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(Eingegangen am 16. März 1989)

E 7029

Alkali Metal Picrate Complexes of "Crowned"-Phthalocyanines. Solid State Structures and Electrical Properties

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Complex Compounds / Electrical Properties / Molecular Structure / Phthalocyanines / Transport Properties

Molecules of copper phthalocyanine substituted with four 18-crown-6 moieties, were aggregated with the help of K^+ , Rb^+ , and Cs^+ picrates. Possible structures were proposed based on computer analysis of X-ray powder diffraction patterns: for the crowned phthalocyanine an orthorhombic cell with: $a = 50.77$, $b = 25$, $c = 8.7$ Å. For its metal picrate complexes, tetragonal structures were found: $a = b = 22.76$, $c = 12.99$ Å (K^+ -complex); $a = b = 29.44$, $c = 10.63$ Å (Cs^+ -complex); $a = b = 29.44$, $c = 10.40$ Å (Rb^+ -complex). A.c. impedance spectroscopy showed an increase in the electronic conductivity of 2 to 3 powers of ten, if crowned phthalocyanine was aggregated by means of a metal picrate salt. In the K^+ complex only electronic conductivity could be detected. The Rb^+ and Cs^+ complexes exhibited cation conductivity as well.

Introduction

Recently much effort has been directed to the construction of low dimensional organic conductors comprising phthalocyanines (Pc's). Well known are single crystals of partially oxidized (metallo-) Pc's [1], Pc's as discotic liquid crystals [2], and metallo-Pc's polymerized through suitable bidentate ligands [3]. All of these systems consist of columns of face to face stacked macrocycles with small inter-planar distances. Charge transport of electrons or holes occurs via $\pi-\pi$ overlap of the macrocyclic ligands, via a one dimensional chain of metal centres, or via a metal-ligand-metal chain. We achieved an alternative way of stacking by adding cations to Pc's to which four crown ether rings are attached [4].

In solution "crowned"-phthalocyanine 1 tends to form aggregates. Aggregation is induced by alkali metal ions which coordinate to the crown ether rings. This aggregation is particularly notable when the diameter of the ion exceeds the inner diameter of the crown ether rings. In these aggregates the cations are sandwiched between two crown ether rings. Also, by using cations with different diameters, we are able to influence the interplanar distance and staggering angles between the Pc ligands. In an earlier communication [5], we reported on the electrical conductivity of 1 in its

solid state. This conductivity increases when 1 is complexed with alkali metal picrates. Picrate salts were used to reduce anion conduction by steric hindrance.

In the present paper we propose a structure of 1 and of its K^+ , Rb^+ , and Cs^+ picrate complexes on the basis of X-ray powder diffraction patterns. Moreover, the electrical properties of the solid state compounds were studied by a.c. impedance spectroscopy. CuPc was used as a reference compound.

Experimental

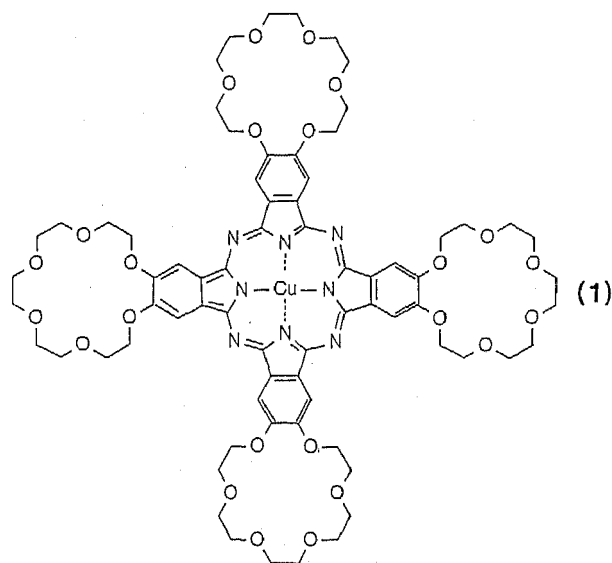
Preparation of alkali metal picrate complexes of (4,5,4',5',4'',5'',4''',5'''-tetrakis(1,4,7,10,13,16-hexaoxa-hexadecamethylene)phthalocyaninato)copper(II) (1)

Compound 1 was synthesized as described previously [4a]. Its K^+ , Rb^+ and Cs^+ picrate complexes were prepared by mixing 1 (0.07 mol) with the appropriate picrate salt in a 1:4 ratio in 20 ml dry chloroform-methanol (1:1 v/v) and stirring for two days at 40°C under an atmosphere of dry nitrogen. A precipitate was formed which was isolated by filtration and washed with hot chloroform, and subsequently with hot methanol until a colourless filtrate was obtained. The product was dried in vacuum over P_2O_5 for two days at 150°C yielding a green, insoluble, micro-crystalline powder. Yield: 80%.

K^+ -picrate complex of 1. T.G.A. 306°C (decomp.); Anal. Calcd. for $CuK_4C_{96}H_{96}N_{20}O_{52}$ (1. (K^+ -picrate)₄): K, 6.10; C, 44.66; H, 3.75;

N, 10.85; O, 32.22. Found: K⁺, 6.3; C, 44.54; H, 3.82; N, 10.68; O, 32.31.

Rb⁺-picrate complex of 1. T.G.A. 306°C (decomp.); Anal. Calcd. for CuRb₄C₉₆H₉₆N₂₀O₅₂ (1. (Rb⁺-picrate)₄): C, 41.67; H, 3.50; N, 10.13; O, 30.05. Found: C, 41.49; H, 3.70; N, 10.08; O, 30.03.



Cs⁺-picrate complex of 1. T.G.A. 306°C (decomp.); Anal. Calcd. for CuCs₄C₉₆H₉₆N₂₀O₅₂ (1. (Cs⁺-picrate)₄): C, 38.99; H, 3.27; N, 9.47; O, 28.13. Found: C, 38.77; H, 3.40; N, 9.56; O, 28.34.

CuPc. CuPc was prepared from phthalonitrile and Cu(I)CN according to literature procedures [7].

X-Ray Diffraction

X-ray powder diffraction patterns of all polycrystalline compounds studied were recorded on a Guinier Johansson FR 552 powder diffractometer (ENRAF-NONIUS-CuK α_1), and on a Kiesig powder diffractometer using Ni-filtered CuK α radiation (100 and 400 mm sample-film distances were used). Unit cells of the studied compounds were generated using CPK-models, and a local computer program based on the trial and error method of Henry, Upton, and Wooster [8].

A.c. Impedance Spectroscopy

To prepare samples the materials were powdered in a mortar and pressed at a load of 3 tons in disc-shaped compacts with a diameter of 6 mm, and a thickness of 0.6 to 1.2 mm. Sputtered platinum electrodes were applied using an Edwards Sputter Coater S 150 B. The samples were mounted in a conventional conductivity cell provided with resistive heating. Samples with sputtered film electrodes were springloaded between two Pt disks. A constant flow of purified nitrogen was used. Impedance spectra were recorded in the frequency range 10^{-1} to 6.5×10^4 Hz using a Solartron 1250 frequency response analyser and a Solartron 1286 electrochemical interface. Reliable conductance values could be measured from about 130°C. The temperature range studied was 130°C to 250°C. Bulk resistances were obtained from analysing the complex plane representations of the recorded impedance spectra. The electrical equivalent circuits describing the impedance spectra were determined by a detailed non-linear least-squares analysis [6] providing information on electrode polarization phenomena as well. The conductivity activation energies, E_a , were calculated from conventional Arrhenius plots of the temperature dependence of the conductivity, $\sigma = \sigma_0 \exp[-E_a/kT]$. Dielectric constants (ϵ) were calculated from the high-frequency capacitance $C_\infty = \epsilon \epsilon_0 \frac{A}{d}$ where $\epsilon_0 = 8.85 \times 10^{-12}$ F/m, while d , and A are the thickness, and electrode surface area of the samples.

Seebeck Measurements

The type of charge carriers in the samples was determined between 150 and 170°C using the hot point probe technique. Seebeck voltages were measured with a Keithly 614 electrometer.

Results and Discussion

Description of the Structure

The sharp X-ray powder diffraction patterns of 1 and of its metal picrate complexes indicate the crystalline nature of the samples. Using a computer program, CPK models, and literature data on Pc's, we tried to derive the structure of each compound from its diffraction data. Since powder patterns do not provide a unique structure, we were only able to propose structures that are not in contradiction with the X-ray patterns.

Recently, structures for a compound similar to 1 but with 15-crown-5 rings, and of its metal free ligand have been proposed by Simon et al. [9]. They observed a crystalline phase which they assigned to an orthorhombic lattice with eclipsed Pc units having a unit cell of $a = 20.5$, $b = 18$, $c = 4.2$ Å ($\alpha = \beta = \gamma = 90^\circ$). They also observed a mesophase comprising staggered Pc's with unit cell parameters $a = b = 20.8$, $c = 8.2$ Å ($\alpha = \beta = \gamma = 90^\circ$). For both structures an interplanar Pc distance of 3.4 Å and a 4.2 Å distance for the crown ethers was proposed.

For 1 and its copper free analogue we observed lattice spacings similar to the crystalline phase observed by Simon et al. [9]. We did not observe a mesophase. However, the crystalline structure did not explain the presence of an additional spacing at 50.77 Å in our diffraction patterns. This 50.77 Å spacing indicates a larger unit cell. An orthorhombic unit cell with parameters $a = 50.77$, $b = 25$, $c = 8.7$ Å fitted our data quite well. For the molecular arrangement in this unit cell a spacing at 3.5 Å was assigned to be the mean interplanar distance of the Pc macrocycles. An eclipsed conformation of the macrocycles was not in agreement with our data. It is known for H₂Pc with an interplanar distance of 3.4 Å, that it has a staggered conformation [10]. The staggering angle of the macrocycles is dependent on the interplanar distance and the substituents on the macrocycle. In this way steric repulsions can be decreased. A structure in accordance with our data with staggered Pc units is depicted in Fig. 1. The Pc molecules are cofacially stacked in parallel columns. For the analysis of the diffraction patterns of the metal picrate complexes of 1 we followed the same procedure, but we also used the information derived from elemental analysis and UV/Vis spectroscopy [4a]. Elemental analysis of the metal picrate complexes of 1 showed a host-guest ratio of 1:4. A potassium ion just fits into the 18-crown-6 ring. UV/Vis experiments, using anhydrous solvents, suggested aggregation of the Pc units upon adding K⁺-picrate [4a]. The picrate anion is located in the neighbourhood of a potassium ion, forming an ion pair with it.

Clustering of the ion pairs leads to stacks of alternating crowned phthalocyanine and picrate anions, as shown in Fig. 2. A spacing of 3.4 Å was assigned to be the interplanar distance. With this model we generated an orthorhombic unit cell with parameters $a = b = 22.76$, $c = 12.91$ Å. These parameters are in agreement with the diffraction data. The large c parameter could be due to the orientation of the

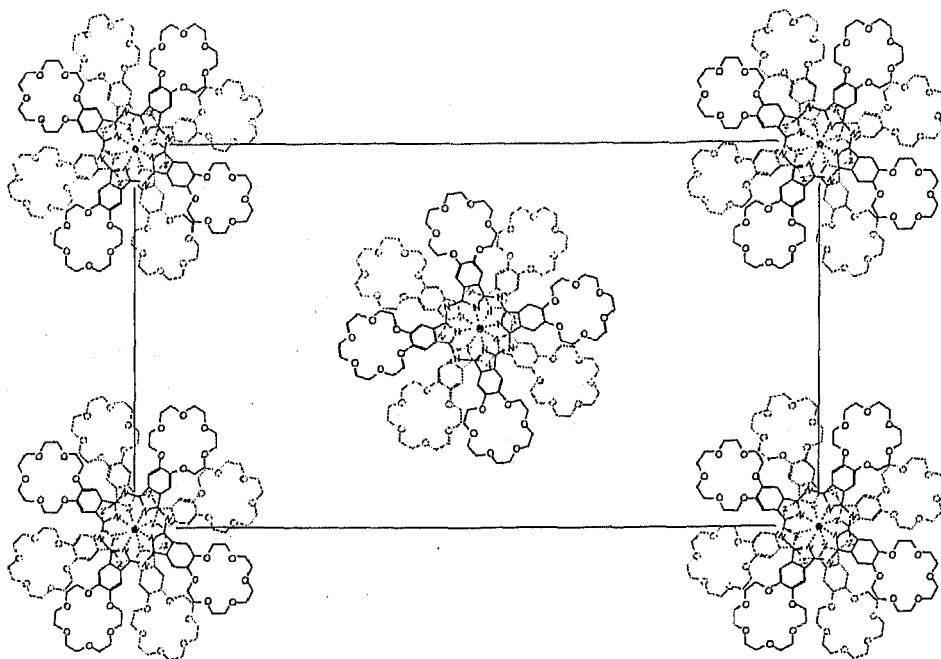


Fig. 1
Schematic representation of the packing of 1

picrate anions. The diffraction patterns of the rubidium, and cesium picrate complexes of 1 were very similar, but different from their potassium counterpart. The powder diffraction patterns of both the rubidium and cesium complex indicated that ordering of the Pc stacking was very high, higher than the Pc stack of the potassium complex of 1. In UV/Vis experiments we observed aggregation upon adding rubidium and cesium salts to a solution of 1 [4a]. In these aggregates the cations are sandwiched between the crowns, and the Pc macrocycles have an eclipsed conformation. Rubidium and cesium ions have diameters that exceed the inner diameter of a planar 18-crown-6 ring. We assumed a similar structure to be possible in the solid state. Because of the resemblance of the powder diffraction patterns and the UV/Vis experiments, we assume the same stacking for both the rubidium and cesium complex of 1. Remarkable in the diffraction pattern of the cesium complex were four sharp reflections in the region between 3.8 and 3.4 Å. In the diffraction pattern of the rubidium complex similar reflections were found, all of them at 0.1 Å shorter distances, i.e. between 3.7 and 3.3 Å. This indicates an interplanar distance that is 0.1 Å smaller in the rubidium as compared to the cesium complex. The data of the cesium picrate complex could be fitted to a tetragonal unit cell $a = b = 29.44$, $c = 10.63$ Å, and those of the rubidium picrate complex to a tetragonal unit cell $a = b = 29.44$, $c = 10.40$ Å. A probable molecular arrangement that fits these unit cells is schematically given in Fig. 3.

Although the X-ray measurements gave sharp powder diffraction patterns, it proved to be impossible to determine exact positions of the molecules in the proposed cells.

Electrical Measurements

The electrical properties of phthalocyanine 1, and of its K^+ , Rb^+ , and Cs^+ picrate complexes were studied in the

solid state by a.c. impedance spectroscopy. CuPc was used as a reference compound. Fig. 4 shows typical impedance spectra for the rubidium picrate complex of 1, $1 \cdot Rb^+$, at 155°C. Similar spectra were obtained for 1 and for its other metal picrate complexes. All spectra suggest that electrode polarisation phenomena are absent and that electronic conductivity predominates.

Seebeck measurements revealed compound 1 and CuPc to be p-type electronic conductors, as has earlier been observed for CuPc¹¹, whereas the K^+ , Rb^+ , and Cs^+ picrate complexes of 1 exhibit n-type electronic conductivity. The rubidium picrate complex of the metal free derivative of 1 showed n-type conductivity as well. For copper phthalocyanine

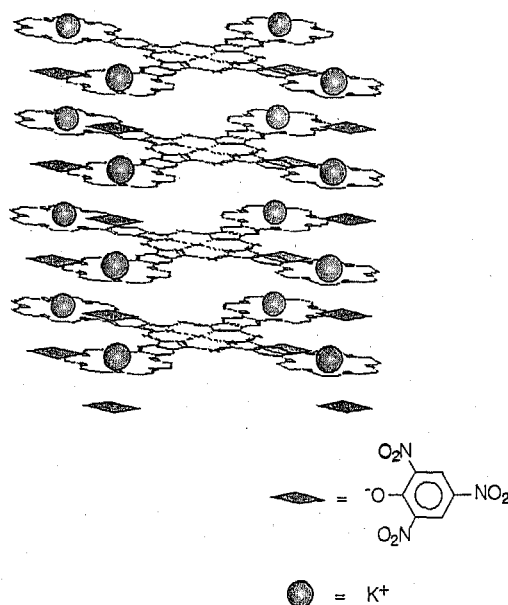


Fig. 2
Schematic representation of the K^+ picrate complex of 1

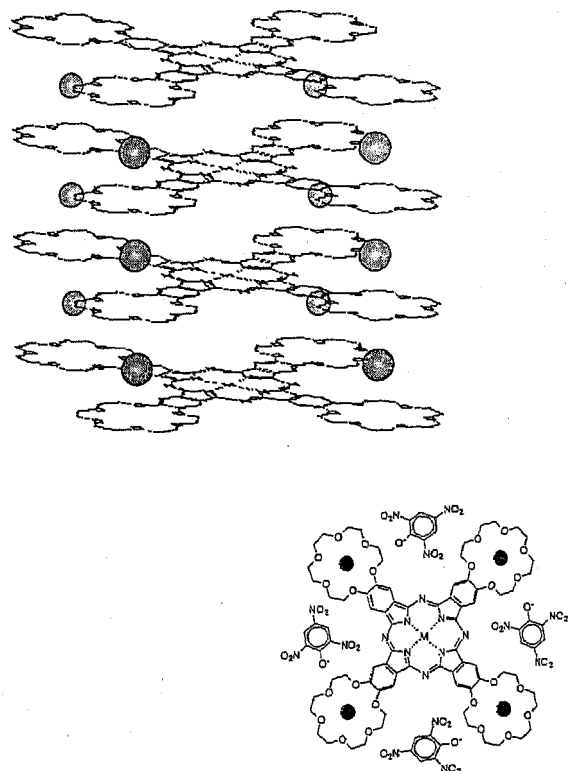


Fig. 3

Schematic representation of complexes of 1 with Rb^+ , and Cs^+ picrate

cyanine it is known that the conduction pathway of the charge carriers is formed by $\pi-\pi$ overlap of the macrocyclic rings [12]. The present data suggest that upon addition of a metal picrate salt to 1 the conduction pathway changes from ligand centred by holes to metal centred by electrons, as a result of interacting d-orbitals of the Cu^{2+} centres [4b, 13].

The impedance spectra of the metal picrate complexes of 1 could be fitted to the equivalent circuit, $C_\infty R_b p Q_1 p Q_2 s$, where s and p stand for series and parallel, respectively (Fig. 5). C_∞ represents the high-frequency capacitance,

$C_\infty = \epsilon \epsilon_0 \frac{A}{d}$, and R_b the bulk electronic conductivity. The

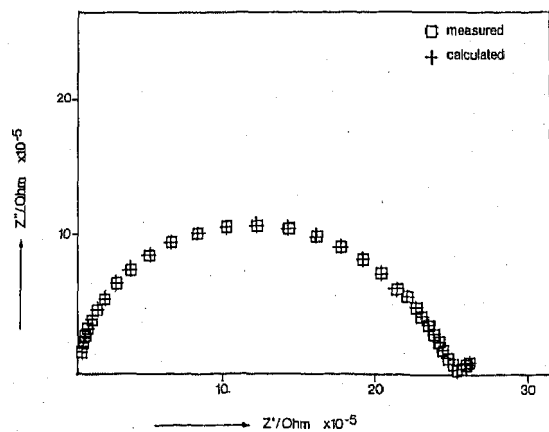


Fig. 4

Measured (\square) and calculated ($+$) impedance spectrum of $1 \cdot \text{Cs}^+$ at 155°C

parallel constant phase element (CPE) Q_1 , with an impedance $Z = (k_1(i\omega)^\alpha)^{-1}$ has values for α of 0.5 to 0.7. This element is related to ionic diffusion. Usually, ionic conduction should be represented with an RCs branch, R^{-1} being the ionic conductance and C the double layer capacitance representing the ion blocking effect of the Pt electrode. Fits with the RCs branch included, led to insignificant values for R , and values for C comparable to k_1 . This may indicate that the mechanism of ionic conduction is dominated by diffusion. Fig. 6 shows the temperature dependence of Q_1 , plotted as $\ln\left(k_1 \cdot \frac{d}{A} \cdot T\right)$ versus $1/T$. This figure points to a

thermally activated transport of Rb^+ and Cs^+ . The slopes of the curves correspond to a conduction activation enthalpy, $\Delta H(Q_1)$, of 0.64 eV for the Rb^+ , and 0.59 eV for the Cs^+ complex of 1. This may be related with binding of Rb^+ and Cs^+ to 18-crown-6 [4a]. The larger Cs^+ -ion has a lower binding energy with the 18-crown-6 rings of 1 than the smaller Rb^+ -ion. It is, therefore, easier to transport Cs^+ through the crystal lattice than Rb^+ . As can be seen in Fig. 6, the K^+ -ion exhibits a different behaviour. The slope of this curve does not refer to thermally activated ion conduction. In fact, CPE Q_1 in Fig. 5, is not required for fitting the impedance spectra of $1 \cdot \text{K}^+$. Adequate fit results are obtained also with the equivalent circuit $C_\infty R_b p Q_2 s$. Po-

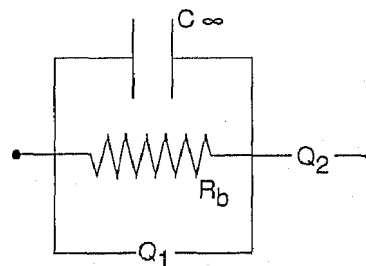


Fig. 5

Equivalent circuit for the a.c. response of the K^+ , Cs^+ , and Rb^+ complexes of 1

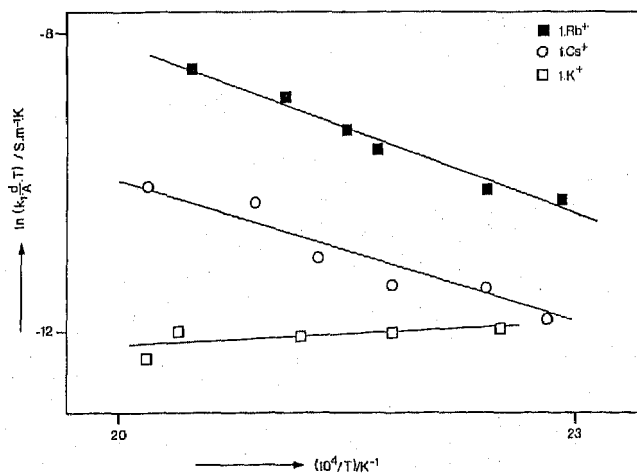


Fig. 6

Temperature dependence of Q_1 plotted as $\ln\left(k_1 \cdot \frac{d}{A} \cdot T\right)$ vs. $1/T$ for the metal picrate complexes of 1

tassium has a much larger binding energy with 18-crown-6 than rubidium and cesium. As can be seen in Fig. 2, the potassium ions fit in the crown-ether rings and are closely packed with picrate anions in between. Hence, the K^+ -ions are practically immobile. Potassium conduction has been demonstrated to occur through an 18-crown-6 channel [14]. For further examination of a possible contribution of K^+ -ions to the conductivity, the open-circuit voltage (OCV) of the concentration cell K-amalgam(I) | $1 \cdot K^+$ | Hg(II) was measured during discharge of this cell. The OCV did not decrease in a subsequent period of discharge of 40 h. From this is concluded that potassium ions are not involved in d.c. transport in $1 \cdot K^+$.

The temperature dependence of the electrical conductivity σ of the prepared compounds, plotted as $\ln \sigma(T)$ versus $1/T$ is shown in Fig. 7. The isothermal electrical conductivity at 180°C and the conductivity activation energy, E_a , are presented in Table 1. As can be seen in Table 1 and Fig. 7 compound 1 shows a higher electrical conductivity, and a lower activation energy than CuPc. A substantial increase in electrical conductivity occurs when 1 is complexed with

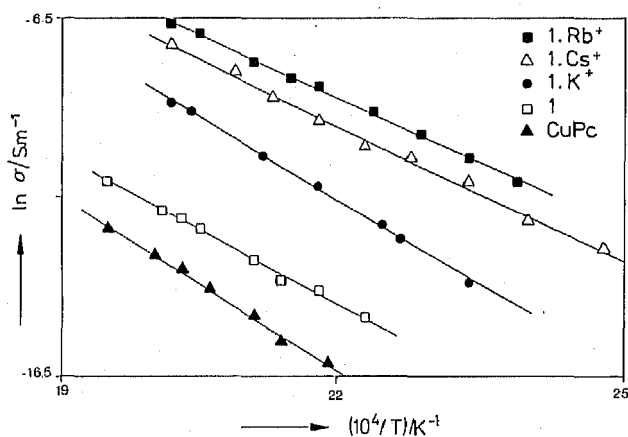


Fig. 7

Temperature dependence of the electrical conductivity (σ), plotted as $\ln \sigma$ versus $1/T$, for 1, and of its metal picrate complexes

an alkali metal ion. This increase is larger for Rb^+ and Cs^+ , than for K^+ . This can be explained by the fact that complexation of an alkali metal ion results in aggregates with eclipsed phthalocyanine units. Rb^+ and Cs^+ ions slightly decrease the interplanar spacing and change the angle of staggering between the macrocycles as is concluded from the X-ray powder diffraction patterns, resulting in an increased $\pi-\pi$ overlap [15]. This overlap could be higher for Rb^+ than for Cs^+ because the latter has a larger diameter. In the K^+ complex of 1, picrate anions are intercalated between eclipsed macrocycles, but the ordering of the Pc stacking is less than for the rubidium and cesium complexes. The overall effect is a higher conductivity activation energy. From the presented data it can be concluded that the electrical properties are affected by a variation in the angle of staggering between the Pc macrocycles.

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

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

For all samples the CPE Q_2 , with an impedance $Z = (k_2(i\omega)^\alpha)^{-1}$, has a value for α between 0.1 and 0.4, and has, therefore, the character of a resistance. We relate the presence of this CPE to current inhomogeneities, which occur due to barriers from cross-linking of the metal picrate aggregates of 1 as visualised in Fig. 8. Charge transport requires hopping between phthalocyanine stacks. The activation energies $E_a(Q_2)$ for this hopping process are given in Table 2. These values are similar to the activation energy, found by Belarbi et al. [16], required for intermolecular electron hopping between Pc_2Lu subunits. The conduction activation energies, E_a , related to charge transport within

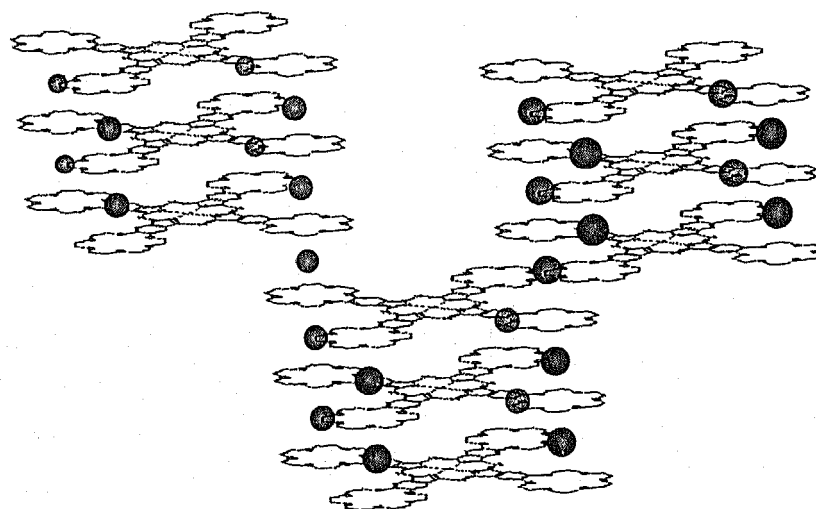


Fig. 8

Cross-linking of phthalocyanine stacks

stacks (Table 1), have larger values than the activation energies for hopping between stacks, $E_a(Q_2)$. E_a must, therefore, be interpreted as: $E_a = \frac{\Delta E_f}{2} + \Delta E_m^{intra}$, with ΔE_f the formation activation energy of the charge carriers, and ΔE_m^{intra} the activation energy of intrastack electron migration. With the rough approximation: $\Delta E_m^{intra} \approx E_a(Q_2)$, values can be estimated for ΔE_f . Estimated values for ΔE_f are 1.56 eV for the K^+ -complex, 1.32 eV for the Cs^+ -complex, and 1.14 eV for the Rb^+ -complex of 1. These values show a linear correlation with the interplanar distances of the metal picrate complexes of 1.

Table 2

Activation energies, $E_a(Q_2)$, for hopping of electronic charge carriers between phthalocyanine stacks

Compound	$E_a(Q_2)/eV$
1 · K^+	0.55
1 · Rb^+	0.45
1 · Cs^+	0.43

The metal picrate complexes of 1 are intrinsic semiconductors with a larger mobility of the electrons than that of the holes.

The n-type K^+ , Rb^+ , and Cs^+ picrate complexes of 1 show Meyer-Neldel behaviour, i.e. a linear relationship between the isothermal conductivity plotted as $\log \sigma(T)$ and E_a [17]. However, the slope of the $\log \sigma(180^\circ C)$ versus 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 semiconducting oxidized cholesterol, retinal, RNA and DNA [18]. A possible explanation for this behaviour is tunneling of thermally excited electrons through intermolecular barriers, according to the Many, Harnik, and Gerlich model. This tunneling leads to an activation energy dependent mobility [19].

The dielectric constant (ϵ), obtained from the high-frequency capacitance C_∞ , of polycrystalline 1, its K^+ , Rb^+ , and Cs^+ complexes, and CuPc are listed in Table 3. These values are higher than earlier published data on phthalocyanines [20]. The ϵ_∞ values are, however, strongly dependent on the morphology, preparation, and compaction methods of the samples. In this respect, the present samples differ from the samples in Ref. [20].

Table 3

Dielectric constant (ϵ) of 1, its K^+ , Rb^+ , and Cs^+ picrate complexes, and of CuPc

Compound	ϵ
1	82.4
1 · K^+	74.0
1 · Rb^+	70.9
1 · Cs^+	65.2
CuPc	67.0

Dr. J. Aerts of AKZO Research, Arnhem, and Mr. A. Schouten of the Department of General Chemistry of the University at Utrecht are gratefully acknowledged for recording the powder diffraction patterns and for their help in the interpretation.

Part of this work was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from The Netherlands Foundation for Scientific Research (NWO).

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(Eingegangen am 6. Februar 1989)

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