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# Crown-ether-substituted phthalocyanines. Control of supramolecular organization by monovalent and divalent metal salts

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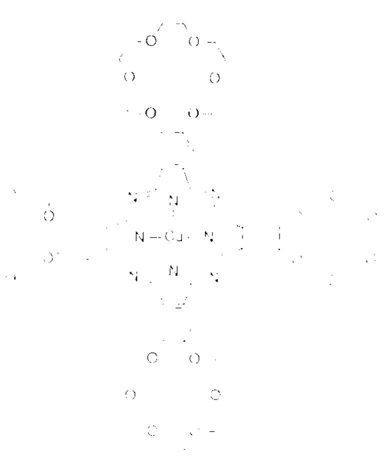
**Abstract.** Aggregation of crown-ether-substituted phthalocyanines with monovalent metal ions ($K^+$, $Rb^+$, and $Cs^+$) results in cofacially ordered phthalocyanine stacks. Aggregation with $Ba^{2+}$ leads to the formation of phthalocyanine networks.

## Introduction

Recently, we reported the synthesis and physical properties of phthalocyanines substituted with crown-ether rings (*e.g.*, compound **1**)[1]. We showed that these molecules can be arranged in cofacial stacks with the help of alkali metal ions which coordinate to the crowns[1,2a]. Metal ions with diameters that match the internal diameter of the crown ethers, *e.g.*, $K^+$, induce stacks in which the crowns are filled by the metal ions. The anions are intercallated in these stacks, occupying positions between the metal ions (Figure 1A). When metal ions are used with a diameter that exceeds the diameter of the crown ether, *e.g.*, $Rb^+$ and $Cs^+$, a sandwich-like structure is obtained in which four metal ions are held between eight crown ethers of two different phthalocyanine molecules (Figure 1B)[2]. In the metal-ion complexes, the distance between the phthalocyanine macrocycles depends on the complexed metal ion, and decreases in the series $K^+ > Cs^+ > Rb^+$. The complexes can be isolated by precipitation from concentrated solutions of the phthalocyanine and metal picrate salt.



**1**

When phthalocyanines are stacked to form columns, their π-electron systems may interact and create a pathway for the transport of electronic charge carriers. AC impedance measurements on the complexed crown-ether phthalocyanines showed that these aggregates are electronic conductors with a small ionic contribution by the metal salts[1c]. The electronic conductivity is dependent on the type of metal salt MX and increases in the series $K^+X^- < Cs^+X^- < Rb^+X^-$. This increase in conductivity is parallel to the decrease in the spacing between the phthalocyanine planes. The impedance study, furthermore, revealed that the electronic conduction process involves many steps, including the formation of free charge carriers and the hopping of charges between phthalocyanine stacks. Alkali metal ions appeared to be involved in each of these steps.

As an extension of this work, we now report the aggregation behaviour of phthalocyanine **1** in the presence of a metal ion that has a valency of two and a diameter smaller than that of $Rb^+$ and larger than that of $K^+$. Such an ion was expected to give a very stable complex with an even smaller interplanar phthalocyanine spacing and a smaller barrier for hopping of electronic charge carriers between the stacks. $Ba^{2+}$ seemed to be a good candidate, as this ion is known to exhibit binding properties towards crown ethers that are superior to those of the alkali metal ions[4]. Surprisingly, barium salts were found to cause a supramolecular ordering of the crown-ether phthalocyanines that differed from the ordering obtained with monovalent metal salts.

## Results and discussion

The free energies of complexation ($\Delta G^0$) between **1**, its 15-crown-5 and 21-crown-7 analogs, and barium picrate were determined by the picrate extraction technique[5]. The data calculated for a 1:1 crown/metal-ion complex are presented in Table I together with the values obtained for

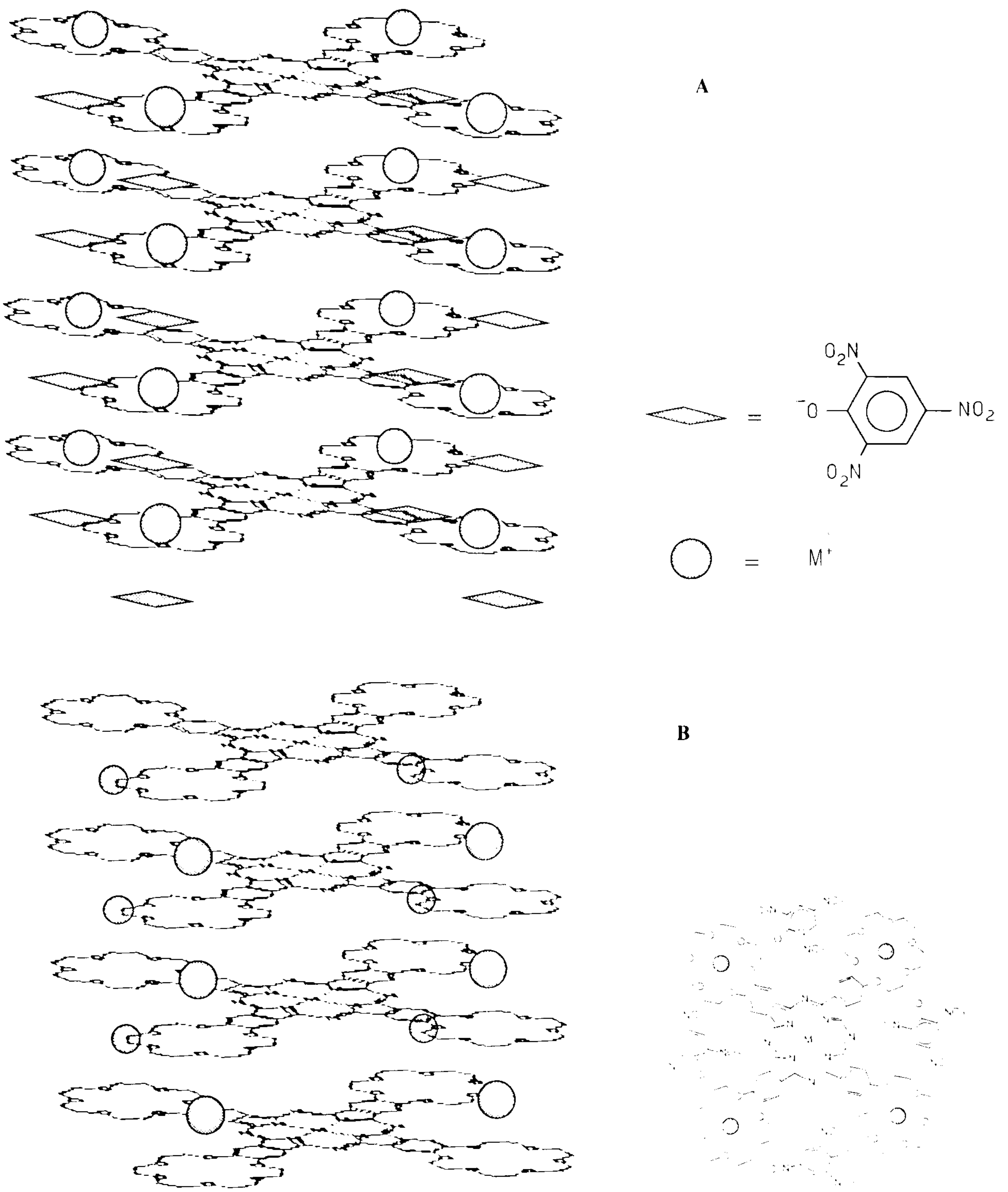


*Fig. 1. (A) Schematic representation of the structure of the $K^+$-picrate complex of* **1**. *(B) Schematic representation of the complexes of* **1** *with $Rb^+$ and $Cs^+$ picrate.*

rubidium picrate[2a]. The $-\Delta G^0$ values for $Ba^{2+}$ presented in Table I are lower limits, because the distribution constant ($K_d$) of uncomplexed barium picrate between $CHCl_3$ and $H_2O$ could not be accurately measured[6].

As can be seen in Table I, $Ba^{2+}$ is a better complexing agent towards the "crowned" phthalocyanines than $Rb^+$, especially towards the 18-crown-6 and 21-crown-7 derivatives. This is in accordance with published data on the free crown ethers[4]. The driving force for complex formation is mainly the ion-dipole interaction, which is stronger for $Ba^{2+}$ than for $Rb^+$.

The barium-picrate complex of **1** was prepared in a similar

*Table I Free energies of binding ($-\Delta G^0$, kcal·mol$^{-1}$) of 1:1 metal picrate/crowned phthalocyanine complexes*[a].

| Compound | Metal ion | |
|---|---|---|
| | $Rb^+$ | $Ba^{2+}$ |
| $CuPc(15\text{-crown-}5)_4$ | 8.6 | > 9.3 |
| $CuPc(18\text{-crown-}6)_4$ | 9.8 | > 11.7 |
| $CuPc(21\text{-crown-}7)_4$ | 10.1 | > 13.5 |

[a] 1 Cal = 4.19 J.

way to that described for the alkali-metal-picrate complexes of **1**: compound **1** and barium picrate were mixed in a 1:4 molar ratio in dry chloroform/methanol (1:1, v/v). Immediately after mixing, a green precipitate was formed, and an appreciable amount of heat was evolved. The precipitate was isolated as described previously[1c]. Elemental analysis showed that only two-thirds of the added barium picrate had been incorporated in to the complex. The stoichiometry of the precipitate amounted to $\mathbf{1}\cdot(\mathrm{Ba}^{2+}\text{-picrate})_{2.7}$. The most likely reason for the observed fast complex formation is the high solubility of barium picrate in the chloroform/methanol mixture and the high binding affinity of the ion towards **1**.

*Table II Electrical conductivities (σ) at 180°C of crown-ether phthalocyanine* **1** *and of its metal picrate complexes.*

| Compound | $\sigma_{180°C} \times 10^7$ S·m$^{-1}$ |
|---|---|
| **1** | 5 |
| **1**·K$^+$ | 100 |
| **1**·Rb$^+$ | 3000 |
| **1**·Cs$^+$ | 700 |
| **1**·Ba$^{2+}$ | 0.1[a] |

[a] At 200°C.

Unexpectedly, the X-ray powder diffraction pattern of the isolated barium picrate complex showed that no ordering was present within the material. Only two diffuse halos, at spacings of ≈24 Å and ≈9 Å, were visible. AC impedance measurements revealed that the complex had a much lower electrical conductivity at 200°C ($\sigma = 10^{-8}$ S/m) than the monovalent metal picrate complexes of **1** (Table II). The electrical conductivity could not be measured accurately at lower temperatures. A similar low value was found for the barium-picrate complex of the 15-crown-5 derivative of **1**, which was prepared in a similar way.

These data suggest that a different kind of ordering exists in the complexes of crowned phthalocyanines with barium picrate as compared to those with, *e.g.*, rubidium picrate. This prompted us to study the complexation behaviour of Ba$^{2+}$ in more detail, using UV/Vis spectroscopy. This technique is a good tool to study the aggregation behaviour of the phthalocyanines[2]. The changes that occur in the absorption spectrum of compound **1** when Rb$^+$ or Ba$^{2+}$ is added, are shown in Figures 2 and 3. Dimerisation of the phthalocyanine occurs when large ions, such as Rb$^+$, are added. Such dimerisation can be detected by the decrease of the 675-nm band (monomeric band) and the increase of the 630-nm band (the dimer band), as shown in Figure 2A. Compound **1** shows a different behaviour when Ba$^{2+}$ is added (Figure 2B). The result is a decrease in the 675 nm band, while hardly any increase in the 630-nm band is observed. This suggests that no cofacial dimer is formed.

As can be seen from Figure 3, the effect of adding Ba$^{2+}$ or Rb$^+$ on the 675-nm band is similar for both ions, until an alkali metal ion (M) to "crowned" phthalocyanine **1** ratio (M/**1**) of 2 is reached. At higher M/**1** ratios, the 675-nm band increases again for Ba$^{2+}$, but not for Rb$^+$. The addition of larger amounts of Ba$^{2+}$ has little effect on the dimer band at 630 nm. This contrasts with the case of Rb$^+$ where an increase is visible. Similar behaviour was observed when Ba$^{2+}$ was added to the 15-crown-5 derivative of **1**.

A possible explanation of these phenomena is the following. *Lever* and *Kobayashi* have proposed that the formation of the cofacial dimer from "crowned" phthalocyanines proceeds by a step-wise process[2b]. In the concentration range $0 < \mathrm{M}/\mathbf{1} < 0.5$, one alkali metal ion binds to two phthalocyanines to give the non-cofacial dimer of type A (Figure 4)[2b]. In the concentration range $0.5 < \mathrm{M}/\mathbf{1} < 1.0$, a second alkali metal ion is bound and a non-cofacial dimer of type B is formed. Further increasing the alkali-metal-ion

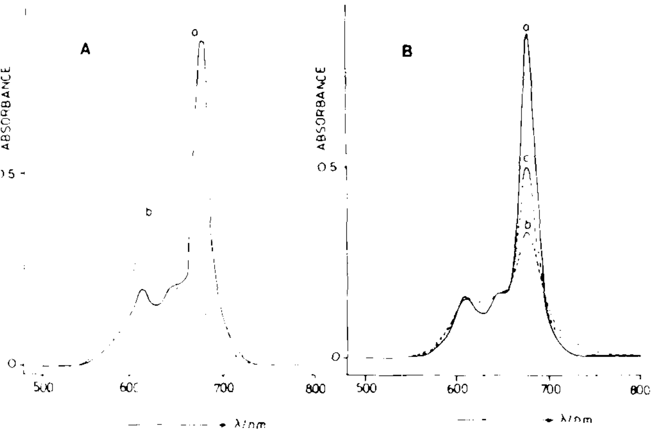


*Fig. 2. (A) Change in the absorption spectrum of* **1** *(CHCl$_3$) by the addition of Rb$^+$ picrate: (a) [Rb$^+$]/*$\mathbf{1}$ *= 0; (b) [Rb$^+$]/*$\mathbf{1}$ *= 2. (B) Change in the absorption spectrum of* **1** *(CHCl$_3$) by the addition of Ba$^{2+}$ picrate: (a) [Ba$^{2+}$]/*$\mathbf{1}$ *= 0; (b) [Ba$^{2+}$]/*$\mathbf{1}$ *= 2; (c) [Ba$^{2+}$]/*$\mathbf{1}$ *= 6.*

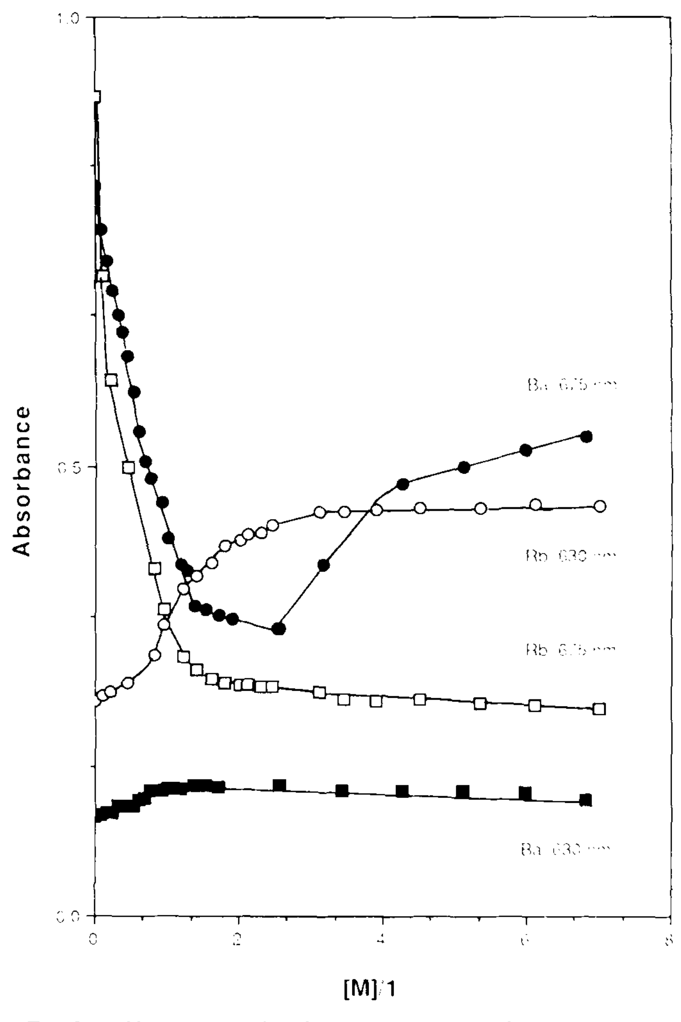


*Fig. 3. Change in absorbance at 675 and 630 nm as a function of the M/*$\mathbf{1}$ *ratio for Rb$^+$ and Ba$^{2+}$*

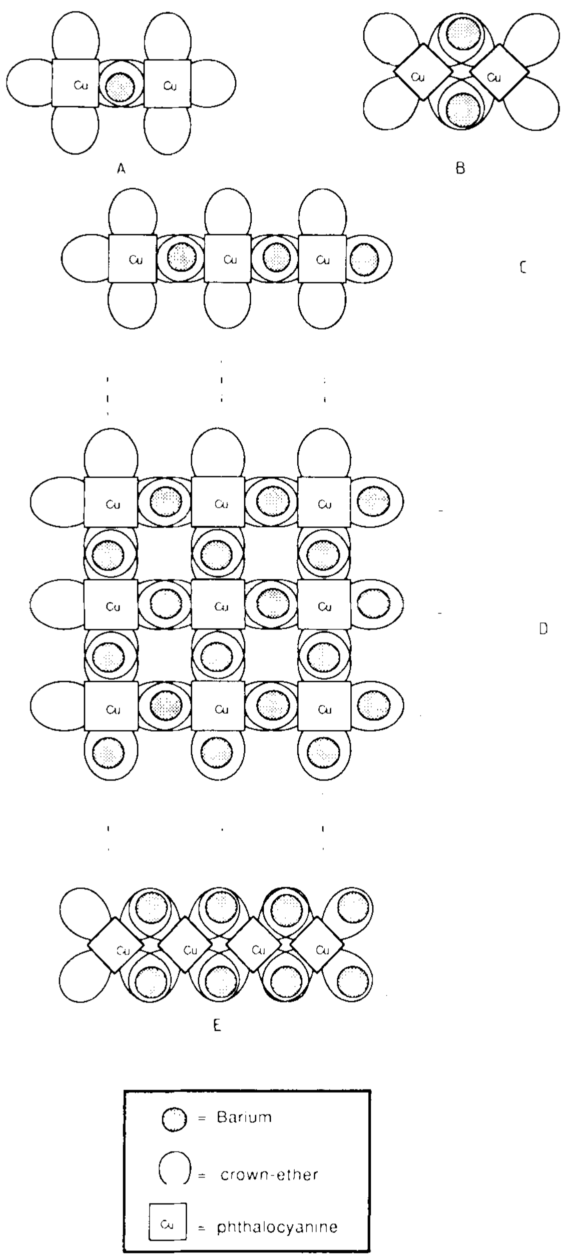


*Fig. 4. Possible structures obtained by the addition of barium picrate to* **1**.

concentration causes rearrangement of the non-cofacial form of dimer to the cofacial form. This takes place in the concentration range $1 < M/\mathbf{1} < 2$. Following this mechanism, the $Rb^+$ complex will undergo complete conversion from a non-cofacial to a cofacial dimer. The $Ba^{2+}$ complex first will have the structure presented in Figure 4A (concentration range $0 < Ba^{2+} < 0.5$). Upon increasing the $Ba^{2+}$ concentration until $[Ba^{2+}]/\mathbf{1} = 1$, the non-cofacial dimer presented in Figure 4B will be obtained. However, at this stage, the structure presented in Figure 4C cannot be excluded, *viz.*, a linear chain of crowned phthalocyanines that is cross-linked by $Ba^{2+}$. Further addition of $Ba^{2+}$ does not lead to a cofacial dimer. Apparently, the non-cofacial dimer is not able to rearrange to the cofacial form. Instead, cross-linked structures as shown in Figure 4D or 4E are obtained. The network presented in Figure 4D will be insoluble and will precipitate from solution (see below). In the range $2 < [Ba^{2+}]/\mathbf{1} < 4$, the cross-linked structures disintegrate, as can be concluded from the increase in intensity of the band at 675 nm. At the ratio $[Ba^{2+}]/\mathbf{1} = 4$, each crown/ether forms a complex with one $Ba^{2+}$. Since each $Ba^{2+}$ carries two picrate anions, aggregation in any from could be prevented by steric hindrance due to these picrate ions. The fact that the monomeric 675-nm band does not return to its initial absorbance may be the result of electronic effects originating from interactions of the picrate anions or $Ba^{2+}$ with the phthalocyanine macrocycle. Since the solid-state sample for the AC impedance measurements was prepared at much higher concentrations than used for UV/Vis spectroscopy, and since the product immediately precipitated after mixing, it is likely that this complex is a mixture of the structures presented in Figures 4D and 4E.These cross-linked structures may explain the low conductivity measured by AC impedance spectroscopy and the lack of ordering shown by X-ray powder diffraction.

The study presented in this paper shows that it is possible to control the organization of phthalocyanines by using different metal salts. Structures can be derived varying from potential electronic conductors to insulators. Further work along there lines is in progress.

## Experimental

The phthalocyanines substituted with 15-crown-5, 18-crown-6, and 21-crown-7 rings were prepared as described before[2a]. The barium picrate complexes were prepared as previously reported by us for the monovalent picrate complexes[1c]. UV/Vis spectra were recorded on a Perkin-Elmer 555 spectrometer. $CHCl_3$ was distilled before use; $CH_3OH$ was of spectrograde quality. AC impedance spectra and X-ray diffraction patterns were taken and analyzed as described previously[1c]. The $\Delta G^0$ values were determined by the picrate extraction technique from $H_2O$ into $CHCl_3$ at 25°C as described previously[5,6]. UV/Vis titration experiments were performed by adding small portions of $10^{-2}$M solutions of the picrate salts in methanol with a micropipette to 5 ml of $10^{-5}$M solutions of crown-ether phthalocyanines in chloroform.

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