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Preliminary Communication

Crystal Structure and Silver Ion Complexation of a Novel Porphyrazine Substituted with Four Dithiacrown Ether Rings

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Abstract. The synthesis of magnesium porphyrazines substituted with sulfur-containing 15-crown-5 and 18-crown-6 macrocycles is reported as well as the single crystal structure of the 18-crown-6 substituted porphyrazine; the larger crown ether compound is shown to form dimers with Ag⁺ ions, unlike the porphyrazine with the smaller crown ether rings.

Supramolecular structures from phthalocyanine and porphyrin building blocks are currently receiving great interest. As part of our program aimed at the development of conducting materials from such structures, we describe here the first synthesis and metal ion binding properties of novel porphyrazines 1(n) (n=1, 2) substituted at the β-positions with crown-ether rings. In addition, we present the first X-ray structure of a crowned porphyrin/phthalocyanine type of molecule.

The crown ether precursors 2(1) and 2(2) were prepared from sodium cis-1,2-dicyano-1,2-ethylenedithiolate 8 and tetraethyleneglycol-dichloride (11% yield) and pentaethyleneglycol-dichloride (23% yield), respectively, according to a slightly modified literature procedure. To a boiling suspension of 5 mmol magnesium in 10 mL n-propanol was added a solution of 1 mmol of 2(n) in 10 mL rt-propanol and the reaction mixture was refluxed for 18 h. The product was isolated and purified by washing with acetone and dry diethylether and subsequently by column chromatography (NaBr impregnated silica, eluent 2% MeOH in CHCl₃ for 1(1), and 10% MeOH in CHCl₃ for 1(2)). Compounds 1(1) and 1(2) were obtained as dark blue powders in yields of 22% and 20%, respectively (m.p. > 320 °C). Single crystals of 1(2) were grown from CHCl₃/MeOH (1:1). X-ray data were collected on an Enraf-Nonius Cad4-T/rotating anode diffractometer [MoKα (Mon); 150 K]. The compound crystallized in a triclinic unit cell, space-group P1, a = 9.584(3) Å, b = 17.672(2) Å, c = 19.620(4) Å, α = 84.904(14)°, β = 85.21(2)°, γ = 89.29(2)°, V = 3298.3(13) Å³, Z = 2. The structure was solved with SIR92 and refined using SHELXL92, resulting in R1 = 0.093, wR2 = 0.252, and S = 0.983. A PLUTON-plot is presented in Figure 1. The magnesium atom in the center of the porphyrazine is coordinated by one water molecule (probably from the solvent), which is linked with two bifurcated H-bonds to the crown ether ring of a neighboring porphyrazine. In this way a linear staircase-like structure is obtained. The nearest distance between the centers of two porphyrazine molecules amounts to 9.58(5) Å. A detailed description of the structure will be published elsewhere.

The binding affinities of compounds 1(n) for silver(I) perchlorate were evaluated by UV/vis spectroscopy. On addition of an AgClO₄ solution to a solution of the 18-crown-6 derivative 1(2) in 5% MeOH in CHCl₃, the products were fully characterized by elemental analysis and spectroscopic techniques. Compound 1(1): UV/vis (CHCl₃) λmax/nm/log ε: 675(4.97), 503(4.07), 378(4.89). 1H NMR (CDCl₃): δ 3.31, 3.40, 3.89 (CH₂O), 4.29 (CH₂S). 13C NMR (CDCl₃): δ 35.02, 70.56, 140.01, 157.36. Anal. calcd for C₄₂H₄₂N₄O₄S₄Mg: C 47.03, H 5.26, N 9.14, S 20.92; found: C 47.01, H 5.34, N 9.04, S 20.64%. Compound 1(2): UV/vis (CHCl₃) λmax/nm/log ε: 675(4.97), 503(4.12), 377(4.91). 1H NMR (CDCl₃): δ 3.32, 3.47, 3.85 (CH₂O), 4.06 (CH₂S). 13C NMR (CDCl₃): δ 34.55, 70.24, 140.04, 157.22. Anal. calcd for C₅₆H₄₀N₈O₁₆S₄Mg: C 58.03, H 5.75, N 9.79, S 18.29; found: C 58.03, H 5.80, N 7.99, S 18.09%.
intensity of the monomeric Q-band at 675 nm gradually decreased up to an Ag⁺ to porphyrazine ratio of ca. 2:1 (Figures 2(a) and 2(b)). This decrease is probably due to an electrostatic effect of the bound Ag⁺ ions. On further addition, the spectrum hardly changed until a guest-host ratio of 4:1 was reached. After this point a further decrease of the monomeric Q-band was accompanied with the appearance of a new peak at 650 nm, which can be attributed to a dimeric complex. The absorption at 650 nm reached a maximum at a guest-host ratio of ca. 6:1. Further addition of AgClO₄ resulted in the dissociation of the dimer.

Figures 2a and 2b clearly indicate that the dimerization of 1(2) is a stepwise process. The mechanism of this reaction is not clear at present. It is however obvious that four silver ions are bound to one porphyrazine molecule prior to dimerization. From the observed downfield (CH₂S) and upfield (CH₂O) shifts in the 13C NMR spectrum at a guest-host ratio of 4:1 we conclude that these silver ions are located in the crown ether rings. A possible structure of the dimer of 1(2) with 12 Ag⁺ ions is shown in Figure 2(c): four cations are sandwiched between the crown ether rings of the two porphyrazine molecules, and four cations are located on each side of the dimer. Notice that both sulfur atoms and aromatic π-systems are known to be ligands for silver ions. At present it is not known whether water molecules, which are present in the crystal structure, are involved in the dimerization process. The 15-crown-5 porphyrazine derivative 1(1) displayed a different complexion behavior. On adding AgClO₄ a decrease in the absorbance at 675 nm was observed up to four equivalents of Ag⁺, but after that no further change of the spectrum took place. Apparently, porphyrazine 1(1) does not dimerize in the presence of Ag⁺ ions. We propose that the small crown ether units in 1(1) cause steric hindrance, and, as a result, aggregation is prevented. In support of this explanation are the X-ray structure of 2(1), which has been reported in the literature, and the X-ray structures of 2(2) and the AgClO₄ complex of 2(1), which we have determined recently. AgClO₄ the crown ether rings are perpendicular to the dicyanoethylene plane, whereas in 2(2) these rings are lying more or less in this plane. Also from Figure 1 it is evident that the larger 18-crown-6 ring has more flexibility and can be located in the plane of the porphyrazine core, probably unlike the crown ether rings in 1(1).

The crystal structure of the 1:1 complex of 2(1) with AgClO₄ shows that the Ag⁺ ion is bound between the crown ether ring of one molecule and a cyano group of a neighboring molecule. In this way a linear chain is formed.

Figure 1. PLUTON representation of the structure of 1(2).H₂O: side view of two molecules.

Figure 2. UV/vis absorption spectra of 1(2) in 5% MeOH/CHCl₃ (a), after addition of 2 equiv. of AgClO₄ (---), and after addition of 6 equiv. of AgClO₄ (...) (a); Absorbance change vs ratio of Ag⁺ to 1(2) at 675 nm (O) and at 650 nm (D) (b); Proposed structure of the [1(2)]₂[Ag⁺]₁₂ complex (c).

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