Polytopic Ligand Systems: Synthesis and Complexation Properties of a 'Crowned' Phthalocyanine†

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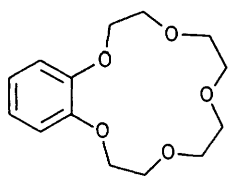
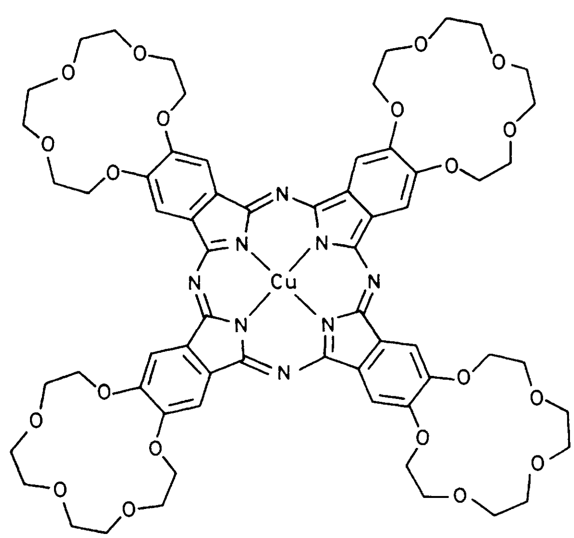
The synthesis is described of a phthalocyanine that contains four 15-crown-5 rings; K^+ ions induce dimerization of the phthalocyanine, whereas Li^+ and $Bu^tNH_3^+$ ions do not.

We designed the polytopic ligand (**2**) as part of a programme aimed at the development of multifunctional catalysts and carrier systems from easily accessible host molecules. Compound (**2**) contains a metal centre that is complexed by a phthalocyanine ring and four crown ether binding sites. Its synthesis and binding properties are described.

Benzo-15-crown-5 (**1**)[1] was brominated (Fe–Br_2, solvent CH_2Cl_2) to give 4,5-dibromobenzo-15-crown-5 in 65% yield. The latter compound (1.0 mmol) was refluxed for 20 h with CuCN (5 mmol) in *N,N*-dimethylformamide (1.5 dm^3). A small amount of pyridine (0.1 dm^3) was added as a catalyst. After work-up (aqueous ammonia, extraction with chloroform) the solid residue was subjected to column chromatography (neutral alumina, eluant $CHCl_3$–MeOH, 10:1 v/v). Compound (**2**) was obtained as a green, almost black powder in 35% yield (m.p. > 200 °C).‡



(**1**)



(**2**)

The complexation properties of compound (**2**) were evaluated by u.v.–visible spectroscopy. The free host shows a spectrum which is characteristic for a monomeric copper phthalocyanine.[2] On addition of KBr this spectrum changes and a new spectrum, attributable to dimeric phthalocyanine appears (Figure 1, inset). On increasing the concentration of

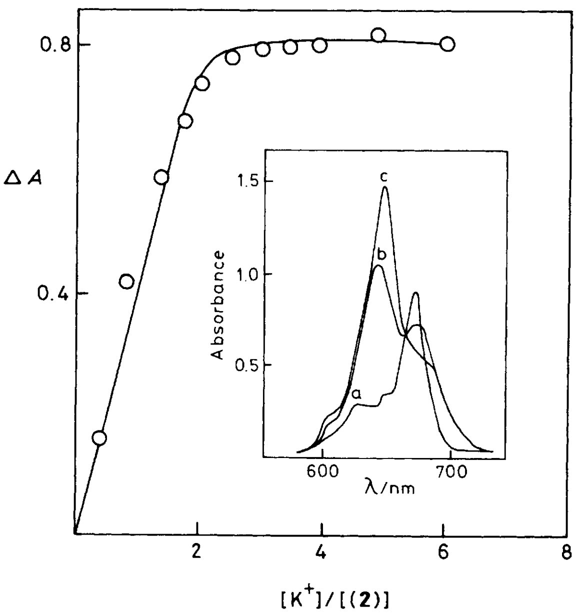


Figure 1. Absorbance increase, Δ*A*, *vs.* ratio of cation to crown–phthalocyanine. Inset: visible absorption spectra of (a) host (**2**) in chloroform (10^{-5} mol dm^{-3}), (b) (**2**) +1.5 equiv. of KBr and (c) (**2**) +6 equiv. of KBr.

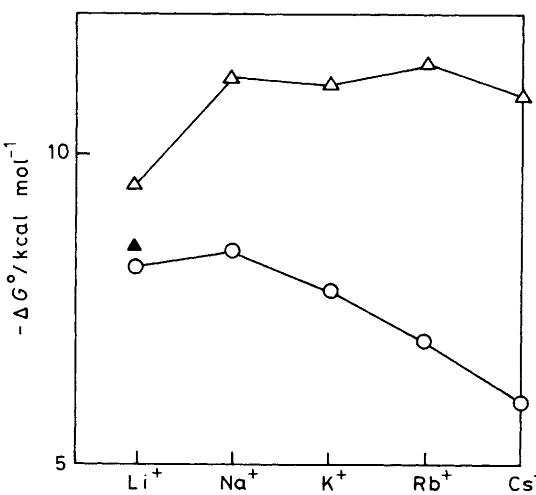


Figure 2. Free energies of binding of picrate salt guests to host (**1**) (1:1 complex, (○) and to host (**2**) (2:1 complex: △; 1:1 complex ▲).

† Since the submission of this communication, related work was published by A. R. Koray, V. Ahsen, and O. Bekaroglu, *J. Chem. Soc., Chem. Commun.*, 1986, 932. The preceding communication submitted independently, also reports related work.

‡ Compound (**2**) gave analytical and spectroscopic data consistent with its structure.

KBr the spectrum of monomeric phthalocyanine gradually disappears. A plot of the increase in absorption at 630 nm as a function of the amount of added KBr (Figure 1) shows an inflection point at a K^+ to phthalocyanine ratio of *ca.* 2:1. This indicates that the crown ether rings of (**2**) and K^+ ions form complexes of stoicheiometry 8:4 (host:guest). Adding Li^+ and t-butylammonium ions to (**2**) did not change the u.v.–visible spectrum of this compound. From this we assume that these ions form 4:4 complexes with (**2**).

The free energies of complexation ($-\Delta G^\circ$) for a number of cations by host molecules (**1**) and (**2**) were determined by the picrate extraction method.[3] Figure 2 compares the apparent $-\Delta G^\circ$ values (kcal mol^{-1}§) for Li^+, Na^+, K^+, Rb^+, and Cs^+ picrate complexes of (**2**), assuming 2:1 complexation, with those of (**1**), which forms 1:1 complexes.¶ The latter compound displays the normal binding profile for this type of host, *i.e.* the $-\Delta G^\circ$ values become smaller when the diameter of the guest molecule increases. Compound (**2**), however, shows a different behaviour. It has a high affinity for Na^+, K^+, Rb^+, and Cs^+ ions, with little or no structural recognition within the series, but a relatively low affinity for Li^+ ions. This binding profile supports the idea that large ions induce dimerization of the phthalocyanine rings.

A number of possible applications can be envisaged for molecule (**2**), for instance in the field of catalysis (*e.g.* binding of substrate molecules to the crown ether rings and reaction with ligands co-ordinated to the metal centre) and in the field of ion transport. Regarding the latter application, it is of interest that metal phthalocyanines (Pc) with suitable ligands L (–O–, CN^-, pyrazine) will readily form cascade complexes of the type $[Pc–L–Pc–L]_n$.[4] For (**2**) this will lead to stacking of the crown ether rings and the formation of extended channels. Such channels can bind and transport ions as we have shown previously.[5] Work along these lines is in progress and details will be published in a full paper.

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§ 1 cal = 4.184 J.

¶ Compound (**1**) [$K \times 10^{-5}/(dm^3\ mol^{-1})$, $-\Delta G^\circ$/kcal mol^{-1} for 1:1 complex]: Li^+, 11, 8.2; Na^+, 14.5, 8.4; K^+, 6.5, 7.9; Rb^+, 1.4, 7.0; Cs^+, 0.3, 6.1; Li^+–(**2**) complex: 25, 8.7; compound (**2**) [$K \times 10^{-7}/(dm^3\ mol^{-1})^2$, $-\Delta G^\circ$/kcal mol^{-1} for 2:1 complex]; Li^+, 1.1, 9.6; Na^+, 18, 11.3; K^+, 16, 11.2; Rb^+ 23, 11.4; Cs^+ 9.0, 11.0.

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