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

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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. 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.

In a previous paper we described the synthesis and aggregation behaviour of phthalocyanines which contain crown ether subunits, e.g. (1). Compound (1) forms aggregates in the presence of alkali metal ions (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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Table 1. Electrical conductivity ($\sigma$) at 180 °C, activation energy ($E_a$), and type of conductivity of (1), its metal picrate complexes, and CuPc.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\sigma_{180°C}$/S m$^{-1}$</th>
<th>$E_a$/eV</th>
<th>Type of conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuPc</td>
<td>$6 \times 10^{-8}$</td>
<td>1.39</td>
<td>p</td>
</tr>
<tr>
<td>(1)</td>
<td>$5 \times 10^{-7}$</td>
<td>1.18</td>
<td>p</td>
</tr>
<tr>
<td>(1):K$^+$</td>
<td>$1 \times 10^{-5}$</td>
<td>1.33</td>
<td>n</td>
</tr>
<tr>
<td>(1):Rb$^+$</td>
<td>$3 \times 10^{-4}$</td>
<td>1.02</td>
<td>n</td>
</tr>
<tr>
<td>(1):Cs$^+$</td>
<td>$7 \times 10^{-5}$</td>
<td>1.09</td>
<td>n</td>
</tr>
</tbody>
</table>

The electrical equivalent circuit corresponding to the impedance spectra of Figure 2 is an RCp circuit. The electrical conductivity ($\sigma$) 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 $E_a$. However, the slope of the log $\sigma_{180°C}$ 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. 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.

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 as follows: Complexation of an alkali metal ion induces aggregation of the phthalocyanines which might result in increased 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.

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