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

Ron Hendriks, Ot E. Sielcken, Wiendelt Drenth, and Roeland J. M. Nolte*
Department of Organic Chemistry, University at Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands

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'NH₃⁺ 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–Br₂, solvent CH₂Cl₂) 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 dm³). A small amount of pyridine (0.1 dm³) was added as a catalyst. After work-up (aqueous ammonia, extraction with chloroform) the solid residue was subjected to column chromatography (neutral alumina, eluant CHCl₃-MeOH, 10:1 v/v). Compound (2) was obtained as a green, almost black powder in 35% yield (m.p. > 200°C).‡

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. On addition of KBr this spectrum changes and a new spectrum, attributable to dimeric phthalocyanine appears (Figure 1, inset). On increasing the concentration of

† 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.

Figure 1. Absorbance increase, ΔA, 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: Δ; 1:1 complex ▲).
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 stoichiometry 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. 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.$^\ddagger$ 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 (Pe) with suitable ligands L (--O–, CN–, pyrazine) will readily form cascade complexes of the type [Pe-L-Pc-L]$_n$. 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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References

Regiospecific Synthesis of Terminal, Oxyfunctionalized Methyl Ketone Enamines via Catalytic Aminomercuriation of Prop-2-ynyl Esters and Ethers
José Barluenga,* Fernando Aznar, Ramón Liz, and Carmen Postigo
Departamento de Química Orgánica, Facultad de Química, Universidad de Oviedo, 33071 Oviedo, Spain

Catalytic aminomercuriation of 1-substituted prop-2-ynyl esters and ethers (5) provides a mild, simple, and regiospecific route to the terminal functionalized enamines (6) despite the fact that they are potentially isomerisable to their internal form; hydrolysis of (6) furnishes α-oxyketones (7).

Enamines$^1$ derived from alkyl methyl ketones, obtained by a variety of methods, have usually been reported to exist as a mixture of isomers differing in the terminal (1) or internal (3) double bond position.$^2$ In fact, apart from a series of enol ether- and enol sulphide-enamines (3) and (4), recently prepared by us via catalytic aminomercuriation of prop-2-ynyl ethers and sulphides,$^3$ only some isolated instances are known in which the location of the double bond is unambiguous [e.g., (1a)$^{26}$ (2a)$^4$]. Since both electronic and steric factors$^{27,5}$ seem to influence the regiosomer distribution, we decided to employ the more hindered 1-substituted prop-2-ynyl esters and ethers (5) as unsaturated substrates in catalytic aminomercuriation processes.$^6$

When a 1-substituted prop-2-ynyl ester or ether (5) was treated with an excess of piperidine or morpholine, in the presence of mercury(ii) acetate as catalyst, the corresponding $\beta'$-oxy substituted enamine (6) was regiospecifically obtained, the internal isomer not being detected in the crude reaction mixture, according to the $^1$H n.m.r. spectra (90 MHz)$^6$

$\ddagger$ Compound (1) [K × 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 × 10$^{-5}$/(dm$^3$ mol$^{-1}$)], $-\Delta G^\circ$/kcal mol$^{-1}$ for 2:1 complex: Li$^+$, 11, 9.6; Na$^+$, 18, 11.3; K$^+$, 16, 11.2; Rb$^+$, 23, 11.4; Cs$^+$, 9.0, 11.0.

§ 1 cal = 4.184 J.

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† In some instances, ca. 5% of the corresponding acetamide was observed as by-product.