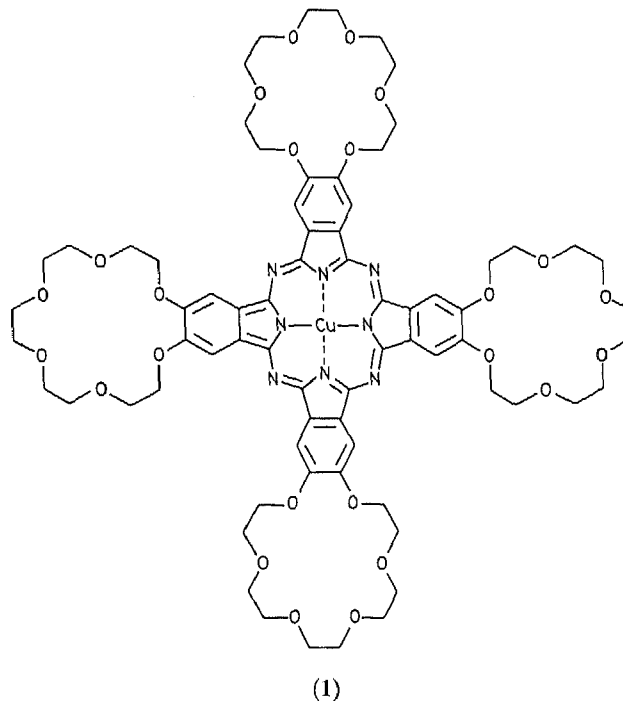
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Aggregation of 'crowned' phthalocyanines by metal salts increases the electrical conductivity compared to the non-aggregated phthalocyanines.

Recently, there has been much interest in the design and synthesis of low dimensional organic conductors.^{1,2} Efforts are being directed towards the linear arrangement of metallo-phthalocyanines (MPc) (*e.g.* M = Fe, Co, or Sn). Such an arrangement can be achieved by using suitable bidentate ligands (L) (*e.g.* L = pyrazine, CN, or O) which bridge the central metal atoms. In these linear systems charge transport may occur *via* π - π overlap of the macrocyclic rings which are held at small distances, or *via* the M-L-M stack.³

In a previous paper we described the synthesis and aggregation behaviour of phthalocyanines which contain crown ether subunits, *e.g.* (1).⁴ Compound (1) forms aggregates in the presence of alkali metal ions⁵ (Figure 1). We now report that these aggregates exhibit increased electrical conductivity as compared to uncomplexed (1) and unsubstituted phthalocyanines.

K⁺, Rb⁺, and Cs⁺ picrate complexes of (1) were prepared by mixing the latter compound and the appropriate metal picrate in a 1 : 4 ratio in chloroform-methanol (1 : 1 v/v) and stirring at ~40 °C for two days. The green precipitates were isolated by filtration, washed with hot methanol and chloroform until a colourless filtrate was obtained, and dried



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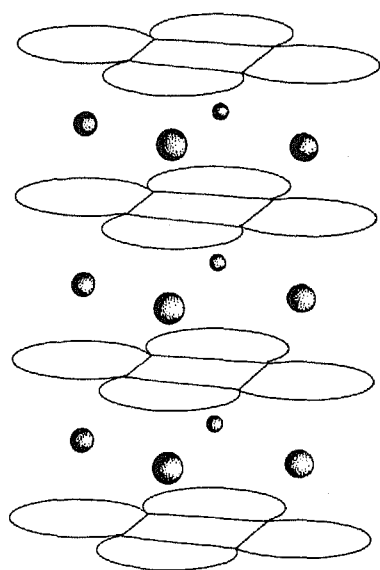


Figure 1. A stack of crowned phthalocyanines obtained by intercalation of alkali metal ions.

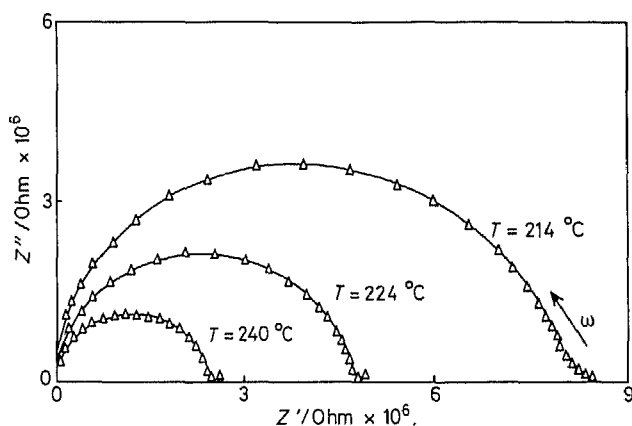


Figure 2. The impedance spectrum of (1) at three temperatures. Frequency range 10^{-1} to 6.5×10^4 Hz.

in vacuo for two days at 25°C. According to elemental analyses (C, H, N, O, M) the stoichiometry of the complexes is 1:4 (Pc: metal picrate).

The electrical properties of phthalocyanine (1), and of its K^+ , Rb^+ , and Cs^+ picrate complexes were studied in the solid state by impedance measurements[‡] as described previously.⁶ Electronically conducting CuPc was used as a reference compound. Figure 2 shows typical impedance spectra for uncomplexed (1) taken at different temperatures. Similar impedance spectra were obtained for CuPc and for the metal picrate complexes of (1). All the spectra suggest that in these samples electronic conductivity predominates. In addition, Seebeck measurements revealed compound (1) and CuPc to be p-type electronic conductors, whereas the K^+ , Rb^+ , and Cs^+ picrate complexes of (1) exhibit n-type electronic conductivity.

‡ Impedance spectra were recorded in the frequency range 10^{-1} to 6.5×10^4 Hz using a Solartron frequency response analyser (1250).

Table 1. Electrical conductivity (σ) at 180°C, activation energy (E_a), and type of conductivity of (1), its metal picrate complexes, and CuPc.

| Compound | $\sigma_{180^\circ\text{C}}/\text{S m}^{-1}$ | E_a/eV | Type of conductivity |
|-------------|--|-----------------|----------------------|
| CuPc | 6×10^{-8} | 1.39 | p |
| (1) | 5×10^{-7} | 1.18 | p |
| (1)· K^+ | 1×10^{-5} | 1.33 | n |
| (1)· Rb^+ | 3×10^{-4} | 1.02 | n |
| (1)· Cs^+ | 7×10^{-5} | 1.09 | n |

The electrical equivalent circuit corresponding to the impedance spectra of Figure 2 is an RCp circuit. The electrical conductivity (σ) at 180°C and the conductivity activation energies are presented in Table 1. The latter data were calculated from conventional Arrhenius plots of the temperature dependence of the conductivity, $\sigma = \sigma_0 \exp(-E_a/kT)$.

The n-type K^+ , Rb^+ , and Cs^+ picrate complexes of (1) show Meyer-Neldel behaviour, *i.e.* a linear relationship between $\log \sigma_T$ and E_a .⁷ However, the slope of the $\log \sigma_{180^\circ\text{C}}$ vs. E_a curve is smaller than the expected value of $0.434/kT$, indicating an additional temperature-independent term preceding the term $\exp(-E_a/kT)$ as has been found for semi-conducting oxidised cholesterol, retinal, and RNA and DNA.⁸ A possible explanation for this behaviour is tunnelling of thermally excited electrons through intermolecular barriers, according to the so-called Many, Harnik, and Gerlich model. This tunnelling leads to an activation-energy-dependent mobility.⁹

As seen in Table 1, an appreciable increase in the electrical conductivity occurs when the crown ether rings in (1) are complexed with an alkali metal ion. This increase is larger for Rb^+ than for Cs^+ and K^+ . We explain this in the following way: Complexation of an alkali metal ion induces aggregation of the phthalocyanines⁴ which might result in increased π - π overlap of the central core. This overlap could be higher in Rb^+ than for Cs^+ because the latter ion has a larger diameter. K^+ has the same diameter as the 18-crown-6 ring and will, therefore, be more embedded in the crowns leading to less efficient stacking of the rings.

Received, 14th September, 1987; Com. 1342

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