

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 porphyrazine complexes. In the case of the dithia-18-crown-6-substituted porphyrazines, 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 porphyrazine MgPz(18) are presented. Compound C₁₄H₂₀N₂O₄S₂ (**2(2)**) crystallizes in the monoclinic space group *P*2₁/*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 *R*_w = 0.0504. Compound C₅₆H₈₂MgN₈O₁₇S₈ (MgPz(18)) crystallizes in the triclinic space group *P*1̄ 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 *R*1 = 0.0839 and *wR*2 = 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. It is 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.^{2,3}

Phthalocyanines (Pcs), porphyrins (Pps), and porphyrazines (Pzs) are compounds of another class receiving great interest as components in molecular ionics.⁴ Pps containing pendant crown ether macrocycles were first described by Thanabal and by Kobayashi.⁵ Of particular interest are phthalocyanines

substituted with four crown ether rings,^{2,3} which were reported independently by the groups of Bekâroglu, Kobayashi, and Nolte.⁶ These compounds display solvent and metal ion induced aggregation behavior.⁷ 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 thiocrown ether substituents,

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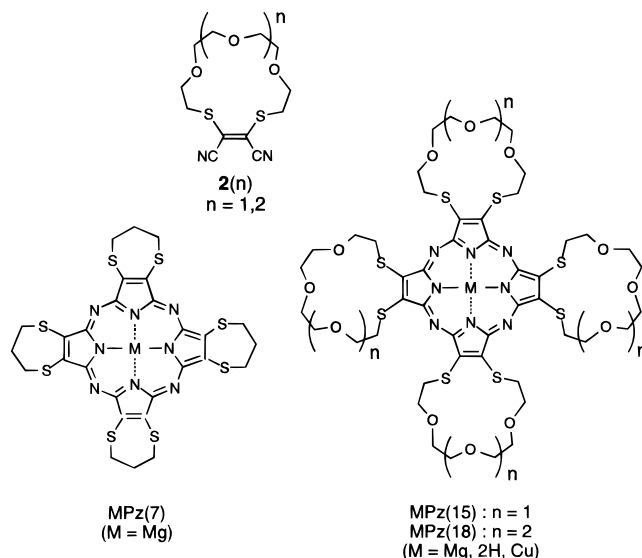
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which are capable of binding transition-metal ions.¹² Furthermore, variations in the connection of the crown ether rings to the Pc core have been introduced,¹³ and linear and two-dimensional network polymers have been prepared.^{14,15}

Recently, we and Hoffman independently reported the preparation of crowned porphyrazines.^{16,17} 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.^{18,19} Thiocrown ethers **2**(*n*) (*n* = 1–2) containing 1,2-dicyano-1,2-dithioethane were used as the precursors for the crowned porphyrazines. These compounds were previously synthesized by Holdt,²⁰ Märkl,²¹ and Hoffman²² and were shown to bind Ag⁺, Pd²⁺, and Hg²⁺ ions.^{22–24}

Recently, Hoffman published the single-crystal structures of the 1:1 complexes of **2**(1) with AgBF₄.²² We independently solved the crystal structure of the AgClO₄ complex of this crown ether.¹⁶ 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.²²

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 H₂Pz(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.²⁵ Tetraethylene glycol dichloride and pentaethylene glycol dichloride were prepared as described by Pedersen.²⁶ All other reagents were used as supplied without further purification.

¹H and ¹³C NMR spectra were obtained using Bruker WH-90, AC-100, 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 with 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 at 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 ca. 1 ton in disk-shaped compacts with diameters of 7 to 10 mm and thicknesses of ca. 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 electrical equivalent circuits describing the impedance spectra were determined by a detailed nonlinear least-squares analysis.²⁷

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Table 1. Crystallographic Data for **2(2)** and MgPz(18)

	2(2)	MgPz(18) ^a
formula	C ₁₄ H ₂₀ N ₂ O ₄ S ₂	C ₅₆ H ₈₂ MgN ₈ O ₁₇ S ₈
mol wt	344.46	1420.14
cryst syst	monoclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1 ^b
<i>a</i> , Å	10.9310(13)	9.584(3)
<i>b</i> , Å	19.383(3)	17.672(2)
<i>c</i> , Å	8.6976(14)	19.620(4)
α, deg		84.904(14)
β, deg	108.898(11)	85.21(2)
γ, deg		89.29(2)
<i>V</i> , Å ³	1743.5(5)	3298.4(14)
<i>D</i> _{calc} , g cm ⁻³	1.312	1.430
<i>Z</i>	4	2
<i>F</i> (000)	728	1500
μ, cm ⁻¹	3.1	3.5
data set	-14:14, 0:25, -11:11	-10:10, 0:19, -21:21
final <i>R</i> , ^c no. of data	0.0366 [3056, <i>I</i> > 2.5σ(<i>I</i>)]	0.0839 [4457, <i>F</i> ² > 4.0σ(<i>F</i> ²)]
final <i>R</i> _w , ^d no. of data	0.0504 [3056]	
final wR ₂ , ^e no. of data		0.2196 [8603]
<i>S</i>	0.54	1.03

^a Excluding additional H₂O. ^b In our preliminary communication^{16a} this space group was erroneously reported to be *P*1 instead of *P*1̄. ^c *R* = Σ||*F*_o| - |*F*_c||/Σ|*F*_o|. ^d *R*_w = [Σ[w(|*F*_o| - |*F*_c||)²]/Σ[w(*F*_o²)]]^{1/2}. ^e wR₂ = [Σ[w(*F*_o² - *F*_c²)²]/Σ[w(*F*_o²)²]]^{1/2}.

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 × 0.10 × 0.63 mm, was mounted on a Lindemann-glass capillary and placed on an Enraf-Nonius CAD4-T diffractometer on rotating anode in a cold dinitrogen stream (150 K). Data were collected in ω/2θ mode, λ (Mo Kα) 0.71073 (Zr-filtered), θ in the range 1.0–22.5°. Scan angle was Δω = (0.90 + 0.35 tan θ)°. Unit-cell dimensions and standard deviations were obtained by least-squares fit (SET4²⁸) of the setting angles of 25 reflections in the range 9.9° < θ < 15.4°. Reduced-cell calculations did not indicate higher lattice symmetry (SPEK²⁹). One reflection was monitored periodically (720) and showed approximately 2% variation in intensity during the 55 h of data collection. The data were scaled accordingly. Intensity data were corrected for Lorentz, polarization, and absorption effects (an empirical absorption/extinction correction was applied (DIFABS³⁰ correction range 0.265–1.000)) and averaged into a unique set of reflections. Total data of 8948 reflections were collected of which 8608 were independent (*R*_{int} = 0.105). Structure MgPz(18) was solved by automated direct methods (SIR-92).³¹ Refinement on *F*² was carried out by full-matrix least-squares techniques (SHELXL-93);³² final *R*₁ value 0.0839 for 813 parameters and 4457 reflections with *I* > 2.0σ(*I*), wR₂ = 0.2196 for all 8603 reflections, *w* = 1/[σ²(*F*_o²) + (0.0753*P*)² + 12.05*P*] where *P* = (Max(*F*_o², 0) + 2*F*_c²)/3 and *S* = 1.034. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were refined with a fixed isotropic thermal parameter 1.2 or 1.5 times the value of the equivalent isotropic thermal parameter of the carrier atoms C and O, respectively. Because the crown ether rings showed some extreme large ellipsoids, for two rings a disorder model was refined. Weights were optimized in the final refinement cycles. Packing analysis³³ showed that MgPz(18) contains a small void at a position consistent with the presence of an additional water molecule, at hydrogen-bond distance in between two crown ether oxygens of (via inversion related) adjacent molecules. The site-occupation factor of a

tentative water molecule refined to 0.17. This additional water molecule, however, was not taken into account.

A final difference Fourier showed no residual density outside -0.40 and +0.68 e Å⁻³. Neutral atom scattering factors and anomalous dispersion corrections were taken from ref 34.

Compound **2(2).** A colorless crystal of **2(2)**, 0.30 × 0.50 × 0.80 mm, was mounted on a glass fiber and placed on an Enraf-Nonius CAD4-F sealed tube diffractometer at 298 K. Data were collected in ω/2θ mode, λ (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 (SET4²⁸) 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).²⁹ Three reflections were monitored periodically (-1, 2, -2; 2, 2, -2; -2, 5, -1) and showed approximately 2% variation in intensity during the 116 h of data collection. The data were scaled accordingly. Intensity data were corrected for Lorentz and polarization but not for absorption effects and averaged into a unique set of reflections. Total 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).³⁵ Refinement on *F* was carried out by full-matrix least-squares techniques (SHELX76);³⁶ final *R* = 0.0366, *R*_w = 0.0504, for 200 parameters and 3056 reflections with *I* > 2.5σ(*I*), *w* = 1/[σ²(*F*) + 0.000481*F*²], and *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 were taken from Cromer and Mann,³⁷ 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)). Dithiolate **1** (2.34 g, 12 mmol) was suspended in refluxing acetonitrile (150 mL) under a nitrogen atmosphere, and a solution of tetraethylene 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 × 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, 100 MHz): δ 3.31 (t, 4H, CH₂S), 3.61 (s, 8H, CH₂O), 3.71 (t, 4H, CH₂O). MS (EI): *m/z* 300 (M⁺). Anal. Calcd for C₁₂H₁₆N₂O₃S₂: 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.

1,2-Dicyano-3,18-dithia-6,9,12,15-tetraoxacyclooctadecene (2(2)). This compound was synthesized from **1** and pentaethylene glycol dichloride as described for **2(1)**. Yield: 23% of slightly yellow crystals, mp 64–65 °C (lit.²² mp 62–65 °C). IR (KBr): 2210 (CN) cm⁻¹. ¹H NMR (CDCl₃, 100 MHz): δ 3.31 (t, 4H, CH₂S), 3.67 (s, 12H, CH₂O), 3.76 (t, 4H, CH₂O). MS (EI): *m/z* 344 (M⁺). Anal. Calcd for C₁₄H₂₀N₂O₄S₂: C, 48.82; H, 5.85; N, 8.13; S, 18.62. Found: C, 48.95; H, 5.76; N, 8.09; S, 18.74.

1,2-Dicyano-3,7-dithiacycloheptene (3). A suspension of dithiolate **1** (1.0 g, 5.3 mmol) in acetonitrile (10 mL) was added to a solution of 1,3-dibromopropane (10 g, 50 mmol) in acetonitrile (15 mL) under a

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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). 1,10-Dibromo-5,6-dicyano-4,7-dithia-5-decene **4** was obtained as an oily side product in 33% yield. Compound **3** was collected as a white solid. Yield: 0.45 g (46%). Mp: 104–106 °C. IR (KBr): 2210 (CN) cm⁻¹. ¹H NMR (CDCl₃, 100 MHz): δ 2.26 (q, 2H, C-CH₂-C), 3.71 (t, 4H, CH₂S). MS (EI): *m/z* 182 (M⁺). Anal. Calcd for C₇H₆N₂S₂: C, 46.13; H, 3.32; N, 15.37; S, 35.18. Found: C, 46.26; H, 3.33; N, 14.73; S, 35.55.

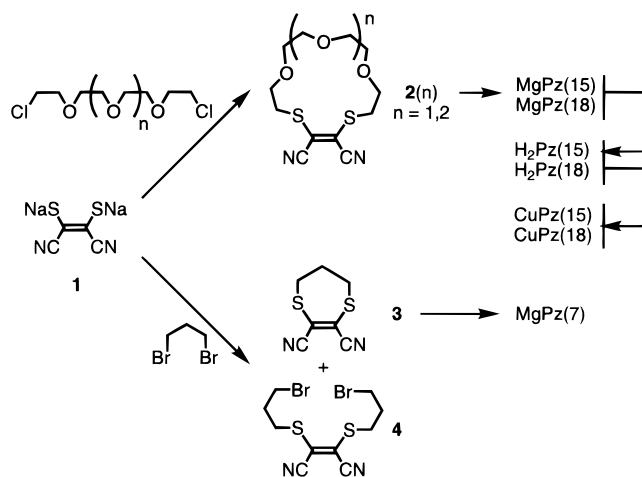
{Tetrakis([1,5]dithiacyclohepteno)[6,7-b:6',7'-g:6''-l:6''',7''-q]-porphyrazinato}magnesium(II) (MgPz(7)). Magnesium metal (0.67 g, 12.75 mmol) and a small crystal of I₂ were added to *n*-propanol (30 mL) under a nitrogen atmosphere. The mixture was refluxed until the magnesium had completely reacted to form a suspension of magnesium propoxide. Dicyanocrown ether **3** (1.0 g, 5.5 mmol) in *n*-propanol (30 mL) was added dropwise to the refluxing suspension during 1 h. After 24 h the reaction mixture was filtered while hot and the residue was washed with acetone (3 × 50 mL). The combined organic solutions were concentrated under vacuum. The resulting solid was purified by chromatography (silica gel, eluent CHCl₃-MeOH 93:7, v/v), and subsequently extracted in a Soxhlett apparatus with dichloromethane. After evaporation of the solvent the product was dissolved in hot benzene and precipitated by adding hexane to this solution. Yield: 0.95 g (12%) of a dark blue powder, mp >320 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 2.59 (q, 2H, C-CH₂-C), 3.96 (t, 4H, CH₂S). ¹³C NMR (400 MHz, DMSO-*d*₆): δ 31.3 (C-S), 32.3 (C-C-C), 137.8 (C=C), 155.8 (C=N). MS (FAB): *m/z* 753 (M⁺). Anal. Calcd for C₂₈H₂₄MgN₈S₈: C, 44.68; H, 3.22; N, 14.9; S, 34.01. Found: C, 45.35; H, 3.57; N, 14.79; S, 33.76.

{Tetrakis([1,4,7,10,13]trioxadithiacyclopentadeceno)[11,12-b:11'-12'-g:11'',12''-l:11''',12'''-q]porphyrazinato}magnesium(II) (MgPz(15)). This compound was synthesized from **2**(1) as described for MgPz(7). The product was purified as follows. The hot reaction mixture was filtered and the residue was washed with dichloromethane until the washings were clear. The combined organic solutions were evaporated under reduced pressure, and the resulting solid was purified by column chromatography over NaBr impregnated silica gel. Impurities were first removed by elution with CHCl₃. The product was collected by elution with CHCl₃-MeOH (93:3, v/v). The product was finally washed with hot benzene. Yield: 32% of a dark blue powder, mp >320 °C. ¹H NMR (400 MHz, CDCl₃): δ 3.28 (s, 4H, CH₂O), 3.37 (s, 4H, CH₂O), 3.86 (s, 4H, CH₂O), 4.24 (s, 4H, CH₂S). ¹³C NMR (400 MHz, CDCl₃): δ 35.0 (C-S), 70.0, 70.5, 70.6 (C-O), 140.1 (C=C), 157.1 (C=N). MS (FAB): *m/z* 1225.5 (M⁺ + 1), 1223.4 (M⁺ - 1). Anal. Calcd for C₄₈H₆₄MgN₈O₁₂S₈: C, 47.03; H, 5.26; N, 9.14; S, 20.40. Found: C, 47.09; H, 5.34; N, 9.04; S, 20.36.

{Tetrakis([1,4,7,10,13,16]tetraoxadithiacyclooctadeceno)[14,15-b:14',15'-g:14'',15''-l:14''',15'''-q]porphyrazinato}magnesium(II) (MgPz(18)). This compound was synthesized from **2**(2) as described for MgPz(7). The product was purified as follows. The hot reaction mixture was filtered, and the residue was washed with acetone until the washings were clear. The combined organic solutions were concentrated under reduced pressure, and the resulting solid was purified by chromatography (NaBr impregnated silica gel, eluent CHCl₃-MeOH 9:1, v/v). The product was dissolved in hot benzene and precipitated by adding hexane to the solution. Yield: 52% of a dark blue powder, mp >320 °C. ¹H NMR (400 MHz, CDCl₃): δ 3.32 (s, 8H, CH₂O), 3.47 (s, 4H, CH₂O), 3.85 (s, 4H, CH₂O), 4.06 (br s, 4H, CH₂S). ¹³C NMR (400 MHz, CDCl₃): δ 34.5 (C-S), 70.1, 70.2 (C-O), 140.0 (C=C), 157.2 (C=N). MS (FAB): *m/z* 1401.4 (M⁺ + 1), 1399.5 (M⁺ - 1). Anal. Calcd for C₅₆H₈₀MgN₈O₁₆S₈: C, 47.97; H, 5.75; N, 7.99; S, 18.29. Found: C, 48.03; H, 5.80; N, 7.99; S, 18.09.

Tetrakis([1,4,7,10,13]trioxadithiacyclopentadeceno)[11,12-b:11'-12'-g:11'',12''-l:11''',12'''-q]porphyrazine (H₂Pz(15)). MgPz(15) (0.10 g, 0.08 mmol) was dissolved in a minimum amount of trifluoroacetic acid and poured onto ice. The mixture was neutralized with concentrated ammonia and extracted with chloroform. The chloroform solution was washed with water until the latter was neutral, dried over

Scheme 1



MgSO₄, and concentrated in vacuum. Yield: 0.075 g (76%) of a dark blue/purple powder, mp >320 °C. ¹H NMR (90 MHz, CDCl₃): δ -1.6 (s, 2H, NH), 3.6 (s, 8H, CH₂O), 3.95 (t, 4H, CH₂O), 4.25 (t, 4H, CH₂S). Anal. Calcd for C₄₈H₆₆N₈O₁₂S₈: C, 47.90; H, 5.53; N, 9.31; S, 21.31. Found: C, 47.45; H, 5.46; N, 9.16; S, 22.22.

Tetrakis([1,4,7,10,13,16]tetraoxadithiacyclooctadeceno)[14,15-b:14',15'-g:14'',15''-l:14''',15'''-q]porphyrazine (H₂Pz(18)). This compound was synthesized from MgPz(18) as described for H₂Pz(15). Yield: 85% of a dark blue/purple powder, mp >320 °C. ¹H NMR (100 MHz, CDCl₃): δ -1.8 (s, 2H, NH), 3.3 (s, 8H, CH₂O), 3.5 (s, 4H, CH₂O), 3.85 (s, 4H, CH₂O), 4.05 (br s, 4H, CH₂S). Anal. Calcd for C₅₆H₈₂N₈O₁₆S₈: C, 48.75; H, 5.99; N, 8.12; S, 18.59. Found: C, 49.55; H, 5.95; N, 8.01; S, 18.61.

{Tetrakis([1,4,7,10,13]trioxadithiacyclopentadeceno)[11,12-b:11'-12'-g:11'',12''-l:11''',12'''-q]porphyrazinato}copper(II) (CuPz(15)). H₂Pz(15) (0.066 g, 0.055 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 H₂Pz(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 C₄₈H₆₄CuN₈O₁₂S₈·CH₄O: 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.

{Tetrakis([1,4,7,10,13,16]tetraoxadithiacyclooctadeceno)[14,15-b:14',15'-g:14'',15''-l:14''',15'''-q]porphyrazinato}copper(II) (CuPz(18)). This compound was synthesized from H₂Pz(18) as described for CuPz(15). The product was purified by chromatography (silica gel, eluent CHCl₃-MeOH 95:5, v/v). Yield: 86%. Anal. Calcd for C₅₆H₈₀CuN₈O₁₆S₈·CH₄O: 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 porphyrazines 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 dicyanocrown ethers **2**(1) and **2**(2), respectively. The syntheses 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 by recrystallization. The smaller dicyanocrown ether **3** was obtained in a yield of 46% by reaction of dithiolate **1** with a large excess of dibromopropane. The side product **4**, which

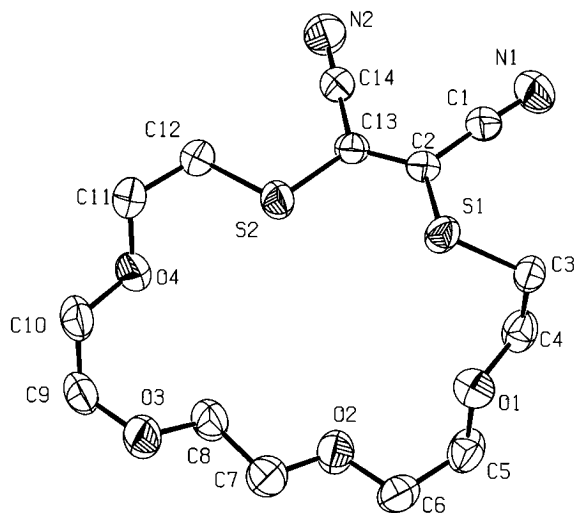


Figure 1. Thermal motion ellipsoid plot (50% probability level) of crown ether **2(2)**.³³ For clarity the hydrogen atoms have been omitted.

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.³⁹ 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 acid⁴⁰ to give the metal-free derivatives H₂Pz(15) and H₂Pz(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 chloroethanol.⁴⁰ 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.⁴¹ In this section we present the single-crystal structures of compound **2(2)** and porphyrazine 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)**.⁴¹ 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 dicyanodithioethene 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 dicyanodithioethene unit. (ii) As

Table 2. Torsion Angles (deg) of Selected Bonds for Crown Ether **2(2)** and for the Different Crown Ether Rings A-D of MgPz(18) (Esds in Parentheses)^a

2(2)	ring A of MgPz(18)			ring B of MgPz(18)			ring C of MgPz(18)			ring D of MgPz(18)			
	C3-S1-C2-C1	38.52(15)	C47-S7-C14-C13	115.2(8)	C26-S2-C3-C4	5.2(11)	C36-S4-C7-C8	74.7(9)	C37-S5-C10-C9	20.4(11)	C37-S5-C10-C11	-167.7(8)	C37-S5-C10-C11
C3-S1-C2-C13	-149.00(14)	C47-S7-C14-C15	-62.7(10)	C26-S2-C3-C2	-176.4(8)	C36-S4-C7-C6	-113.4(10)	C10-S5-C37-C38	-171.3(9)	C10-S5-C37-C38	71.3(9)	C10-S5-C37-C38	71.3(9)
C2-S1-C3-C4	81.79(14)	C14-S7-C47-C48	166.3(7)	C3-S2-C26-C25	80.0(9)	C7-S4-C36-C35	148.7(10)	C11-S6-C46-C45	-59.3(9)	C11-S6-C46-C45	-59.3(9)	C11-S6-C46-C45	-59.3(9)
C13-S2-C12-C11	178.50(15)	C15-S8-C56-C55	159.7(6)	C2-S1-C17-C18	-77.2(7)	C27-S3-C6-C7	71.4(16)	C46-S6-C11-C10	159.0(9)	C46-S6-C11-C10	159.0(9)	C46-S6-C11-C10	159.0(9)
C12-S2-C13-C2	175.24(15)	C56-S8-C15-C14	148.7(8)	C17-S1-C2-C3	124.6(9)	C27-S3-C6-C5	9.7(14)	C39-S9-C38-C37	-31.5(10)	C39-S9-C38-C37	-31.5(10)	C39-S9-C38-C37	-31.5(10)
C12-S2-C13-C14	-5.74(17)	C56-S8-C15-C16	-42.5(10)	C17-S1-C2-C1	-65.9(8)	C34-S4-C7-C6	-173.3(10)	C38-S9-C39-C40	174.9(9)	C38-S9-C39-C40	174.9(9)	C38-S9-C39-C40	174.9(9)
C5-O1-C4-C3	174.42(16)	C49-O13-C48-C47	-169.3(8)	C24-O4-C25-C26	177.9(9)	C35-S5-C36-C35	-176.1(13)	C41-O10-C40-C39	164.0(10)	C41-O10-C40-C39	164.0(10)	C41-O10-C40-C39	164.0(10)
C4-O1-C5-C6	160.05(17)	C48-O13-C49-C50	-179.0(8)	C25-O4-C24-C23	172.5(8)	C35-O8-C34-C33	88.1(17)	C40-O10-C41-C42	177.4(10)	C40-O10-C41-C42	177.4(10)	C40-O10-C41-C42	177.4(10)
C7-O2-C6-C5	166.76(19)	C51-O14-C50-C49	178.2(8)	C22-O3-C23-C24	77.0(10)	C32-O7-C33-C34	94(2)	C43-O11-C42-C41	-84.3(15)	C43-O11-C42-C41	-84.3(15)	C43-O11-C42-C41	-84.3(15)
C6-O2-C7-C8	-172.51(18)	C50-O14-C51-C52	-179.4(8)	C23-O3-C22-C21	-177.4(8)	C33-O7-C32-C31	98.7(18)	C42-O12-C44-C43	166.1(14)	C42-O12-C44-C43	166.1(14)	C42-O12-C44-C43	166.1(14)
C9-O3-C8-C7	172.85(19)	C53-O15-C52-C51	-173.3(7)	C20-O2-C21-C22	-174.9(7)	C30-O6-C31-C32	-99.3(15)	C44-O12-C45-C46	168(2)	C44-O12-C45-C46	168(2)	C44-O12-C45-C46	168(2)
C8-O3-C9-C10	81.8(2)	C52-O15-C53-C54	177.7(8)	C21-O2-C20-C19	-69.0(10)	C31-O6-C30-C29	159.1(12)	C45-O12-C46-C46	103.6(18)	C45-O12-C46-C46	103.6(18)	C45-O12-C46-C46	103.6(18)
C11-O4-C10-C9	-174.69(19)	C55-O16-C54-C53	-179.1(8)	C18-O1-C19-C20	79.1(10)	C28-O5-C29-C30	157.5(13)	S5-C37-C38-O9	63.7(11)	S5-C37-C38-O9	63.7(11)	S5-C37-C38-O9	63.7(11)
C10-O4-C11-C12	-171.87(18)	C54-O16-C55-C56	-177.2(8)	C19-O1-C18-C17	158.9(7)	C29-O5-C28-C27	-66(2)	O9-C39-C40-O10	-73.9(12)	O9-C39-C40-O10	-73.9(12)	O9-C39-C40-O10	-73.9(12)
S1-C3-C4-O1	58.58(18)	S7-C47-C48-O13	-79.0(9)	O4-C25-C26-S2	62.9(10)	O8-C35-C36-S4	54.7(14)	O10-C41-C42-O11	54.3(15)	O10-C41-C42-O11	54.3(15)	O10-C41-C42-O11	54.3(15)
O1-C5-C6-O2	-75.2(2)	O13-C49-C50-O14	-63.4(10)	O3-C23-C24-O4	-81.1(11)	O7-C33-C34-O8	-168.2(14)	O11-C43-C44-O12	50(3)	O11-C43-C44-O12	50(3)	O11-C43-C44-O12	50(3)
O2-C7-C8-O3	172.36(17)	O14-C51-C52-O15	75.0(10)	O2-C21-C22-O3	72.6(10)	O6-C31-C32-O7	-67.7(17)	O12-C45-C46-S6	-56.6(11)	O12-C45-C46-S6	-56.6(11)	O12-C45-C46-S6	-56.6(11)
O3-C9-C10-O4	-73.0(2)	O15-C53-C54-O16	-60.0(9)	O1-C19-C20-O2	-65.0(10)	O5-C29-C30-O6	-71.0(18)						
O4-C11-C12-S2	65.1(2)	O16-C55-C56-S8	66.0(9)	S1-C17-C18-O1	170.5(6)	S3-C27-C28-O5	178.2(11)						

^a Torsion angles deviating from the Wolf rule are underlined (see text).

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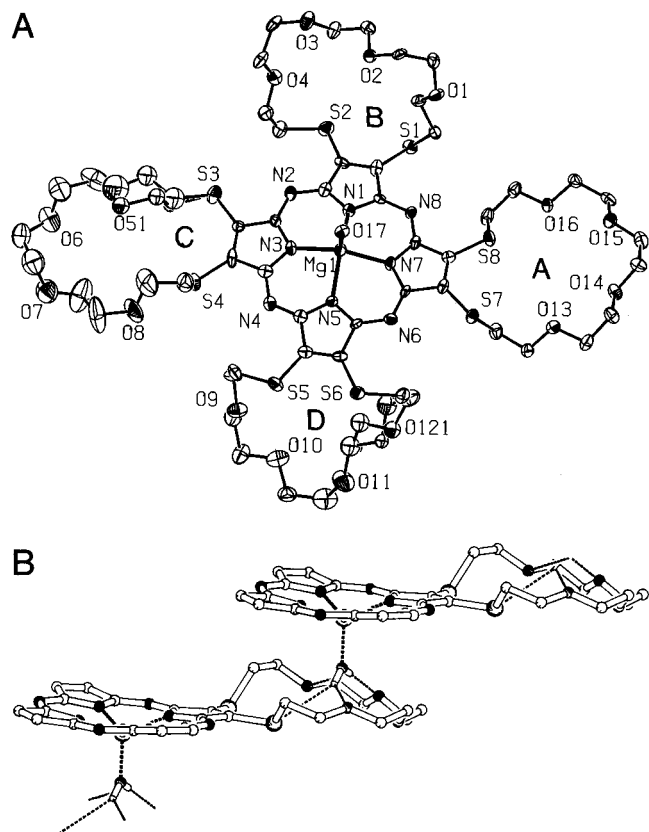


Figure 2. Thermal motion ellipsoid plot (50% probability level) of porphyrazine MgPz(18) (A); side view showing the polymeric chain of molecules (for clarity only one crown ether ring is shown) (B). The hydrogen atoms have been omitted.

can be seen in Table 2, the torsion angles obey Wolf's rule for crown ethers,⁴² *i.e.* the conformations around the C–S and the C–C bonds are gauche whereas those 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 endodentate and the sulfur atoms exodentate,⁴² but in the structure of **2(2)** O3 is exodentate, and the two sulfur atoms are endodentate. 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 porphyrin 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

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Table 3. UV–Vis data of the Porphyrazines^a

compound	λ_{\max}/nm (log $\epsilon/\text{L mol}^{-1} \text{cm}^{-1}$)			
MgPz(7)	669 (4.98)	616 (sh)	542 (4.29)	371 (4.96)
MgPz(15)	675 (4.97)	619 (sh)	503 (4.07)	378 (4.89)
MgPz(18)	675 (4.97)	622 (sh)	503 (4.12)	377 (4.91)
H ₂ Pz(15)	715 (4.63)	642 (4.48)	501 (4.30)	345 (4.67)
H ₂ Pz(18)	714 (4.62)	640 (4.48)	504 (4.33)	351 (4.69)
CuPz(15)	675 (4.80)	618 (sh)	496 (4.23)	341 (4.66)
CuPz(18)	675 (4.79)	622 (sh)	497 (4.26)	355 (4.69)

^a sh = shoulder.

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.⁴³ 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.⁴⁵ 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.^{39,46} From the data of the magnesium derivatives MgPz(7), MgPz(15), and MgPz(18), it

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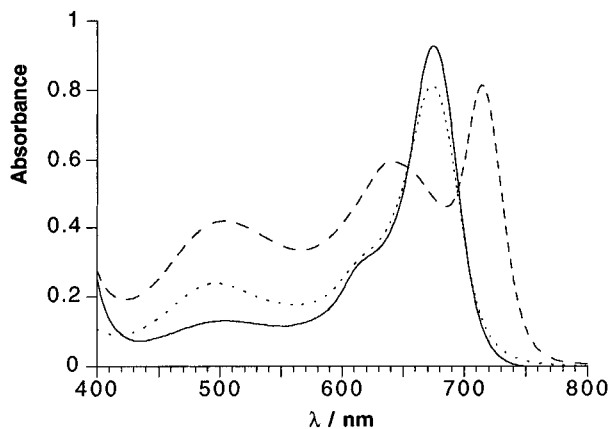


Figure 3. Absorption spectra of dithia-18-crown-6 Pz derivatives in CHCl_3 -MeOH (95:5, v/v): MgPz(18) (—), $\text{H}_2\text{Pz}(18)$ (---), CuPz(18) (···).

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 $\text{H}_2\text{Pz}(18)$ 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 $n-\pi^*$ transition (n is non-bonding electron of sulfur).^{46b,47} 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.^{45,48} 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 alkylthioporphyrazines.⁴⁶

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 AgClO_4 or $\text{Hg}(\text{ClO}_4)_2$ 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 Hg^{2+} , respectively. At the same time the $n-\pi^*$ 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 AgClO_4 an inflection point is visible at a metal to porphyrazine ratio of *ca.* 2.5. The curve for $\text{Hg}(\text{ClO}_4)_2$ 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)). Hg^{2+} 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

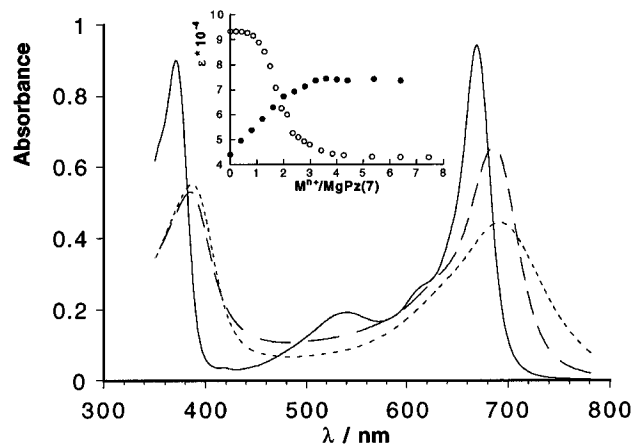


Figure 4. Absorption spectra of MgPz(7) in CHCl_3 -MeOH (95:5, v/v): without metal salt (—), in the presence of 4 equiv of AgClO_4 (---), or in the presence of 4 equiv of $\text{Hg}(\text{ClO}_4)_2$ (···). Inset: plot of the molar extinction coefficient *vs* the metal–porphyrazine ratio: Ag^+ ($\lambda = 686$ nm) (●), Hg^{2+} ($\lambda = 669$ nm) (○).

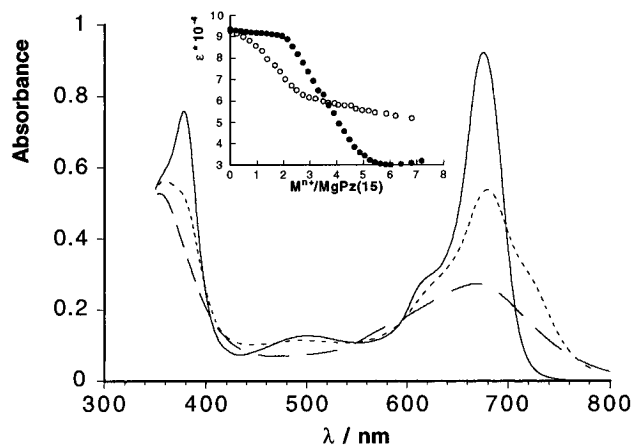


Figure 5. Absorption spectra of MgPz(15) in CHCl_3 -MeOH (95:5, v/v): without metal salt (—), in the presence of 6 equiv of AgClO_4 (---), or in the presence of 4 equiv of $\text{Hg}(\text{ClO}_4)_2$ (···). Inset: plot of the molar extinction coefficient at 675 nm *vs* the metal–porphyrazine ratio: Ag^+ (●); Hg^{2+} (○).

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 AgClO_4 are shown in Figure 6. The titration curve is presented in Figure 6 (inset). Addition of AgClO_4 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 AgClO_4 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 AgClO_4 caused this peak to decrease slightly and to shift to 661 nm. A third set of isosbestic points was now observed. The $n-\pi^*$ transition disappeared gradually between 0 and 6 equiv of AgClO_4 . $\text{Hg}(\text{ClO}_4)_2$ 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 $\text{H}_2\text{Pz}(18)$ was even more complex. Four stages could be distinguished during the titration with AgClO_4 . Each stage had its own set of isosbestic

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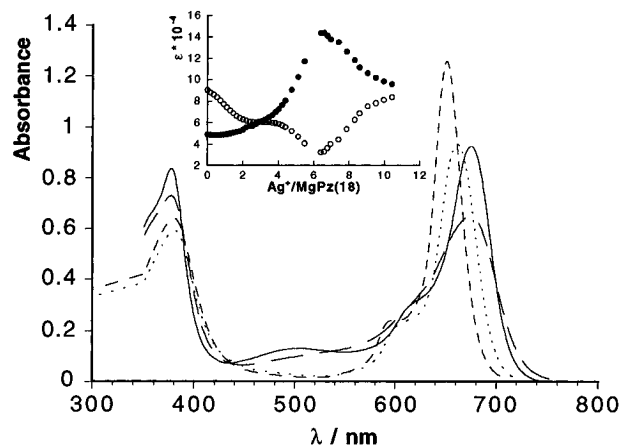


Figure 6. Absorption spectra of MgPz(18) in CHCl_3 -MeOH (95:5, v/v) in the presence of various amounts of AgClO_4 : 0 equiv (—), 2 equiv (---), 6 equiv (- - -), or 12 equiv (· · ·). Inset: plot of the molar extinction coefficient *vs* the Ag^+ -porphyrizine ratio at different wavelengths: 675 nm (○), 650 nm (●).

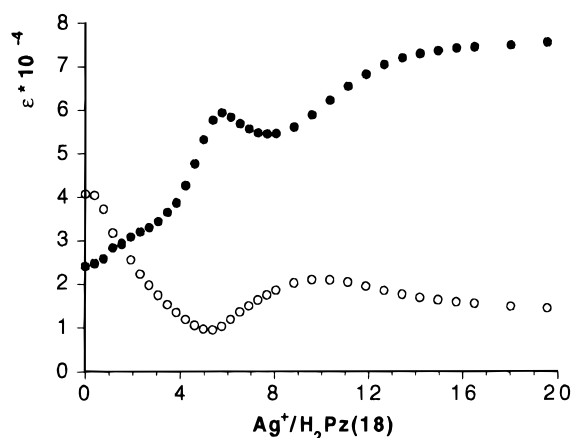


Figure 7. Plot of the molar extinction coefficient of $\text{H}_2\text{Pz}(18)$ in CHCl_3 -MeOH (95:5, v/v) *vs* the Ag^+ -porphyrizine ratio at different wavelengths: 714 nm (○), 676 nm (●).

points. Some spectra are supplied in the Supporting Information. During the addition of the first two equivalents of AgClO_4 the two Q-bands subsided and broadened, and the $n-\pi^*$ transition shifted to the red. On further addition of AgClO_4 , up to 6 equiv, the latter transition disappeared completely, and two new bands appeared, *viz.* at 676 and 626 nm with a shoulder at about 575 nm. Between 6 and 8 equiv these two new peaks slightly shifted to the red and broadened. Finally, at a metal to porphyrizine ratio of about 12, only one broad band at 676 nm with a shoulder at *ca.* 620 nm was left. Further addition of AgClO_4 did not affect the spectra appreciably. The plots of the molar extinction coefficient at 676 and 714 nm *vs* the Ag^+ to porphyrizine ratio are presented in Figure 7.

The copper porphyrizine CuPz(18) behaved similarly as the corresponding magnesium derivative when AgClO_4 was added, except that the blue shift of the Q-band at the metal-porphyrizine ratio of 6 was larger, *i.e.* to 640 nm instead of 650 nm. CuPz(15) reacted with AgClO_4 in a manner similar to the magnesium derivative MgPz(15) with $\text{Hg}(\text{ClO}_4)_2$, as could be concluded from the broadening of the Q-band, which was observed up to a metal-porphyrizine ratio of about 3 (results not shown).

The results presented above indicate that the metal binding behavior of the crowned porphyrizines is rather complex, and at this stage it is not possible to fully explain the results obtained by the UV-vis absorption experiments. Some conclusions can

nevertheless 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 $\text{Hg}(\text{ClO}_4)_2$ and the reaction of MgPz(15) with AgClO_4 . It is possible that in the case of these porphyrizines 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 porphyrizines is the shift of the Q-band which takes place upon complexation of the metal perchlorates. The porphyrizine with the smallest crown ether rings, MgPz(7), shows a red-shift of this band, whereas MPz(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 porphyrizine molecules.

A remarkable phenomenon of all the experiments is the disappearance of the $n-\pi^*$ 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-dithiacyclohexeno) Pz are protonated.^{46b} 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 porphyrizines. 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 porphyrizines, 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 AgClO_4 complexes of this porphyrizine and of CuPz(15) were recorded using a porphyrizine concentration of *ca* 1 mM. Figure 8A shows the spectra of CuPz(18) recorded at various temperatures in CHCl_3 . 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 ($g_{\parallel} = 2.135$, $g_{\perp} = 2.052$, $A_{\parallel} = 205$ 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 tetraphenylporphyrine.⁴⁹ 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 8A) is a triplet spectrum characteristic of two coupled copper nuclei, indicating that in the frozen solution dimers are present.^{7b,50} Two strong perpendicular transitions each containing seven lines are visible in the $g = 2$ region, as well as small signals at half field. It is possible to calculate from the EPR data the distance between the two copper nuclei, using the formula⁵⁰

$$D_2 = 0.65g_2^2/r^3 \quad (1)$$

where g_2 is the average g value of the two perpendicular transitions, D_2 is the difference between g_2 and the g values of the transitions in cm^{-1} , and r is the Cu-Cu distance (see also Figure 8A). The calculated values of D_2 and g_2 , from which a distance of $r = 4.1$ Å can be derived, are given in Table 4.

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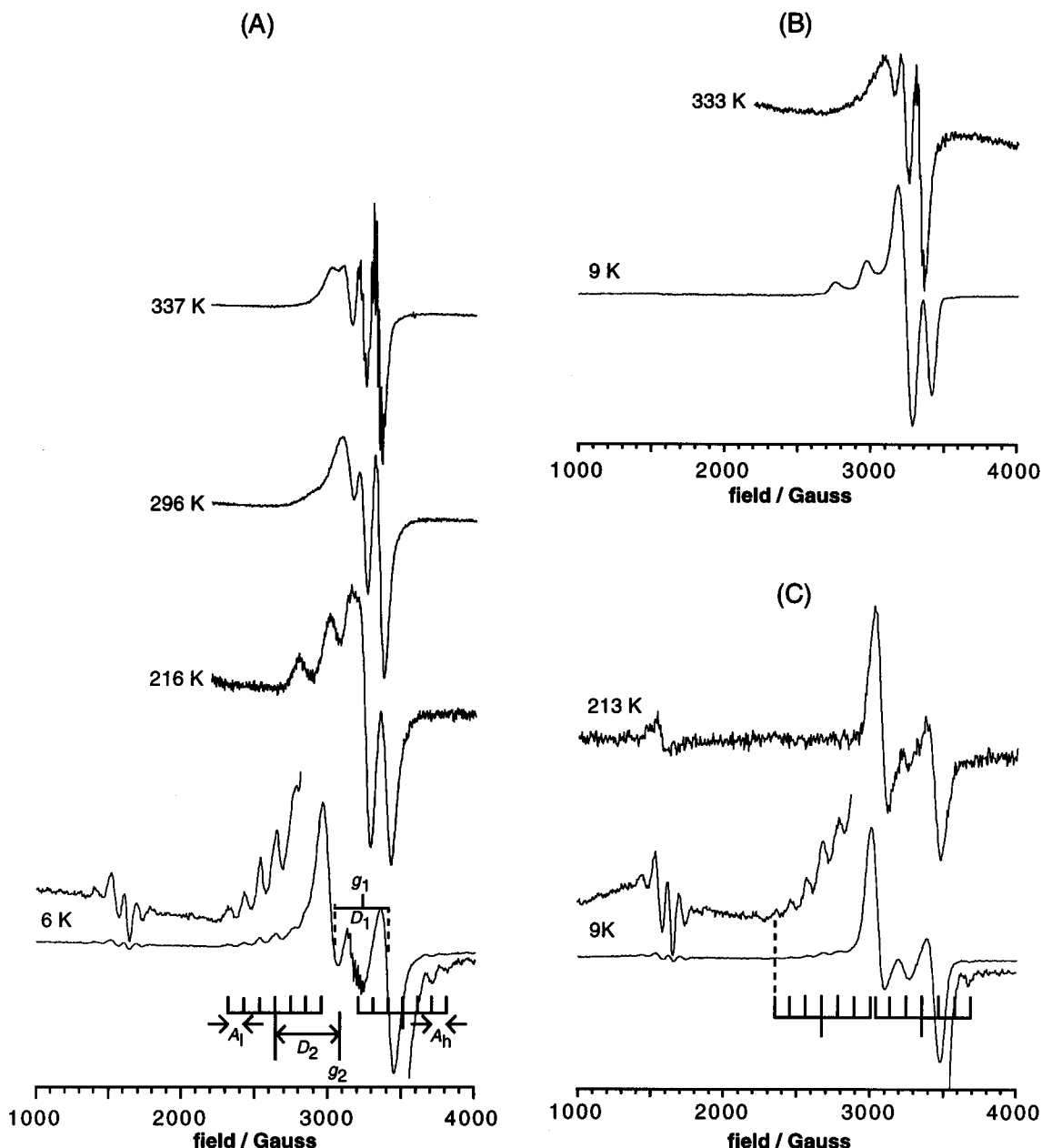


Figure 8. EPR spectra of copper Pzs in CHCl_3 -MeOH (95:5, v/v) at various temperatures: CuPz(18) (A), CuPz(18) in the presence of 6 equiv of AgClO_4 (B), or CuPz(15) in the presence of 6 equiv of AgClO_4 (C).

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

compound	g_1	g_2	A_1/G	A_2/G	D_1/G	D_2/G	$r/\text{\AA}$
CuPz(18)	2.045	2.136	112	105	346	424	4.1
CuPz(15) + 6 AgClO_4	2.058	2.226	108	108	343	335	4.5

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

It is highly probable that, in the absence of AgClO_4 , the molecules of CuPz(15) are monomers in solution at room temperature, like those of CuPz(18), since the UV-vis spectra of both compounds are almost identical (see Table 3).

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): $g_{\parallel} = 2.18$, $g_{\perp} = 2.06$, $A_{\parallel} = 206$ G). In the case of CuPz(15) only a

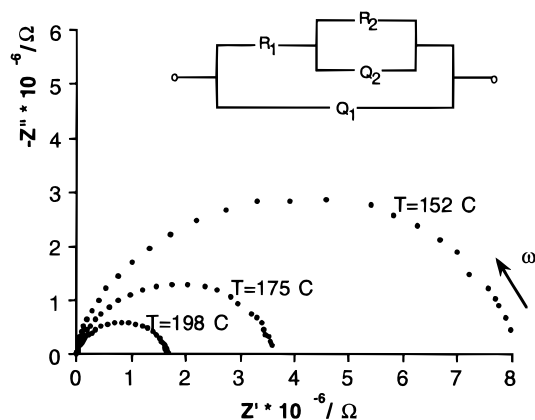
small temperature dependence was observed. The increased size of the dimeric species probably prevents the development of a fully isotropic spectrum at elevated temperatures. The spectrum recorded at 9 K was sufficiently resolved to calculate the Cu-Cu distance. We assume that the small peak which is 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_2 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 Pcs have been extensively studied before.^{8,9,12b,51} We carried out preliminary ac conductivity experiments with one of the crowned Pzs, *viz.* the metal-free dithia-18-crown-6 derivative $\text{H}_2\text{Pz}(18)$. Figure 9

Table 5. Values of the Equivalent Circuit Parameters at 150 °C Obtained from Fitting of the Impedance Spectra of H₂Pz(18)^a

$\sigma_1/\text{S m}^{-1}$	$E_{a,1}/\text{eV}$	$k_{Q_1}^{-1}$	α_1	ϵ_r	$\sigma_2/\text{S m}^{-1}$	$E_{a,2}/\text{eV}$	$k_{Q_2}^{-1}$	α_2
5.94×10^{-6}	0.54	1.62×10^{-11}	0.98	11	2.69×10^{-6}	0.73	4.13×10^{-10}	0.68

^a σ_1 and σ_2 , conductivity related to resistances R_1 and R_2 ; $E_{a,1}$ and $E_{a,2}$, activation energy of conduction related to resistances R_1 and R_2 ; k_Q , preexponential factor for impedance of constant-phase element Q ; α , exponential factor for impedance of Q ; ϵ_r , relative dielectric constant.

**Figure 9.** Impedance spectra of H₂Pz(18) at different temperatures in the frequency range 10¹–10⁶ Hz. Inset: equivalent circuit used for fitting the ac responses of H₂Pz(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 picrate complexes.⁸ 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 $Z_{Q_1} = (k_{Q_1}(i\omega)^\alpha)^{-1}$, has a value of α 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 ϵ_r = relative dielectric constant, ϵ_0 = the permittivity of free space, *i.e.* 8.85×10^{-12} F m⁻¹, A = electrode surface area, and d = sample thickness. C_∞ 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,⁸ 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, $\sigma_1 = \sigma_0(\exp(-E_{a,1}/kT))$, the activation energy $E_{a,1}$ was found to be 0.54 eV. This value is lower than that for 18-crown-6-Pc,⁸ but similar to the activation energies for intercolumnar electron hopping in mesogenic Pcs.^{52c,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.⁸ 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_2Q_2) 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 σ_2 could be derived. The value of α 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 $Z_W = k_W^{-1}(i\omega)^{-1/2}$.

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.⁵⁴ 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^{16,22} indicate that such a binding indeed takes place. In a number of cases this leads to aggregation of the porphyrazines, *e.g.* when AgClO₄ or Hg-(ClO₄)₂ is added to solutions of MgPz(7) and to the dithia-15-crown-5 porphyrazines.⁵⁵ 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]₆. These complexes display 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.⁵⁶ 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)**,^{16,22} 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 accommodate a silver ion and the coordination sites of the latter ion can be completely filled by the atoms of a single macrocycle.⁵⁷ 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

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 (53) Belarbi, Z.; Maitrot, M.; Ohta, K.; Simon, J.; André, J. J.; Petit, P. *Chem. Phys. Lett.* **1988**, *143*, 400.

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(55) In our previous communication,^{16a} we concluded that MPz(15) remains monomeric and that MPz(18) dimerizes in the presence of 6 equiv of silver perchlorate. On the basis of the results presented in this paper, we have to withdraw these conclusions.

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(57) A polymeric structure was also observed for the Ag⁺ complex of **2(2)** in the solid state, but the Ag⁺ ion is probably fully surrounded by a single crown ether ring in solution (see ref 22).

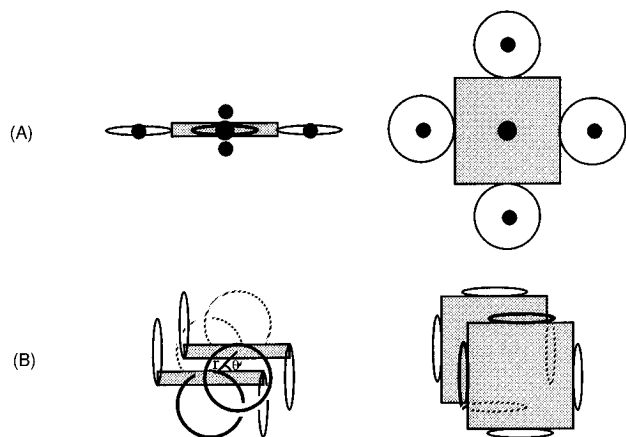


Figure 10. Side view and top view of the proposed structures of the monomeric complexes between MPz(18) and 6 Ag^+ ions (A) and of the dimeric complex of MPz(15) and Ag^+ ions with $r = 4.5 \text{ \AA}$ and $\theta \approx 54.7^\circ$ (B). The squares and rectangles represent the aromatic cores, the 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 AgClO_4 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 a slipped-stacked orientation with a tilt angle (angle between the normal of the porphyrazine plane and the center-to-center line) of approximately 35.3° .⁵⁸ The dimeric AgClO_4 and $\text{Hg}(\text{ClO}_4)_2$ 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 r in the complex of CuPz(15) with AgClO_4 amounts to 4.5 \AA . From this value the interplanar distance can be calculated to be approximately $r \times \cos 35.3 = 3.67 \text{ \AA}$. The centers of the porphyrazine rings are shifted $r \times \sin 35.3 = 2.60 \text{ \AA}$ 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.^{16,22} This makes it likely that the crown ether rings in the AgClO_4 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 ionoelectronics. As postulated by Simon^{2,3} 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 Hg^{2+} (Figure 4), MgPz(15) with Ag^+ (Figure 5), and MgPz(18) with Hg^{2+} and Ag^+ (Figure 6) and from the curves of $\text{H}_2\text{Pz}(18)$ 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.

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Supporting Information Available: A figure showing absorption spectra of $\text{H}_2\text{Pz}(18)$ 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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