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

O. E. Sielcken,[a] J. Schram,[b] R. J. M. Nolte,[a]† J. Schoonman,[b] and W. Drenth[a]

[a] *Department of Organic Chemistry, University at Utrecht, 3584 CH Utrecht, The Netherlands*
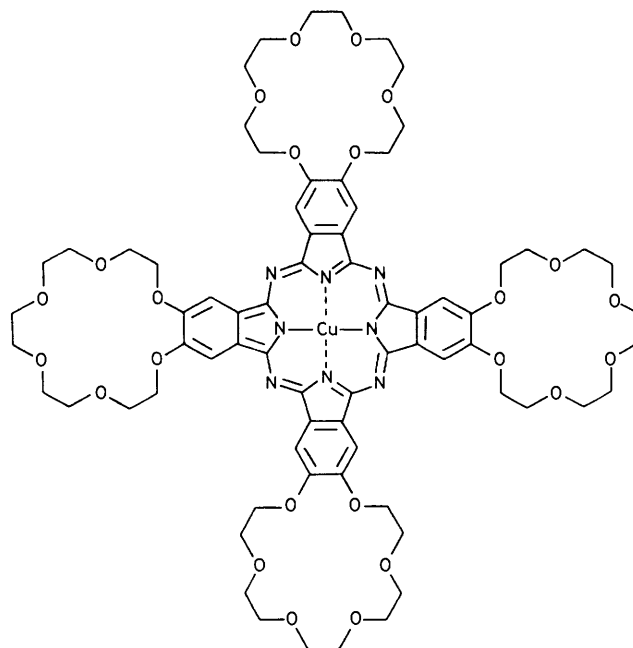[b] *Laboratory of Inorganic and Physical Chemistry, Delft University of Technology, 2628 BL Delft, The Netherlands*

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 metallophthalocyanines (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 ions[5] (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
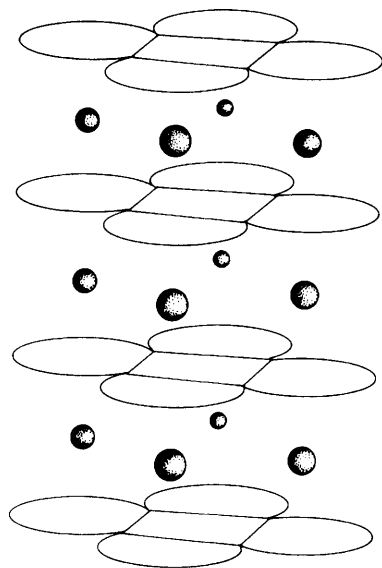
(**1**)

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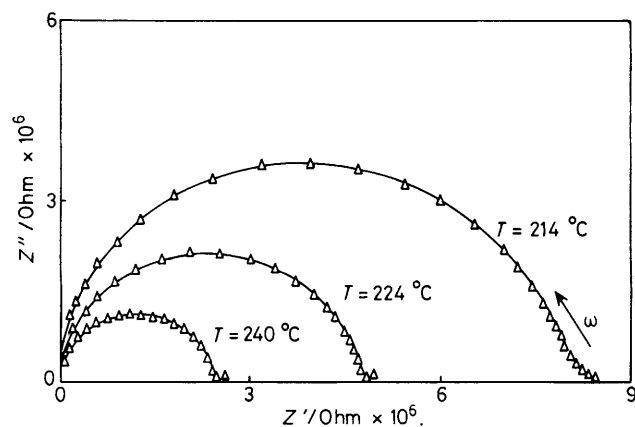

Figure 2. The impedance spectrum of (1) at three temperatures. Frequency range 10^{-1} to 6.5×10^4 Hz.

in vacuo for two days at 25 °C. According to elemental analyses (C, H, N, O, M) the stoicheiometry 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	$\sigma_{180\,°C}$/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 σ_T and E_a.[7] 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.[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 is the following way: Complexation of an alkali metal ion induces aggregation of the phthalocyanines[4] 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.

References

1 M. Y. Ogawa, J. Martinsen, S. M. Palmer, J. L. Stanton, J. Tanaka, R. L. Greene, B. M. Hoffman, and J. A. Ibers, *J. Am. Chem. Soc.*, 1987, **109**, 1115; B. W. Dirk, T. Inabe, K. F. Schoch, and T. J. Marks, *ibid.*, 1983, **105**, 1539; C. F. Piechocki, J. Simon, A. Skoulios, D. Guillon, and P. Weber, *ibid.*, 1982, **104**, 5245.
2 M. Hanack and R. Fay, *Recl. Trav. Chim. Pays-Bas*, 1986, **105**, 427.
3 A. Datz, J. Metz, O. Schneider, and M. Hanack, *Synth. Met.*, 1984, **9**, 31.
4 R. Hendriks, O. E. Sielcken, W. Drenth, and R. J. M. Nolte, *J. Chem. Soc., Chem. Commun.*, 1986, 1464.
5 O. E. Sielcken, M. M. van Tilborg, M. F. M. Roks, R. J. M. Nolte, and W. Drenth, *J. Am. Chem. Soc.*, 1987, **109**, 4261.
6 J. H. van der Linden, J. Schoonman, R. J. M. Nolte, and W. Drenth, *Recl. Trav. Chim. Pays-Bas*, 1984, **103**, 260.
7 W. Meyer and H. Neldel, *Z. Techn. Phys.*, 1937, **18**, 588.
8 B. Rozenberg, B. B. Bhowmik, H. C. Harder, and E. Postow, *J. Chem. Phys.*, 1968, **49**, 4108.
9 D. D. Eley, *J. Polym. Sci.*, 1967, **17**, 73.