Dithiacrown Ether Substituted Porphyrazines: Synthesis, Single-Crystal Structure, and Control of Aggregation in Solution by Complexation of Transition-Metal Ions

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The synthesis of novel magnesium, copper, and metal-free porphyrazines, peripherally substituted with dithia-7-crown-2 (MPz(7)), dithia-15-crown-5 (MPz(15)), and dithia-18-crown-6 (MPz(18)) macrocycles is reported. These compounds are prepared starting from dicyanoethylene containing crown ethers 3, 2(1), and 2(2), respectively, which contain sulfur as well as oxygen heteroatoms. The “crowned” porphyrazines bind silver(I) and mercury(II) perchlorates. UV/vis spectroscopy and electron paramagnetic resonance measurements reveal that addition of the transition-metal ions leads to dimerization of the porphyrzone complexes. In the case of the dithia-18-crown-6-substituted porphyrzones, the dimers break up to form monomeric 6:1 guest-host complexes when more than 2 equiv of the metal ion is added. The single-crystal structures of the crown ether 2(2) and the porphyrzone MgPz(18) are presented. Compound C8H6MgN2O12S2 (2(2)) crystallizes in the monoclinic space group P21/c with a = 10.9310(13) Å, b = 19.383(3) Å, c = 8.6976(14) Å, β = 108.898(11)°, V = 1743.5(5) Å3, and Z = 4. The structure refinement converged to R = 0.0366 and Rw = 0.0504. Compound C8H6MgN2O12S2 (MPz(18)) crystallizes in the triclinic space group PI with 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 = 3298.4(13) Å3, and Z = 2. The structure refinement converged to R1 = 0.0839 and wR2 = 0.2196. The electrical properties of H2Pz(18) have been studied by complex impedance spectroscopy. The bulk electrical conductivity of this compound is approximately 1 order of magnitude higher than that of the corresponding 18-crown-6 phthalocyanine.

Introduction

Molecular ionics is a rapidly developing area in chemistry, as aimed at the development of molecular systems and devices that can handle and store information using ions as the basic species.1-3 Crown ethers, which are capable of selectively binding alkali metal ions, are important building blocks for constructing such devices because metal complexation can lead to a specific response, e.g., a change in electrical conductivity. In order to maximize the reliability, the response must be highly nonlinear, which can be achieved by introducing a cooperative effect in the binding process.2,4 Phthalocyanines (Pcs), porphyrins (Pps), and porphyrazines (Ppz) are compounds of another class receiving great interest as components in molecular ionics because metal complexation can lead to a specific response, e.g., a change in electrical conductivity. We have prepared complexes of crown ether Pcs with various alkali metal picrates and studied the electrical properties of these systems.8,9 The ac electrical conductivities of the K+, Rb+, and Cs+ complexes of 18-crown-6 Pc were shown to be 2-3 orders of magnitude higher than those of the free molecules. It was demonstrated that these higher conductivities are due to the fact that in the complexes the phthalocyanines have a cofacially stacked arrangement. With Ba2+, noncofacial aggregates are formed, which show lower conductivities. The most promising application of crown ether phthalocyanines and their complexes is as sensor materials in gas sensors.10,11 Other crowned Pcs that have been synthesized and studied are Pcs with azacrown ether and thiacrown ether substituents.


which are capable of binding transition-metal ions. Furthermore, variations in the connection of the crown ether rings to the Pc core have been introduced, and linear and two-dimensional network polymers have been prepared.

Recently, we and Hoffman independently reported the preparation of crowned porphyrazines. In this paper we give a full account of the synthesis and physical properties of porphyrazines to which four sulfur-containing crown ether rings of various sizes are connected: dithia-7-crown-2 (MPz(7)), dithia-15-crown-5 (MPz(15)), and dithia-18-crown-6 (MPz(18)). The presence of the sulfur atoms in the crown ether rings gives the opportunity to bind soft transition-metal ions. The compounds were previously synthesized by Holdt, and Hoffman were shown to bind Ag⁺, Pb⁺, and Hg⁺ ions.

Recently, Hoffman published the single-crystal structures of the 1:1 complexes of 2(1) with AgBF₄. We independently solved the crystal structure of the AgClO₄ complex of this crown ether. Both crystal structures contain a monomeric as well as a polymeric complex. The Ag⁺ ion appears to be coordinated to the S and O atoms of the crown ether ring. The polymeric complex contains Ag⁺ ions that are bound to the crown ether ring of one molecule as well as to the cyano group of a neighboring molecule. The X-ray structure of 2(2)-AgBF₄ only revealed the presence of a polymeric complex.

In this paper we present the first single-crystal structure of a porphyrin-like derivative with peripheral crown ether rings (MgPz(18)). The single-crystal structure of its precursor 2(2) is also presented. The binding of silver and mercury ions to the porphyrazines has been studied and will be discussed, together with results on the electronic properties of the metal-free H₃Pz(18).

Experimental Section

Materials and Methods. All solvents were dried before use. Silica gel used for chromatography (Kieselgel 60H) was obtained from Merck. Disodium cis-1,2-dicyano-1,2-ethylenedithiolate, 1, was prepared by the method of Davison and Holm. Tetraethyleneglycol dichloride and pentaethyleneglycol dichloride were prepared as described by Pedersen. All other reagents were used as supplied without further purification.

H and ¹³C NMR spectra were obtained using Bruker WH-90, AC-300, and WM-400 instruments. Electronic ionization (EI) and fast atom bombardment (FAB) mass spectra (MS) were obtained using a VG-7070E apparatus and a Finnigan MAT 90 spectrometer. Elemental analyses were carried out on an EA 1108 Carlo Erba instrument. Infrared (IR) spectra were obtained using a Perkin-Elmer 1720-X infrared fourier-transform spectrometer. Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 5 spectrophotometer. Melting points were determined with a Reichert hot-stage microscope and are uncorrected.

Electron paramagnetic resonance (EPR) spectra were measured with a X-band frequency (9 GHz) using a Bruker ESP 300 instrument equipped with a helium continuous flow cryostat.

The ac impedance spectra were recorded using a Solartron Schlumberger 1260 impedance/gain-phase analyzer under ambient atmosphere. Powdered samples were pressed at a load of 1 ton in disk-shaped compacts with diameters of 7 to 10 mm and thicknesses of 0.5 mm. Sputtered gold electrodes with diameters of 6 mm were applied using an Edwards sputter coater S 150B. The samples were spring-loaded between two platinum disks and mounted in a heated cell. Bulk resistances were obtained from analyzing the complex plane representations of the recorded impedance spectra.

The ac impedance spectra were recorded using a Solartron Schum-berger 1260 impedance/gain-phase analyzer under ambient atmosphere. Powdered samples were pressed at a load of 1 ton in disk-shaped compacts with diameters of 7 to 10 mm and thicknesses of 0.5 mm. Sputtered gold electrodes with diameters of 6 mm were applied using an Edwards sputter coater S 150B. The samples were spring-loaded between two platinum disks and mounted in a heated cell. Bulk resistances were obtained from analyzing the complex plane representations of the recorded impedance spectra.

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Dithiacrown Ether Substituted Porphyrazines

Table 1. Crystallographic Data for MgPz(18) and MgPz(18)*

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<th>MgPz(18)</th>
<th>MgPz(18)*</th>
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<tbody>
<tr>
<td>formula</td>
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<td>8603</td>
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<tr>
<td>final wR2, no. of reflections</td>
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<td>0.2196 (8603)</td>
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</table>

*Excluding additional H-0. In our preliminary examination of this space group, it was erroneously reported to be P11 instead of P1. R = \[\sum ||F_o| - |F_c||/\sum |F_o|\]. 

X-ray Crystallography on Compounds MgPz(18) and 2(2).

Crystal data are collected in Table 1.

Compound MgPz(18). A dark blue crystal of MgPz(18), 0.10 x 0.10 x 0.63 mm, was mounted on a Lindemann-glass capillary and placed on an Enraf-Nonius CAD4-T diffractometer on rotating anode a cold dinitrogen stream (150 K). Data were collected in o/20 mode, (Mo Kα) 0.71073 (Zr-filtered), θ in the range 1.0–27.5°. Scan angle was Δω = 0.50 (0.35 tan θ'). Unit-cell dimensions and standard deviations were obtained by least-squares fit (SETA43) of the setting angles of 25 reflections in the range 9.9° < θ < 13.9°. Reduced-cell calculations did not indicate higher lattice symmetry (SPEK). Three reflections were monitored periodically (1, -2, 2; 2, -2, -2; -2, 2, -1) and showed approximately 2% variation in intensity during the 55 h of data collection. The final data of 8774 reflections were collected of which 3996 were independent (R(int) = 0.021). Structure 2(2) was solved by automated direct methods (SHELXS86). Refinement on F was carried out by full-matrix least-squares techniques (SHELXL76); final R = 0.0366, R = 0.0504, for 200 parameters and 3056 reflections within |θ| > 2.5σ(F). S = 0.54 (based on the variance). Hydrogen atoms were included in the refinement on calculated positions (C—H = 0.98 Å) riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters; the hydrogen atoms were refined with one common isotropic displacement parameter. Weights were optimized in the final refinement cycles. The final difference Fourier showed no residual density outside -0.29 and 0.46 e Å^-3. Neutral atom scattering factors and anomalous dispersion corrections, from Cromer and Liberman.38 All geometrical calculations and the ORTEP illustrations were performed with PLATON.33 Positional parameters are listed in the Supporting Information. Computing was conducted on a DEC-station 5000 cluster.

Syntheses. 1,2-Dicyano-3,15-dithia-6,9,12-trioxacyclopentadecene (2(1)). Dithiole 1 (2.34 g, 12 mmol) was suspended in refluxing acetonitrile (150 mL) under a nitrogen atmosphere, and a solution of tetraethyl glycol dichloride (1.92 g, 8 mmol) in acetonitrile (25 mL) was added dropwise during 1 h. The reaction mixture was refluxed for 48 h. The solvent was evaporated under reduced pressure, and the resulting orange oil was dissolved in dichloromethane (100 mL), washed with water (2 x 100 mL), and dried over MgSO4. The organic solvent was evaporated under reduced pressure and the product was purified by column chromatography (silica gel, eluent CHCl3-MeOH 1:1; v/v). The slightly yellow solid was recrystallized from hexane–benzene (1:1; v/v). Yield: 0.3 g (13%) of white crystals, mp 131–132 °C (lit.22 mp 129–131 °C). IR (KBr): 2210 (CN) cm^-1. 1H NMR (CDCl3, 300 MHz): δ 3.31 (t, 4H, CH2S), 3.61 (t, 8H, CH2O), 3.71 (t, 4H, CH2S) MS (EI): m/z 300 (M^+). Anal. Caled for C_{24}H_{16}N_{2}O_{8}S_{4}: C, 47.98; H, 5.37; N, 9.33; S, 21.35. Found: C, 48.95; H, 5.73; N, 9.33; S, 21.35. Compound 2(2), 1.2-Dicyano-3,15-dithia-6,9,12-tetraoxacyclooctadecene (2(2)). This compound was synthesized from 1 and pentaethylene glycol dichloride (1.92 g, 8 mmol) in acetonitrile (25 mL) was added dropwise during 1 h. The reaction mixture was refluxed for 48 h. The solvent was evaporated under reduced pressure, and the resulting orange oil was dissolved in dichloromethane (100 mL), washed with water (2 x 100 mL), and dried over MgSO4. The organic solvent was evaporated under reduced pressure and the product was purified by column chromatography (silica gel, eluent CHCl3-MeOH 1:1; v/v). The slightly yellow solid was recrystallized from hexane–benzene (1:1; v/v). Yield: 0.3 g (13%) of white crystals, mp 64–65 °C (lit.22 mp 62–65 °C). IR (KBr): 2210 (CN) cm^-1. 1H NMR (CDCl3, 300 MHz): δ 3.31 (t, 4H, CH2S), 3.61 (t, 8H, CH2O), 3.71 (t, 4H, CH2S) MS (EI): m/z 344 (M^+). Anal. Caled for C_{24}H_{16}N_{2}O_{8}S_{4}: C, 48.82; H, 5.85; N, 8.13; S, 18.64. Found: C, 48.95; H, 5.76; N, 8.09; S, 18.74. 1,2-Dicyano-3,7-dithiaoctacycloheptane (3). A suspension of dithiaole 1 (1.0 g, 5.3 mmol) in acetonitrile (10 mL) was added to a solution of 1.3-dibromopropene (10 g, 50 mmol) in acetonitrile (15 mL) under a slight warming to 60 °C. A precipitate was formed, filtered, and the filtrate was concentrated to dryness. The residue was recrystallized from acetonitrile (5 mL) and dried under reduced pressure. Yield: 0.5 g (80%) of white crystals, mp 130–131 °C (lit.23 mp 131–132 °C). IR (KBr): 2210 (CN) cm^-1. 1H NMR (CDCl3, 300 MHz): δ 3.31 (t, 4H, CH2S), 3.61 (t, 8H, CH2O), 3.71 (t, 4H, CH2S) MS (EI): m/z 530 (M^+). Anal. Caled for C_{24}H_{16}N_{2}O_{8}S_{4}: C, 47.98; H, 5.37; N, 9.33; S, 21.35. Found: C, 47.92; H, 5.24; N, 9.23; S, 21.83.

Supporting Information. Computing was conducted on a DEC-station 5000 cluster.


nitrogen atmosphere. This mixture was stirred for 48 h at room temperature. The solvent was evaporated under reduced pressure, and the resulting orange oil was dissolved in dichloromethane (25 mL). The resulting solution was washed with water (2 × 50 mL), dried over MgSO₄, and concentrated in vacuum. The product was purified by column chromatography (silica gel, eluent CHCl₃—hexane 3:2, v/v). The resulting solution was washed with water (2 × 50 mL), dried over nitrogen atmosphere. This mixture was refluxed until the washings were clear. The combined organic solutions were concentrated under vacuum, and the resulting solid was purified by column chromatography over NaBr impregnated silica gel. Impuri-

yields the dicyanocrown ethers 2(1) and 2(2), respectively. The product was synthesized from MgPz(18) as described for H₂Pz(15). MgPz(15) (0.10 g, 0.066 mmol) was dissolved in chloroethanol (13.5 mL) at 100 °C. CuCl₂·2H₂O (0.046 g, 0.27 mmol) and sodium acetate (0.018 g, 0.22 mmol) were dissolved in hot ethanol (5 mL) and added to the hot solution of MgPz(15). The mixture was refluxed for 15 min. The solvent was evaporated under reduced pressure, and water and chloroform were added. The chloroform layer was washed twice with water, dried over MgSO₄, and concentrated in vacuum.

The product was purified by chromatography (silica gel, eluent CHCl₃—MeOH 96:4, v/v). Yield: 0.058 g (83%). Anal. Calcd for Ca₄H₆N₅O₇S₄·CH₂O: C, 45.37; H, 5.28; N, 8.64; S, 19.77. Found: C, 45.64; H, 5.14; N, 8.42; S, 19.30.

{Tetakis[1,4,7,10,13]tetraoxadithiacyclooctadecatetraeno}[14,15-b:14',15'-g:14,15'-f:14',15'-e:14',15'-d:14',15'-c:14',15'-b]porphyrinato(copper(II)) (CuPz(18)). This compound was synthesized from H₂Pz(18) as described for H₂Pz(15). CuPz(18) (0.066 g, 0.055 mmol) was dissolved in chloroethanol (135 mL) at 100 °C. CuCl₂·2H₂O (0.046 g, 0.27 mmol) and sodium acetate (0.018 g, 0.22 mmol) were dissolved in hot ethanol (5 mL) and added to the hot solution of CuPz(15). The mixture was refluxed for 15 min. The solvent was evaporated under reduced pressure, and water and chloroform were added. The chloroform layer was washed twice with water, dried over MgSO₄, and concentrated in vacuum. The product was purified by chromatography (silica gel, eluent CHCl₃—MeOH 95:5, v/v). Yield: 86%. Anal. Calcd for Ca₄H₆N₅O₇S₄·CH₂O: C, 46.47; H, 5.75; N, 7.61; S, 17.41. Found: C, 46.68; H, 5.57; N, 7.34; S, 16.79.

Results

Synthesis. The magnesium, copper, and metal-free derivatives of the dithiacrown ether substituted porphyrinato(II) compounds were prepared starting from cis-1,2-dicyano-1,2-ethylenedithiolate 1 as shown in Scheme 1. Reaction of the latter compound with tetraethylene glycol dichloride or pentaethylene glycol dichloride yielded the dicyanogem ethers 2(1) and 2(2), respectively. The synthesis of these crown ethers was previously described by Holdt,20 and was recently improved by Hoffman.22 We applied a high-dilution method in which we made use of the low solubility of the starting compound 1 in acetonitrile. The products were purified by column chromatography and recrystallization. The smaller dicyanogem ether 2 was obtained in a yield of 46% by reaction of dithiolate 1 with a large excess of dibromopropene. The side product 4, which

Scheme 1

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Figure 1. Thermal motion ellipsoid plot (50% probability level) of crown ether 2(2). For clarity the hydrogen atoms have been omitted.

was isolated after purification in 33% yield, is an interesting starting compound for the future synthesis of other crown ethers. From compounds 2(1), 2(2), and 3 we synthesized the corresponding magnesium Pzs according to the procedure described in the literature for the synthesis of alkylthio substituted Pzs. The products were purified by column chromatography. We obtained the dithia-15-crown-5 derivative MgPz(15) in 32% yield, the dithia-18-crown-6 derivative MgPz(18) in 52% yield, and the dithia-7-crown-2 derivative MgPz(7) in 12% yield, all as dark blue powders. MgPz(15) and MgPz(18) were quantitatively demetalated with trifluoroacetic acid to give the metal-free derivatives H,Pz(15) and H,Pz(18) as dark blue to purple powders. The copper derivatives CuPz(15) and CuPz(18) were finally obtained by reaction of the metal-free compounds with copper chloride in the presence of sodium acetate in a mixture of ethanol and chloroform. The yields of the dark blue CuPzs after purification by column chromatography amounted to approximately 85%. Elemental analysis showed that probably one molecule of methanol (from the eluent) is coordinated to the CuPzs. All products were soluble in chloroform.

Single-Crystal X-ray Structures. The single-crystal structures of compounds 2(0) and 2(1) have been published in the literature. In this section we present the single-crystal structures of compound 2(2) and porphyrin MgPz(18).

Dicyanocrown ether 2(2). Single-crystals of 2(2) were grown from methanol and the X-ray structure of this compound was solved by standard methods. Crystal data are given in Table 1. Selected torsion angles are listed in Table 2. Figure 1 shows a plot of the molecular conformation of compound 2(2). The density in the solid form is close to that of 2(0) and 2(1). Conclusions that can be drawn from the structural data of 2(2) are as follows. (i) The angle between the least-squares planes through the dicyanodithieothene unit and the crown ether unit amounts to 131.74(4)°. Holdt has reported angles of 70.2 and 61.6° for 2(0) and 2(1), respectively. This difference is related to the size and flexibility of the macrocyclic rings. The dithia-18-crown-6 ring of 2(2) possesses more conformational freedom, which makes it easier for this ring to be stretched out in the direction of the plane of the dicyanodithieothene unit. (ii) As

can be seen in Table 2, the torsion angles obey Wolf's rule for crown ethers, i.e. the conformations around the C—S and the C—C bonds are gauche whereas around the C—O bonds are trans. Exceptions are the conformations around the S2—C12 and C7—C8 bonds, which are trans, and the conformation around the O3—C9 bond, which is gauche. (iii) In the X-ray structures of crown ethers the oxygen atoms are mostly oriented endoentact and the sulfur atoms exoentact, but in the structure of 2(2) O3 is exoentact, and the two sulfur atoms are endoentact. The latter is unusual and is related to the large angle between the dicyanodithioethene plane and the crown ether segment.

Dithia-18-crown-6 Porphyrazine MgPz(18). Although several phthalocyanine and porphin derivatives with peripheral crown ether rings directly attached to the aromatic core have been synthesized, no structural information has been reported so far from single crystals. We were able to grow single-crystals of MgPz(18) from chloroform-methanol, which were of sufficient quality to determine the X-ray structure. Crystal data are listed in Table 1. The molecular structure of the compound is shown in Figure 2A. A water molecule is found to be present on the central magnesium ion of the porphyrazine ring, and is coordinated to the oxygen and sulfur atoms of one of the crown ether rings (A) of a second porphyrazine molecule via two bifurcated hydrogen bonds. In this way a polymeric chain of molecules is formed as can be seen in Figure 2B. The water molecule might add to the stability of the large and flexible porphyrazine complex in the crystalline phase. As a result of the coordination of the water molecule, the aromatic core of the porphyrazine ring is not perfectly flat and the magnesium ion is displaced 0.570(4) Å from the N1—N3—N5—N7 plane. The dihedral angles between the least-squares plane of the porphyrazine ring (defined by all its C, N, and Mg atoms) and the least-squares planes of crown ether rings A and C are 177.99(11) and 176.39(17)°, respectively. This is quite different from the single-crystal structures of the dicyanocrown ethers 2(n) (vide supra). The least-squares planes of crown ether rings B and D are more tilted and make angles of 115.66(11) and 110.02(13)° respectively, with the porphyrazine plane, which is close to the angle found in compound 2(2). The sulfur atoms of rings A and D are oriented to one side of the Pz plane; those of rings B and C point to the other side. Crown ether A is the most ordered ring, as would be expected because it is hydrogen bonded to the water molecule. As can be seen in Table 2, all C—C and C—O torsion angles of ring A obey Wolf's rule, i.e. the C—C bonds have a gauche conformation and the conformation around the C—O bonds is trans. The only exceptions from this rule are the S1—C3 and S2—C12 bonds which have almost trans instead of gauche conformations. The conformations of ring D deviates from the Wolf rule at the O3—C8 and O4—C11 bonds, which are gauche. Of the other two rings, ring C is the most deviating one: five out of the eight C—O bonds have a gauche conformation, and the conformations of the C5—C6 and C11—C12 bonds are trans instead of gauche.

The hydrogen-bonded polymeric structure found for MgPz(18) is very similar to the structure that was previously reported for a chlorophyll a derivative. In the latter case a one-dimensional chain is formed by water molecules, which link the magnesium centers of the chlorophyll a molecules to the carbonyl oxygen atoms of adjacent chlorophyll molecules. Water is known to play an important role in the dimerization of chlorophyll a in solution.44 As will be shown in the next sections our compounds also display interesting dimerization properties in solution.

Electronic Absorption Spectra. Porphyrazines. The electronic spectral properties of porphyrazines have been less thoroughly investigated than those of the phthalocyanines. Some spectral data can however be found in the literature. The electronic transitions are strongly dependent on the presence of substituents and on the type of central metal ion.

The absorption maxima and extinction coefficients of the novel porphyrazines MPz(7), MPz(15), and MPz(18), in chloroform solutions, are listed in Table 3. The absorption spectra of these compounds are very similar to those reported for octa(alkylthio) substituted porphyrazines. From the data of the magnesium derivatives MgPz(7), MgPz(15), and MgPz(18),

### Table 3. UV—Vis data of the Porphyrazines

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<th>compound</th>
<th>λmax/nm (log ε/L mol⁻¹ cm⁻¹)</th>
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<td>669 (4.98) 616 (sh) 542 (4.29) 371 (4.96)</td>
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<tr>
<td>MgPz(15)</td>
<td>675 (4.97) 619 (sh) 503 (4.07) 378 (4.89)</td>
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<tr>
<td>MgPz(18)</td>
<td>675 (4.97) 622 (sh) 503 (4.12) 377 (4.91)</td>
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<td>H2Pz(15)</td>
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<tr>
<td>H2Pz(18)</td>
<td>714 (4.62) 640 (4.48) 504 (4.33) 351 (4.69)</td>
</tr>
<tr>
<td>CuPz(15)</td>
<td>675 (4.80) 618 (sh) 496 (4.23) 341 (4.66)</td>
</tr>
<tr>
<td>CuPz(18)</td>
<td>675 (4.79) 622 (sh) 497 (4.26) 355 (4.69)</td>
</tr>
</tbody>
</table>

*sh = shoulder.*

can be concluded that the size of the crown ether ring has hardly any influence on the electronic properties. The spectra of the three dithia-18-crown-6 derivatives are displayed in Figure 3. The metalated compounds MgPz(18) and CuPz(18) exhibit a single Q-band maximum at 675 nm, whereas the metal-free H2-Pz(18) displays two broad bands with maxima at 714 nm and 640 nm. The broad band around 500 nm which is observed for the metalated as well as the metal-free porphyrazine has been attributed to an n–π* transition (n is non-bonding electron of sulfur). The intense absorption at 350–380 nm (Table 3) is tentatively assigned to the so-called N-band, which is strengthened with respect to the B (Soret) band because of configuration mixing with the latter. It is of interest to note that the spectra are broad compared to the spectra of substituted phthalocyanines and most other porphyrazines. This phenomenon seems to be related to the presence of the sulfur substituents, since it is also observed for other alkylthioporphyrins.

**Influence of Transition-Metal Ions.** Addition of silver(I) perchlorate or mercury(II) perchlorate to solutions of the porphyrazines in chloroform-methanol caused the absorption spectra of the ligands to change. These changes varied for the different ligands and sometimes also for the different perchlorates, as will be discussed next.

As can be seen in Figure 4 the Q-band of MgPz(7) broadens and shifts to the red when AgClO4 or Hg(ClO4)2 is added. This spectral change points to some kind of aggregation. The peak-shifts amounted to 16.5 nm and 25 nm for Ag+ and Hg2+, respectively. At the same time the n–π* transition at 500 nm disappeared, probably because of complexation of the metal ions to the sulfur atoms (vide infra). The titration curves for the two metal ions are plotted in Figure 4 (inset). In the case of AgClO4 an inflection point is visible at a metal–porphyrazine ratio of ca 2.5. The curve for Hg(ClO4)2 shows two inflection points: one at a metal to porphyrazine ratio of 1 and another one at a ratio of ca 2.5.

MgPz(15) behaves differently. No red-shift of the Q-band was observed upon titration with the perchlorates. Instead a slight blue shift, viz. from 675 nm to 668 nm, and a considerable broadening took place, as shown in Figure 5. The complex stoichiometry appeared to be different for the two metal ions (Figure 5 (inset)). Hg2+ caused a gradual decrease of the Q-band absorption during titration, up to a metal–porphyrazine ratio of about 2.5. In the case of Ag+ the spectrum was not affected up to 2 equiv of the metal ion. Hereafter, a decrease of the Q-band absorption took place up to a metal–porphyrazine ratio of ca. 5. Further addition of Ag+ did not change the spectrum.

Porphyrazine MgPz(18) displayed a remarkable behavior. Some of the spectra that were recorded during its titration with AgClO4 are shown in Figure 6. The titration curve is presented in Figure 6 (inset). Addition of AgClO4 first caused a decrease and broadening of the Q-band up to a metal–porphyrazine ratio of ca 2. At least five isosbestic points were present during this stage of the titration. With increasing amounts of AgClO4 the color of the solution changed from purple to blue. A further decrease of the 675 nm band was accompanied with the development of a sharp peak at 650 nm and the appearance of new isosbestic points. The absorption at the latter wavelength reached a maximum at a metal–porphyrazine ratio of 6. Further addition of AgClO4 caused this peak to decrease slightly and to shift to 661 nm. A third set of isosbestic points was now observed. The n–π* transition disappeared gradually between 0 and 6 equiv of AgClO4. Hg(ClO4)2 gave virtually the same results, except that the second peak-shift beyond 6 equivalents was less distinctive (results not shown).

The behavior of the metal-free derivative H2Pz(18) was even more complex. Four stages could be distinguished during the titration with AgClO4. Each stage had its own set of isosbestic points.
points. Some spectra are supplied in the Supporting Information. During the addition of the first two equivalents of AgClO₄, the two Q-bands subsided and broadened, and the n→π* transition shifted to the red. On further addition of AgClO₄, the two Q-bands subsided and broadened, and the n→π* transition shifted to the red. On further addition of AgClO₄, the n→π* transition disappeared completely, and the molar extinction coefficient at 676 and 714 nm never be drawn. In most of the experiments, the addition of the perchlorates results in an immediate spectral change. Exceptions are the reaction of MgPz(7) with Hg(ClO₄)₂ and the reaction of MgPz(15) with AgClO₄. It is possible that in the case of these porphyrazines some kind of cooperative binding process is operative. The reason why these compounds differ from the rest is unclear at present.

The most striking difference between the porphyrazines is the shift of the Q-band which takes place upon complexation of the metal perchlorates. The porphyrazine with the smallest crown ether rings, MgPz(7), shows a red-shift of this band, whereas MgPz(18), which has the largest crown ether rings, shows a considerable blue-shift. The behavior of the dithia-15-crown-5 derivative is intermediate, because no appreciable shift is observed. These spectral shifts will be discussed below in terms of the aggregation and deaggregation behavior of the porphyrazine molecules.

A remarkable phenomenon of all the experiments is the disappearance of the n→π* absorption around 500 nm. This is probably caused by binding of the metal ions to the n-orbitals of the peripheral sulfur atoms. A similar effect has been reported to take place when the sulfur atoms of tetrakis(1,4-dithiaacyclohexeno) Pz are protonated. Of interest is the broadening of the Q-band which is observed in the experiments with the dithia-7-crown-2 and the dithia-15-crown-5 porphyrazines. Also in the case of the dithia-18-crown-6 derivative a broadening occurs when the first 2 equiv of the metal perchlorate are added. These effects may be related to the formation of aggregates. In order to get further insight in the aggregation behavior of the porphyrazines, we carried out EPR experiments. The results are presented in the next section.

Electron Paramagnetic Resonance. The EPR spectra of the copper derivative CuPz(18), and the AgClO₄ complexes of this porphyrazine and of CuPz(15) were recorded using a porphyrazine concentration of ca 1 mM. Figure 8 shows the spectra of CuPz(18) recorded at various temperatures in CHCl₃. Large variations with temperature are observed. The spectrum at 216 K is clearly axial and characteristic of a powder spectrum of a monomeric copper complex (g₁ = 2.135, g₂ = 2.052, A₁ = 205 G). When the complex was heated, a gradual change toward an isotropic spectrum occurred, which can be explained from a more rapid tumbling of the molecules at higher temperatures, resulting in an averaging of the g-tensor anisotropy. Similar effects have been reported in the literature for copper tetrathienylporphyrine. When the solution was cooled below the freezing point of the solvent (210 K), a sudden change in the spectrum took place. The spectrum at 6 K (Figure 8) is a triplet spectrum characteristic of two coupled copper nuclei, indicating that in the frozen solution dimers are present. Two strong perpendicular transitions each containing seven lines are visible in the g = 2 region, as well as small signals at higher field. It is possible to calculate from the EPR data the distance between the two copper nuclei, using the formula

\[ D₂ = 0.65g₂r³ \] (1)
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Figure 8. EPR spectra of copper Pzs in CHCl$_3$–MeOH (95:5, v/v) at various temperatures: CuPz(18) (A), CuPz(18) in the presence of 6 equiv of AgClO$_4$ (B), or CuPz(15) in the presence of 6 equiv of AgClO$_4$ (C).

Table 4. Parameters and Calculated Cu–Cu Distance (r) from EPR Spectra of Dimeric Porphyrazines at Low Temperatures$^a$

| compound       | $|g_1|$/G | $|g_2|$/G | $D_1$/G | $D_2$/G | r/Å  |
|----------------|---------|---------|---------|---------|-------|
| CuPz(18)       | 2.045   | 2.136   | 112     | 105     | 346   |
| CuPz(15) + 6AgClO$_4$ | 2.058   | 2.226   | 108     | 108     | 343   |

$^a$ See Figure 8A for explanation of the parameters.

Next the effect of the addition of 6 equiv of AgClO$_4$ on the EPR spectra of CuPz(15) and CuPz(18) was studied. The two compounds appeared to behave differently. At all temperatures between 6 and 333 K, i.e. both in frozen solution and in the liquid, CuPz(15) gave an EPR spectrum characteristic of a dimeric species (Figure 8C), whereas that of CuPz(18) was clearly indicative of a monomeric species (Figure 8B): $g_{||} = 2.045$, $g_{\perp} = 2.06$, $A_{||} = 206$ G). In the case of CuPz(15) only a small temperature dependence was observed. The increased size of the dimeric species probably prevents the development of a fully isotropic spectrum at elevated temperatures. The spectrum recorded at 9 K was sufficiently resolved to calculate the Cu−Cu distance. We assume that the small peak which is observed at approximately 3700 G, is the outmost of the seven lines of the corresponding transition, and that the line separation is equal for the two transitions (see Figure 8C). Then a distance of $r = 4.5$ Å can be calculated from the values of $D_1$ and $g_2$ given in Table 4. The EPR spectrum of CuPz(18) in the presence of 2 equivalents of AgClO$_4$ was less well-resolved. It suggested that between 213 and 333 K a mixture of monomeric and dimeric complexes was present, as a small signal was observed at half-field (results not shown).

Conductivity. The electrical properties of complexed and uncomplexed crown ether substituted Ps have been extensively studied before.$^{8,9,12,51}$ We carried out preliminary ac conductivity experiments with one of the crowned Pzs, viz. the metal-free dithia-18-crown-6 derivative H$_2$Pz(18). Figure 9


The frequency dependence of the ac conductivity was analyzed and can be described as follows. At low frequencies (<10 kHz) the ac conductivity is independent on the frequency ($\sigma(\omega) \approx 10^{-6} S m^{-1}$), which means that the conductivity is limited by grain boundary effects. At higher frequencies the conductivity follows the relationship $\sigma(\omega) = A\omega^n$, where $n$ was found to be 1.5. The exponent $n$ can be correlated with the degree of order in the sample. A value of 0.5 is usually found for highly ordered structures, while this value increases with increasing disorder. Therefore, the degree of order in our sample turned out to be low.

**Discussion**

The presence of two sulfur atoms in our crown ether porphyrazines affords the possibility of binding transition-metal ions. The spectroscopic studies presented in the Results section and the recently published X-ray structures indicate that such a binding indeed takes place. In a number of cases this leads to aggregation of the porphyrazines, e.g. when AgClO$_4$ or Hg(ClO$_4$)$_2$ is added to solutions of MgPz(7) and to the dithia-15-crown-5 porphyrazines. The EPR data and the broadening of the Q-bands in the UV–vis spectra suggest that dimers are formed. Dimerization also occurs when 2 equiv of the metal perchlorates are added to solutions of the dithia-18-crown-6 porphyrazines. Remarkably, further addition of perchlorate to the latter compounds results in a complete dissociation of the dimers and the formation of monomeric complexes with the stoichiometry [MPz(18)][metal perchlorate], suggesting a sharp Q-band which is blue-shifted with respect to the Q-band of the uncomplexed monomeric porphyrazine. This shift is probably caused by strong interactions of the transition-metal ions with the aromatic cores of the macrocycles. The changes in the absorption spectra which occur upon addition of more than 6 equiv of metal perchlorate to the dithia-18-crown-6 Pzs suggest that reaggregation takes place.

The remarkably different complexation behavior of the dithia-15-crown-5 and dithia-18-crown-6 porphyrazines toward silver ions can be explained as follows. As shown by the single-crystal structure of the silver complex of 2(1), the silver ion does not fit in the cavity of the dithia-15-crown-5 macrocycle and one coordination site of the ion is connected to a perchlorate ion or to a neighboring ligand. A similar situation may be present in the dimeric silver complexes of MPz(15), where the silver ions can form bridges between the two porphyrazine molecules. On the contrary, the cavity of the dithia-18-crown-6 macrocycle is large enough to accomodate a silver ion and the coordination sites of the latter ion can be completely filled by the atoms of a single macrocycle. Any formed dimer will break up easily when more silver perchlorate is added. The fact that MPz(18) eventually forms a 6:1 guest–host complex.

**Table 5.** Values of the Equivalent Circuit Parameters at 150 °C Obtained from Fitting of the Impedance Spectra of H$_3$Pz(18)$^\alpha$

<table>
<thead>
<tr>
<th>$\sigma$ (S m$^{-1}$)</th>
<th>$E_a$ (eV)</th>
<th>$k_0$ (Ω$^{-1}$)</th>
<th>$\alpha_1$</th>
<th>$\alpha_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.94 x 10$^{-6}$</td>
<td>0.54</td>
<td>1.62 x 10$^{-11}$</td>
<td>0.98</td>
<td>11</td>
</tr>
<tr>
<td>$E_a$ (eV)</td>
<td>$k_0$ (Ω$^{-1}$)</td>
<td>$\alpha_1$</td>
<td>$\alpha_2$</td>
<td></td>
</tr>
<tr>
<td>2.69 x 10$^{-6}$</td>
<td>0.73</td>
<td>4.13 x 10$^{-10}$</td>
<td>0.68</td>
<td></td>
</tr>
</tbody>
</table>

* $\sigma$ and $\alpha_1$ conductivity related to resistances $R_1$ and $R_2$; $E_a$ and $E_{a2}$ activation energy of conduction related to resistances $R_1$ and $R_2$; $k_0$ pre-exponential factor for impedance of constant-phase element $Q$; $\alpha$, exponential factor for impedance of $Q$; $\alpha_2$, relative dielectric constant.

\[ T=175^\circ C \]

\[ \text{Inset: equivalent circuit used for fitting the ac responses of H$_3$Pz(18).} \]

Figure 9. Impedance spectra of H$_3$Pz(18) at different temperatures in the frequency range 10–10$^{10}$ Hz. Inset: equivalent circuit used for fitting the ac responses of H$_3$Pz(18).

shows the impedance spectra for this compound recorded at different temperatures. Similar spectra were obtained previously for 18-crown-6 Pc and its metal picate complexes. The impedance spectra could be fitted to the equivalent circuit that is shown in the inset of Figure 9. The parameters obtained from this fitting procedure are presented in Table 5.

The parallel constant-phase element (CPE) $Q_1$, with an impedance $Z_{Q_1} = (k_0\omega)^{\alpha_1}$, has a value of $\alpha_1$ that is close to unity. Therefore, this CPE can be interpreted as the high-frequency capacitance, $C_\infty = \epsilon_r\epsilon_0 A/d$, where $\epsilon_r$ is relative dielectric constant, $\epsilon_0$ is the permittivity of free space, i.e. 8.85 x 10$^{-12}$ F m$^{-1}$, $A$ is the electron surface area, and $d$ is sample thickness. $C_\infty$ is on the order of magnitude of 10$^{-11}$ F. The relative dielectric constant amounts to 11 at 150 °C. This value is lower than the previously reported value for 18-crown-6 Pc, but close to the values found for other Pcs.\(^{52}\) Element $R_1$ of the equivalent circuit is related to the electronic bulk resistance. From the temperature dependence of the bulk conductivity, $\alpha_1 = \sigma_\infty \exp(-E_a/kT)$, the activation energy $E_a$ was found to be 0.54 eV. This value is lower than that for 18-crown-6 Pc, but similar to the activation energies for intercolumnar electron hopping in mesogenic Pcs.\(^{52,53}\) The value of the bulk conductivity at 175 °C is approximately 1 order of magnitude higher than the value found for 18-crown-6 Pc near this temperature. It should be emphasized that the latter results are obtained under nitrogen atmosphere, while we carried out our experiments in air. Therefore, an oxygen doping effect can not be ruled out. The $(R_1Q_1)$ section of the equivalent circuit might be related to conduction and diffusion across grain boundaries. An activation energy of 0.73 eV for the corresponding conductivity $Q_2$ could be derived. The value of $\alpha_2$ for $Q_2$ amounts to approximately 0.7. Therefore, this CPE can also be considered as a parallel combination of a capacitance $C$ and a Warburg element $W$ with impedance $Z_W = k_0^{-1}(\omega)^{\alpha_2}$.\(^{51}\)


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Figure 10. Side view and top view of the proposed structures of the monomeric complexes between MPz(18) and 6 Ag⁺ ions (A) and of the dimeric complex of MPz(15) and Ag⁺ ions with r = 4.5 Å and θ ≈ 54.7° (B). The squares and rectangles represent the aromatic cores, the open circles are the crown ether rings, and the filled circles are the silver ions (the latter are omitted in the complex of MPz(15) because the exact number and positions of these ions are not known).

with AgClO₄ is remarkable. We tentatively propose the following structure for this species: four metal ions are bound in the crown ether rings, while two ions are complexed to the aromatic core (Figure 10A).

The Q-band maxima of the dimeric complexes of MPz(15) and MPz(18) are almost unshifted when compared with the maxima of the monomeric porphyrazines. This suggests that the molecules in the dimers are not cofacially stacked, but have slipped-stacked orientation with a tilt angle (angle between the normal of the porphyrazine plane and the center-to-center interplanar distance) of approximately 35.3°. The dimeric AgClO₄ and HgClO₄ complexes of MgPz(7) display Q-bands that are slightly red-shifted with respect to the monomer. The tilt angle of the porphyrazine moieties in these dimers must therefore be larger than 35.3°. From the EPR data we know that the copper-to-copper distance in the complex of CuPz(15) with AgClO₄ mounts to 4.5 Å. From this value the interplanar distance can be calculated to be approximately r × cos 35.3° = 3.67 Å. The centers of the porphyrazine rings are shifted r × sin 35.3° = 60 Å along the molecular planes. The single-crystal structure of the Ag⁺ complex of dithia-15-crown-5 ether 2(1) shows that the crown ether rings are oriented approximately perpendicular to the plane of the dicyanoethylene unit. This makes it likely that the crown ether rings in the AgClO₄ complex of CuPz(15) also have a perpendicular orientation. On the basis of this assumption and the above presented structural data from the EPR spectra, we propose that the dimeric CuPz(15) complex has the structure shown in Figure 10B. The porphyrazine molecules are held together by silver ions which are sandwiched between neighboring crown ether rings.

Both the oxygen and sulfur atoms of the crown-ether rings as well as the aromatic cores of the porphyrazine rings are potential binding sites for the silver and mercury ions. This may explain why our compounds display such a great variety in complexation behavior. This feature is of great interest in view of the possible applications of our molecules in the field of molecular ionic electonics. As postulated by Simon, a nonlinear complexation of ions is a prerequisite for developing a reliable molecular device which switches between two states. Several of our compounds meet this criterion, as can be concluded from the titration curves of MgPz(7) with Hg²⁺ (Figure 4), MgPz(15) with Ag⁺ (Figure 5), and MgPz(18) with Hg²⁺ and Ag⁺ (Figure 6) and from the curves of H₂Pz(18) and CuPz(18) with Ag⁺ (Figure 7). The aggregation or deaggregation processes in all these cases take place above a critical concentration of ions. If also the conductivity of the porphyrazines would change in a nonlinear way upon complexation, then a switching device can be developed. Work along this line is in progress.

Acknowledgment. We would like to thank Rob van Landschoot for his assistance with the impedance measurements. The research was financially supported by the Dutch Innovation Oriented Research Programme (IOP) of the Ministry of Economic Affairs. The X-ray investigations (Utrecht University) were supported by the Netherlands Foundation of Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

Supporting Information Available: A figure showing absorption spectra of H₂Pz(18) and tables giving further details of the structure determinations, including crystallographic data, atomic coordinates, bond lengths and angles, and thermal parameters for MgPz(18) and 2(2) (20 pages). Ordering information is given on any current masthead page.

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