Synthesis and Properties of a (Phthalocyaninato)copper(II) Complex Symmetrically Substituted with Eight Crown Ethers

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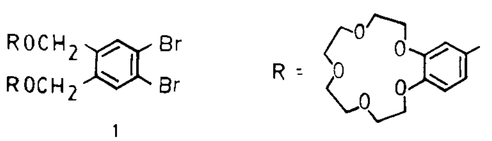
A soluble (phthalocyaninato)copper(II) complex containing eight symmetrical benzo-15-crown-5 substituents, namely {2,3,9,10,16,17,23,24-octakis[[benzo-15-crown-5)-4′-yl]oxymethyl]phthalocyaninato}copper(II) (**2**) from 1,2-bis{[(benzo-15-crown-5)-4′-yl]oxymethyl}-4,5-dibromobenzene (**1**) and CuCN in quinoline or pyridine was synthesized. The crown-ether groups in **2** were shown to prefer intramolecular complexation with alkali metal ions.

The solubility and ion-binding property of phthalocyanines containing crown ethers are receiving considerable attention in view of their effects on aggregation of the molecules[1-6]. It has recently been demonstrated that phthalocyanines substituted with four 15-crown-5 moieties are capable of forming ion channels allowing the migration of alkali or alkaline earth cations[7]. Phthalocyanines with long alkyl or alkoxy groups as well as with crown ethers are also reported to form a new type of liquid crystals, namely the discotic mesophases[7-9].

The alkyl substitution increases the solubility of phthalocyanines, and the effect of bulkyl substituents is shown to be higher than that of the smaller ones, e.g. methyl[10]. Substitution of a phthalocyanine with eight crown ether groups, therefore, is expected to enhance the solubility and improve the intermolecular stacking. In this paper we describe the synthesis and properties of a copper phthalocyanine with eight benzo-15-crown-5 moieties as the first example of a new type of phthalocyanines.

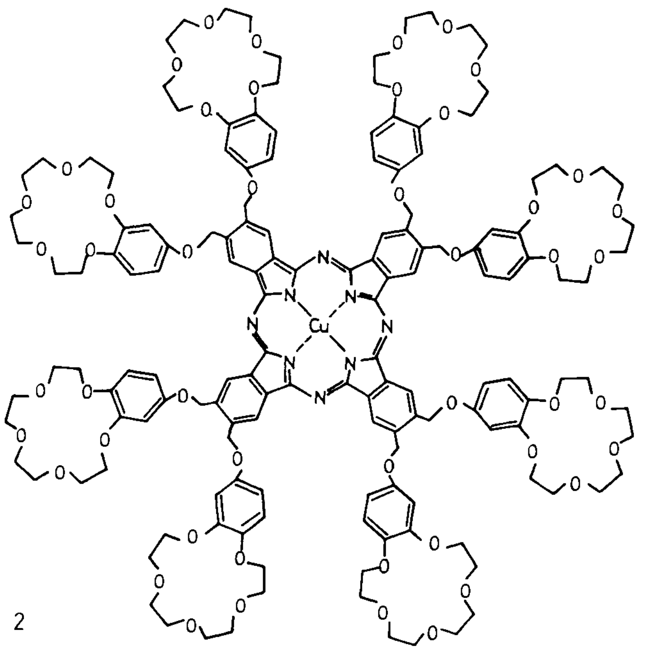
Results and Discussion

1,2-Bis{[(benzo-15-crown-5)-4′-yl]oxymethyl}-4,5-dibromobenzene (**1**), obtained by condensation of 4′-hydroxybenzo-15-crown-5[11] with 4,5,α,α′-tetrabromo-*o*-xylene, was treated with CuCN in refluxing quinoline under argon for 4 h to yield 2,3,9,10,16,17,23,24-octakis[[(benzo-15-crown-5)-4′-yl]oxymethyl]phthalocyaninato}-copper(II) (**2**). The reaction of **1** with CuCN in pyridine in a sealed glass tube at 200°C gave the same product **2**. Crude **2** was dissolved in dichlormethane and isolated by column chromatography on alumina. The yield of the dark green product was 37%.



1

The structures of dibromo compound **1** and phthalocyanine **2** were confirmed by elemental analyses and IR, ^{1}H-NMR, and UV/VIS spectra.



2

The visible portion of the spectrum of **2** was solvent-dependent; while the single intense π→π* transition (Q band) was observed at 690 nm and a shoulder at 650 nm in chloroform, they were shifted to 685 and 632 nm in pyridine. This change in the spectra can be attributed to monomeric and oligomeric phthalocyanine species, the latter being more favorable in polar solvents[1,2,4].

In order to see the effect of alkali cations on the aggregation behavior of the phthalocyanine crowns by visible spectra, **2** was dissolved in dichloromethane, and the metal salt (LiCl, NaSCN, KSCN), dissolved in ethanol, was added. In contrast to the blue shifts obtained with the tetrakis(crown ether)-substituted phthalocyanines[1,2,4], there was no observable change in the spectra due to the various metal ions. Especially with K^+, which prefers formation of sandwich-type complexes with benzo-15-crown-5 units, these results can be regarded as the indication for an intramolecular complexation of crown ether units rather than for intermolecular phthalocyanine dimers.

The alkali ion binding ability of **2**, having eight crown ether units, was estimated by solvent extraction of alkali metal picrates from water to chloroform. Examination of the data revealed the highest affinity to potassium among the other cations in the order $K^+ > Na^+ > Rb^+ > Cs^+ > Li^+$.

The physicochemical characterization of the mesogenic properties of **2** and related compounds will be the object a forthcoming publication.

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Experimental

Benzo-15-crown-5[12], 4'-hydroxybenzo-15-crown-5[11], and 1,2-dibromo-4,5-bis(brommethyl)benzene[13] were prepared by reported procedures. The alkali picrate extractions were carried out as given in the literature[2,14].

1,2-Bis{[(benzo-15-crown-5)-4'-yl]oxymethyl}-4,5-dibromobenzene (**1**): To a solution of 4'-hydroxybenzo-15-crown-5 trihydrate (5.0 g, 14.8 mmol) 40 ml of ethanol was added dropwise within 15 min under nitrogen an equivalent amount of NaOH, dissolved in 150 ml of ethanol. The mixture was kept at 40°C for further 40 min. After dropwise addition of a solution of 1,2-dibromo-4,5-bis(bromomethyl)benzene (3.12 g, 7.4 mmol) in 70 ml of ethanol, the mixture was stirred at 60°C for 24 h. Then the solvent was evaporated under reduced pressure, and the residue was treated with 80 ml of chloroform. The chloroform layer was washed with water (40 ml) three times and then dried with Na_2SO_4. The solvent was evaporated and the oily product was dissolved in 100 ml of ethanol, from which a white precipitate was obtained by the addition of petroleum ether. Yield 2.67 g (44%), m.p. 128°C. – IR (KBr): 3070 cm^{-1} (CH aromat.), 2920–2870 (CH aliphat.), 1260–1220 (Ar–O–C), 1180–1125 (C–O–C), 620 (C–Br). – ^1H-NMR ($CDCl_3$): δ = 7.7 (2H, s, Ar-H), 6.82–6.38 (6H, m, Ar-H), 4.98 (4H, s, Ar–CH_2), and 4.11–3.70 (32H, m, CH_2O).

$C_{36}H_{44}O_{12}Br_2$ (828.5) Calcd. C 52.18 H 5.35
Found C 51.92 H 5.48

{2,3,9,10,16,17,23,24-Octakis[[(benzo-15-crown-5)-4'-yl]oxymethyl]phthalocyaninato}copper(II) (**2**): A mixture of **1** (0.20 g, 0.242 mmol), CuCN (0.057 g, 0.636 mmol), and quinoline (0.25 ml) was heated and stirred at 220°C for 4 h under argon. (When pyridine was used as solvent instead of quinoline, the reaction was carried out in a sealed tube at the same temp. for 2.5 h.) After the dark green product was cooled to 40°C, methanol (10 ml) was added, and the mixture was stirred at this temp. for further 30 min and filtered. After having been washed with methanol and ethyl acetate to remove the unreacted organic material, the precipitate was dissolved in dichloromethane (50 ml), the solution was filtered, and the filtrate evaporated to a smaller volume (ca. 10 ml). Flash chromatography of the condensed residue on Al_2O_3 with chloroform/methanol (50:1) as eluant gave 0.070 g (37%) of **2** as dark green powder, m.p. >250°C. – IR (KBr): 3070 cm^{-1} (CH aromat.), 2920–2870 (CH aliphat.), 1640 (C=N), 1260–1220 (Ar–O–C), 1180–1125 (C–O–C), 750 (CH). – UV-VIS (chloroform): λ_{max} (log ε) = 311 nm (4.925), 348 (4.966), 650 (4.641), 690 (4.882).

$C_{152}H_{176}CuN_8O_{48}$ (2946.5) Calcd. C 61.95 H 6.02 N 3.80
Found C 61.60 H 5.78 N 3.97

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[256/88]