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CROWNED PHTHALOCYANINES

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In biological systems, transport of electrons and ions is mediated by special electron carriers and ionophores. As part of a program aimed at the development of new synthetic systems that mimic these features, we designed macrocyclic compound **1** [1]. Compound **1** contains a phthalocyanine ring to which four crown ether rings are attached. It can bind different metal ions at the same time, e.g. a transition metal ion in the phthalocyanine and alkali metal ions in the crowns. This opens the possibility to use the molecule as an electron carrier (*via* the metal phthalocyanine) or as an ionophore (*via* the crown ether rings). In the present communication we report on the former possibility, i.e. charge transport *via* stacks of phthalocyanine rings.

The Cu(II) derivative of compound **1** was synthesized from 4,5-dicyanobenzo-18-crown-6 and CuCN as described previously [1]. In solution, compound **1** tends to form aggregates. This can be seen in the visible spectrum by the appearance of a broad band at ≈ 630 nm [1]. Aggregation is favoured by alkali metal salts that coordinate to the crown ether rings of **1**. Table I shows that for a series of metal picrate salts added to a solution of **1** in dry chloroform, the intensity of the band at 630 nm increases with increasing diameter of the cation. This suggests that large cations promote oligomerization of the phthalocyanine, probably because they are sandwiched between the crown ether rings (Figure 1).

The electrical properties of phthalocyanine **1** and its K⁺ and Rb⁺ complexes were studied in the solid state by impedance measurements [2]. The complexes were prepared by mixing **1** and the appropriate metal picrate in a 1:4 ratio in chloroform-methanol (1:1, v/v). They were isolated by filtration and dried under vacuum for 2 days at 25°C. The electrical conductivity of the samples are presented in Table II. As a reference the electrical conductivity of copper phthalocyanine is also included in this Table. In Table I can be seen that compound **1** is a better charge carrier than copper phthalocyanine. The ratio of the electrical conductivity of the two compounds amounts to ≈ 8 . This ratio further increases when cations are complexed to the crown ether rings of **1**, the effect being largest for the Rb⁺ ion. This result supports the idea that compound **1** forms aggregates when cations are present. When such aggregates occur as extended stacks (Figure 1), charge transport will be facilitated [3].

Table I. Relative intensity of the absorption band at 630 nm in the visible spectrum of phthalocyanine **1** as a function of added metal picrate salt.^a

| Cation | Relative intensity |
|-----------------|--------------------|
| Na ⁺ | 0.41 |
| K ⁺ | 0.53 |
| Rb ⁺ | 0.98 |
| Cs ⁺ | 1 |

^a In dry chloroform at 25°C; [**1**] = 2.5×10^{-5} mol. dm⁻³; metal picrate 1 mmol; chloroform 2ml.

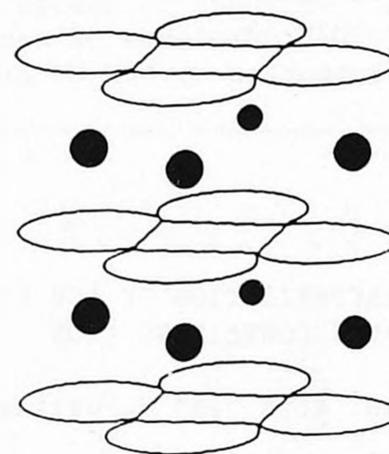
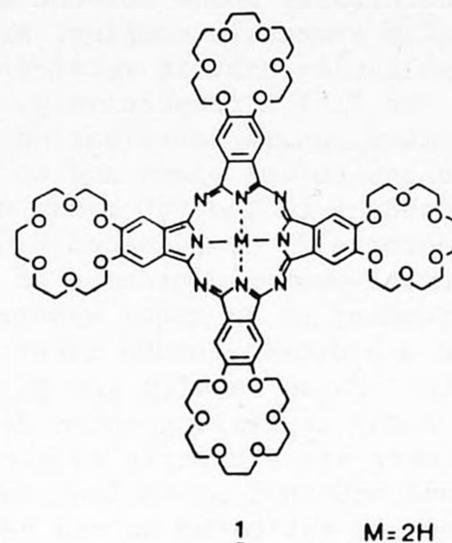


Figure 1.

Table II. Electrical conductivity of phthalocyanine **1** and of its metal picrate complexes^a

| Compound | σ /(S.cm ⁻¹) | σ_{relative} |
|----------------------------|---------------------------------|----------------------------|
| CuPc ^b | 6×10^{-10} | 1 |
| 1 | 5×10^{-9} | 8.3 |
| 1 . K ⁺ | 1×10^{-7} | 166 |
| 1 . Rb ⁺ | 3×10^{-6} | 5000 |

^a At 180°C

^b Pc = phthalocyanine dianion.

[1] O.E. Sielcken, M.M. van Tilborg, M.F.M. Roks, R. Hendriks, W. Drenth, and R.J.M. Nolte, J. Am. Chem. Soc., in press.

[2] More details will be published in a full paper.

[3] O. Schneider, J. Metz, and M. Hanack, Mol. Cryst. Liq. Cryst. **81**, 273 (1982).