Novel Phthalocyanines with Aza Crown Ether Moieties

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Received January 17, 1989

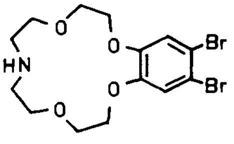
Key Words: Aza crown ethers / (Phthalocyaninato)copper complex / Phthalocyanines, water-soluble

A monoaza crown ether substituted (phthalocyaninato)copper(II) complex 2 and its water-soluble quaternary ammonium salt 3 were prepared from the corresponding dibromomonoaza crown ether derivative 1 and CuCN in pyridine.

Phthalocyanines substituted with crown ether groups have been shown to form discotic mesophases and ion channels for alkali metal cations[1]. At the same time, these compounds have become soluble in common organic solvents as a result of this substitution[2-4]. Monoaza crown ethers have been investigated extensively for their capability of forming branched macrocycles through nitrogen pivot atoms[5,6]. Consequently, the synthesis of monoaza crown ether substituted phthalocyanines will be interesting from two points of view: 1) To compare these new compounds with the previously reported crown ether substituted ones[1-4]. 2) To obtain new phthalocyanines with further substitution of the aza group.

In this communication, the synthesis and properties of monoaza crown ether substituted phthalocyanine and its water-soluble quaternary ammonium salt are described.

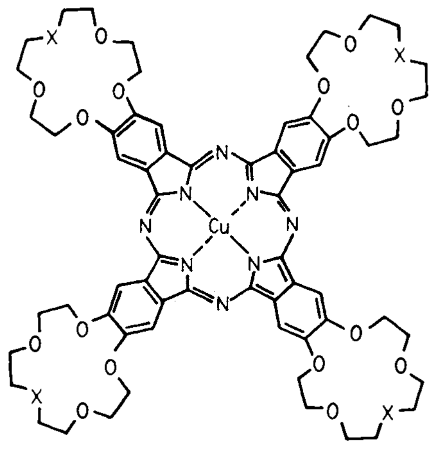
2,3,5,6,8,9,11,12-Octahydro-7*H*-1,4,10,13,7-benzotetraoxaazacyclopentadecine (monoazabenzo-15-crown-5), prepared according to the literature procedure[5], was brominated in acetic acid to obtain the dibromo derivative **1** which was treated with excess CuCN in pyridine in a sealed glass tube at 205–210°C for 3 h to obtain the *N*-unsubstituted phthalocyanine **2**. Methylation of **1** with dimethyl sulfate[7] gives the quaternary ammonium salt which forms the new phthalocyanine **3** with CuCN in pyridine. The common feature of these two phthalocyanines is that both of them are soluble in DMSO, but the extraordinarily high solubility of **3** in water should be especially mentioned.



1

The visible absorption spectra of the phthalocyanines **2** and **3** in DMSO are very similar with an intense Q band around 680 nm. In water, the spectrum of **3** changes, and a new band appears at 635 nm which can be ascribed to the presence of dimeric species. Addition of an alkali metal salt, e. g. KSCN or NaSCN, to a solution of **3** in water causes no appreciable difference in the visible spectra, probably due to the high solvation effect of water and the positively charged N atom in the macrocyclic ring.

The thermal properties of phthalocyanine **2** with initial and main decomposition points around 285 and 360°C are very similar to the previously reported *all*-oxa crown ether substituted phthalocyanines[3]. The insolubility of **2** in water-immiscible solvents such as chloroform or dichloromethane hindered alkali metal extraction experiments from aqueous phase to organic phase[3,8].



2: X = NH
3: X = $N^{\oplus}(CH_3)_2 \cdot CH_3SO_4^{\ominus}$

Further studies are under progress to synthesize new phthalocyanines with *N*-alkyl substituents of changing length.

Experimental

Synthesis of Phthalocyanine **2**: A mixture of **1** (1.50 g, 3.53 mmol), CuCN (0.84 g, 9.28 mmol), and pyridine (3 ml) was fused in a glass tube by gentle heating; after cooling the tube was sealed. The mixture was heated at 205–210°C for 3 h. After cooling to room temp., the dark green mixture was treated with ethanol (10 ml), and the crude product was precipitated. It was suction-filtered and washed with ethanol and diethyl ether to remove any organic residue. The product was further purified by dissolving in H_2SO_4 (15 ml, 90%) and reprecipitating by the addition of ice/water; yield 0.33 g (28%). – IR (KBr): $\tilde{\nu}$ = 3230 cm^{-1}, 2950, 2920, 1605, 1475, 1385, 1290, 1200, 1110, 1030, 930, 745, 620. – UV-VIS (DMSO): λ_{max} (lg ε) = 688 (4.67), 618 (4.24), 416 (4.47), 340 (4.68), 313 (4.71), 291 (4.78).

$C_{64}H_{76}CuN_{12}O_{16}$ (1333) Calcd. C 57.67 H 5.75 N 12.61
Found C 57.55 H 5.52 N 12.64

Preparation of the Quaternary Ammonium Salt of **1**: A 100-ml flask was charged with (5,6-dibromobenzo)monoaza-15-crown-5 (**1**)

(1.70 g, 4 mmol), Na_2CO_3 (0.86 g, 8 mmol), CH_3CN (15 ml), and dimethyl sulfate (1.30 g, 10 mmol) and stirred at reflux for 6 h during which time the reaction progress was followed with TLC for the decrease in **1**. Then the mixture was cooled to room temp., filtered, and the filtrate was evaporated to dryness. The residue was swirled with CH_2Cl_2 (30 ml), cooled, filtered, and the solvent was evaporated. Addition of dry acetone (15 ml) to the orange oily residue gave a white precipitate, which was filtered and washed with cold dry acetone and dried i. vac. The yield of the hygroscopic product was 1.80 g (80%), m. p. 105 – 107 °C. – IR (KBr): $\tilde{\nu}$ = 2930 cm^{-1}, 2880, 1580, 1500, 1250 – 1200, 1130, 1010, 910, 755, 650, 590. – ^{1}H-NMR ($CDCl_3$): δ = 7.04 (s, 2H), 4.14 – 4.03 (m, 11H), 3.94 – 3.83 (m, 8H), 3.29 (s, 6H).

$C_{17}H_{27}Br_2NO_8S$ (565.3) Calcd. C 36.12 H 4.81 N 2.48
Found C 35.96 H 4.79 N 2.16

Synthesis of **3**: A mixture of the quaternary ammonium salt of **1** (0.59 g, 1.05 mmol), CuCN (0.25 g, 2.80 mmol), and pyridine (1 ml) was fused in a glass tube by gentle heating; after cooling, the tube was sealed and then heated at 205 – 210 °C for 1 h. After cooling to room temp., the product was precipitated by the addition of ethanol (10 ml). The precipitate was collected by suction and then treated with a solution of NaCN in water/ethanol (1 : 2) to remove excess CuCN. Finally, the crude product was dissolved in DMSO, filtered, and precipitated with ethanol. The green precipitate was suction-filtered, washed with ethanol and diethyl ether, and dried; yield 0.11 g (22%). This compound was soluble in water and DMSO. – IR (KBr): $\tilde{\nu}$ = 2925 cm^{-1}, 2880, 1605, 1505, 1475, 1405, 1355, 1280, 1205, 1110, 1060, 930, 740, 580. – UV-VIS (DMSO): λ_{max} (lg ε) = 675 (4.88), 648 (4.37), 606 (4.33), 418 (4.35), 353 (4.62), 289 (4.68), 248 (5.60). – UV-VIS (water): λ_{max} (lg ε) = 680 (4.37), 635 (4.42), 410 (4.31), 335 (4.60), 297 (4.59).

$C_{76}H_{108}CuN_{12}O_{32}S_4$ (1894) Calcd. C 48.21 H 5.75 N 8.88
Found C 48.11 H 5.68 N 8.19

CAS Registry Numbers

1: 119877-79-1 / **1** (quanternary ammonium salt): 119877-81-5 / **2**: 119877-82-6 / **3**: 119877-84-8 / CuCN: 544-92-3 / dimethyl sulfate: 77-78-1

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[1] C. Sirlin, L. Bosio, J. Simon, V. Ahsen, E. Yılmazer, Ö. Bekâroğlu, *Chem. Phys. Lett.* **139** (1987) 362.

[2] A. R. Koray, V. Ahsen, Ö. Bekâroğlu, *J. Chem. Soc., Chem. Commun.* **1986**, 932.

[3] V. Ahsen, E. Yılmazer, M. Ertaş, Ö. Bekâroğlu, *J. Chem. Soc., Dalton Trans.* **1988**, 401.

[4] S. Sarıgül, Ö. Bekâroğlu, *Chem. Ber.* **122** (1989) 291.

[5] H. Maeda, S. Furuyoshi, Y. Nakatsuji, M. Okahara, *Bull. Chem. Soc. Jpn.* **56** (1983) 212.

[6] R. A. Schultz, D. M. Dishong, G. W. Gokel, *Tetrahedron Lett.* **22** (1981) 2623.

[7] *Methoden der Organischen Chemie* (Houben-Weyl-Müller), Vol. 11/2, p. 594, Georg Thieme Verlag, Stuttgart 1970.

[8] A. H. Haines, I. Hodgkisson, C. Smith, *J. Chem. Soc., Perkin Trans. 1*, **1983**, 311.

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