A Copper Phthalocyanine with Four Crown Ether Voids†

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A copper phthalocyanine with four crown ether voids has been synthesized; its high tendency towards aggregation, especially K+-induced aggregation, which enables the phthalocyanine to be used as a colorimetric reagent, is reported.

Several reports have appeared on the chemistry of porphyrins with crown ether voids.[1—3] We present here the first example of a phthalocyanine analogue, compound (1), and its high tendency towards aggregation by solvents and cations. In particular, as shown below, K+-triggered aggregation of (1) makes it attractive as a colorimetric reagent for concentrations of K+ as low as 10^{-8} M. This system is one of the most sensitive yet for the quantitative, specific estimation of potassium by colorimetric means.

The dibromo compound (2)‡ was prepared by the bromination[4] of benzo-15-crown-5.[5] Treatment of (2) with a large excess of CuCN[6] gave (1) in 49% yield as a greenish blue powder. Unexpectedly, the solubility of (1) in normal organic solvents was not high, and decreased in the order: CHCl₃ (8.3 mM) > CH₂Cl₂ (6.1 mM) ≫ N,N-dimethylformamide, dimethyl sulphoxide, toluene, benzene, tetrahydrofuran, and ethyl acetate (<0.01 mM).
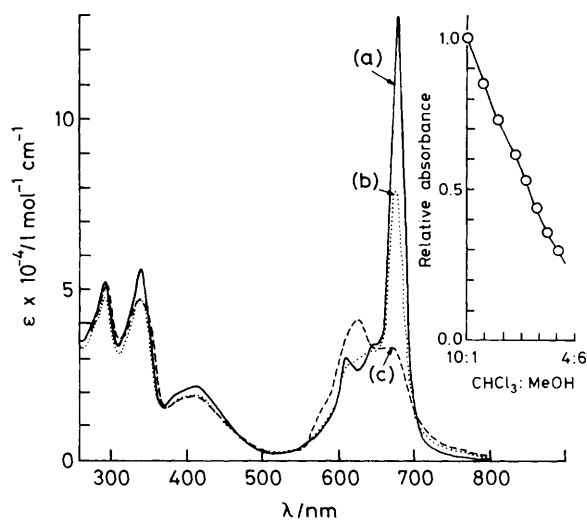
Figure 1 shows the absorption spectra of (1) in various solvents. The absorbance at 676 nm changes dramatically with change of solvent (see also the inset) and the concentration of

(1). Assuming that the bands around 676 and 630—640 nm are due to monomeric and aggregated species, respectively,[7] the aggregated forms prevail over the monomeric form even at *ca.* 10^{-6} M in all solvents except CHCl₃ and CH₂Cl₂.


(1)

(2)

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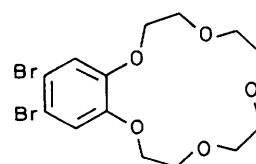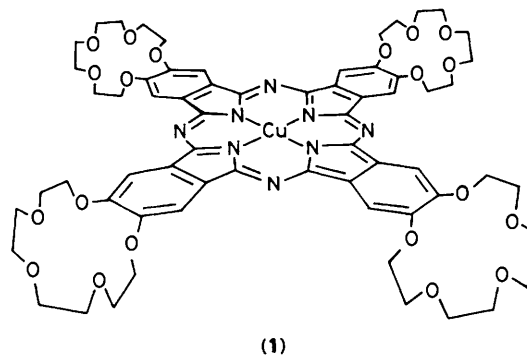
† Since the submission of this communication, related work was published by A. R. Koray, V. Ahsen, and O. Bekaroglu, *J. Chem. Soc., Chem. Commun.*, 1986, 932. The following communication submitted independently also reports related work.

‡ All new compounds gave satisfactory elemental, i.r., and n.m.r. data.

Figure 1. The u.v.–visible absorption spectra of (1) in (a) $CHCl_3$, (b) CH_2Cl_2, and (c) toluene–MeOH (8:2 v/v). The inset shows the relative absorbance at 676 nm for various $CHCl_3$–MeOH mixtures. The absorbance in $CHCl_3$ is set at unity. [(1)] = 7.53×10^{-6} M.
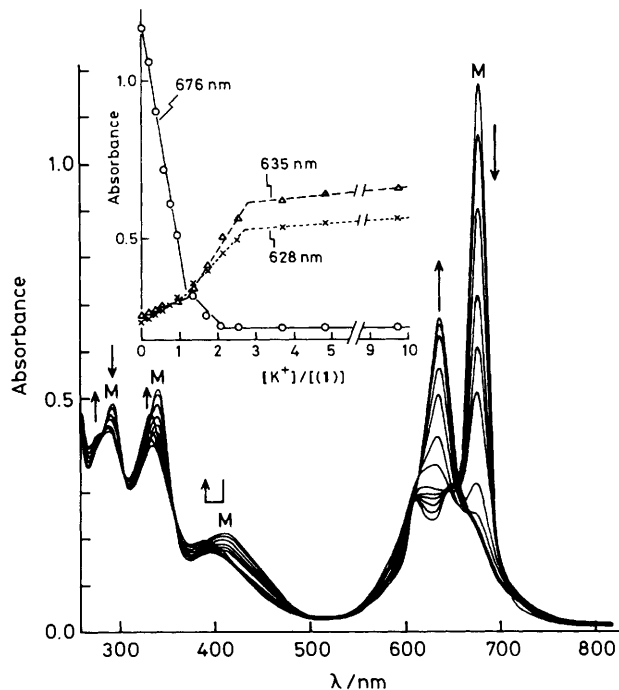
Figure 2. Spectral change of (1) observed on addition of $MeCO_2K$. To 3 ml of a $CHCl_3$ solution of (1) in a 10 mm cell {[(1)] = 8.99×10^{-6} M}, $MeCO_2K$ dissolved in $CHCl_3$–MeOH (95:5 v/v) was added using a microsyringe. Finally, 50 μl was added. M = monomer peak. Arrows indicate the direction of the spectral changes. The inset shows the dependence of absorbance on [K⁺]/[(1)] for several wavelengths.

The changes in the absorption spectrum of (1) in $CHCl_3$ on addition of $MeCO_2K$ are presented in Figure 2. They are clearer and larger in this system than in the porphyrin system.[2]

As shown in the inset, aggregation proceeds in three steps,§ and at [K⁺]/[(1)] < ~4, the final state was attained.¶ If $MeCO_2NH_4$ was used instead of $MeCO_2K$ for the same concentration of (1) as that in Figure 2, the 1st, 2nd, and 3rd steps occurred for [NH₄⁺]/[(1)] ranges of ca. <200, 300—2000, and >3000, respectively. With $MeCO_2Na$, the 1st and 2nd steps occurred for [Na⁺]/[(1)] ranges of <2 and 3—8, respectively, the 3rd step not being observed owing to experimental limitations. Thus, there is no clear correlation between the [cation]/[(1)] ratio and the attainment of the final aggregated forms.‖ However, the influence of cations in promoting the aggregation of (1) in this way is quite obvious.

The mechanism of the above solvent- or cation-induced aggregation is not clear at present. However, it is clear at least that the presence of crown ether void is necessary for the phenomenon, since similar behaviour was not observed for phthalocyanines without the crown ether unit. In particular, we confirmed separately that the K⁺-induced aggregation as observed in Figure 2 could be maintained even at [(1)] = ca. 10^{-8} M. This means, if the linear absorbance change at 676 nm were used {region of [K⁺]/[(1)] ≤ 1}, that concentrations of K⁺ ions of the order of 10^{-8} M can be detected almost quantitatively spectrophotometrically. The large ε (ε_{676} = 129 400 in $CHCl_3$) and the rapid complexation of (1) with K⁺ make it attractive for the colorimetric determination of K⁺ ion.

We thank Prof. H. Yokoi for his courtesy in measuring e.s.r. spectra.

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§ Changes in the position of isosbestic points also clearly demonstrate this. For example, the isosbestic point at 370 nm is that from the 1st to the 2nd step, and that at ca. 418 nm is that from the 2nd to 3rd step.

¶ In order to deduce the state of (1) in solution, its e.s.r. spectra were recorded in $CHCl_3$ in the absence and presence of K⁺. However, (1) existed mostly as an oligomer or polymer even in the absence of K⁺ at e.s.r.-detectable concentrations (≥0.1 mM). Signals of the dimer[8] were recognized, but they were weak. The blue shift of the absorption peaks accompanying the addition of K⁺ (Figure 2) can tentatively be explained by purely excitonic interaction on cofacial dimer formation.[9]

‖ In the case of porphyrins with four 15-crown-5 voids, dimer formation was detected at [K⁺]/[porphyrin] = ~2. Also, it was reported that Na⁺ had no effect on dimer formation.[2]