Acta Chemica Scandinavica, 1999: 53: 1117–1121
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ACTA
CHEMICA SCANDINAVICA
ISSN 0904–213X

Preparation of Octa(alkoxy) Azaphthalocyanines

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Mørkved, E. H., Kjøsen, H. and Ossletten, H., 1999. Preparation of Octa(alkoxy) Azaphthalocyanines. – Acta Chem. Scand. 53: 1117–1121. © Acta Chemica Scandinavica 1999.

5,6-Bis(alkoxy)pyrazine-2,3-dicarbonitriles **3**, with methoxy-, ethoxy- and propoxy-substituents, were allowed to react with magnesium alkoxides to form the corresponding magnesium octa(alkoxy)azaphthalocyanines **5a,d,e**. Compound **5a** was converted into the metal-free azaphthalocyanine **5b**, and to the copper complex **5c**. The propoxy substituted magnesium azaphthalocyanine **5e** was converted to the metal free azaphthalocyanine **5f**. Both **5e** and **5f** are readily soluble in organic solvents. The stable intermediate methyl 2,3-di(methoxy)-6-cyanopyrazine-5-carboximidate **4**, was obtained both from a reaction of 5,6-dichloropyrazine-2,3-dicarbonitrile **1**, with sodium methoxide in methanol, and in a sodium methoxide catalyzed reaction of **3a** with ammonia in methanol. Compound **4** was converted into **5a** with magnesium methoxide, and is therefore an intermediate between **3a** and **5a**.

Substituted azaphthalocyanines (AzaPc's) are generally more soluble than the corresponding phthalocyanines (Pc's), and may, therefore, be more applicable in various areas of technology[1] and in photodynamic therapy.[2] A limited number of substituted AzaPc's have been reported in the literature,[3] where alkyl groups, carboxylic acids or esters are mentioned as substituents. For instance, AzaPc's, substituted with carboxylic acids, were prepared as potential activators for photodynamic cancer therapy.[4]

We have reported[5] some *S*-substituted AzaPc's, but several of the sulfur-containing side chains were replaced by the alkoxide nucleophiles used for the cyclotetramerisations. Recently we found[6] that 5,6-bis-(dialkylamino)pyrazine-2,3-dicarbonitriles were practically inert to cyclisations with magnesium propoxide. However, AzaPc's could be formed from the more reactive diiminoimides, which were formed via stable alkyl carboximidates in an unprecedented reaction.

Presently we report syntheses of alkoxy-substituted pyrazine-dicarbonitriles **3**, and cyclotetramerisations of **3** to AzaPc's (Scheme 1). With reference to previous results with thio- and amino-substituted pyrazines,[5,6] special attention was paid to possible side chain exchange reactions, and to formation of stable alkyl carboximidate intermediates.

Results and discussion

5,6-Dichloropyrazine-2,3-dicarbonitrile (**1**) was reacted with alcohols and triethylamine to give **3a–c** in good to fair yields. A reaction of **1** with phenol and triethylamine in THF gave **3d**.

Compound **1** undergoes mono-substitution far more readily than disubstitution, in accordance with previous observations.[7] Thus, 6-chloro-5-ethoxypyrazine-2,3-dicarbonitrile (**2a**) was observed as an intermediate in the synthesis of **3b**, and 6-chloro-5-propoxypyrazine-2,3-dicarbonitrile (**2b**) was obtained instead of **3c** when the reaction of **1** with triethylammonium propoxide was stopped after 1 h at ambient temperature. There seems to be a fairly small difference in reactivities of the cyano and the chloro groups of **1**. Thus, 5,6-dichloro-3-ethoxypyrazine-2-carbonitrile was obtained as a minor product in the preparation of **3b**.

Attempts to prepare **3a** from **1** and an excess of sodium hydride in methanol, gave the stable methyl carboximidate **4** in 57% yield. A reaction of **3a** with catalytic amounts of sodium hydride and gaseous ammonia in refluxing methanol was expected to yield the diiminoimide derivative of **3a**. Only **4** was observed by TLC after reflux for 3 h. Propanol was added, methanol was distilled off and the reaction mixture was refluxed and flushed with ammonia for another 3 h. The product was shown by mass spectroscopy, ^{1}H and ^{13}C NMR to be a mixture of diiminoimides with methoxy and propoxy side chains.

The formation of **4** as a stable intermediate in the sodium methoxide catalyzed reaction of **3a** with ammonia, parallels the formation of stable alkyl carboximidates from bis(dialkylamino)pyrazine-dicarbonitriles.[6] Sodium alkoxide catalyzed reactions of phthalonitriles and

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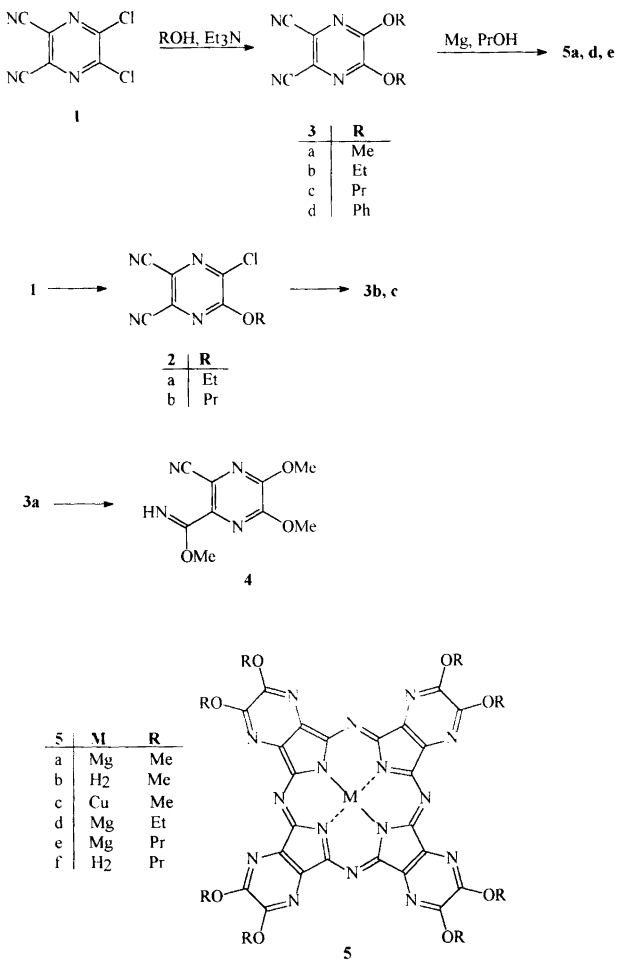

Scheme 1.

ammonia usually give reactive diiminoimides, and the only intermediates between phthalonitriles and diiminoimides have been postulated as unstable alkoxyiminoimides.[8,9]

With the above results in mind, the magnesium AzaPc's **5a,d,e** were prepared from magnesium, and alcohols corresponding to the side chains of dinitriles **3**. Compound **5a** was obtained in 69% yield, from **3a** and magnesium methoxide in refluxing methanol, and in 56% yield from the methyl carboximidate **4** and magnesium methoxide, thus establishing **4** as an intermediate between **3a** and **5a**. However, **5a** was not analytically pure; nitrogen and magnesium contents were considerably lower than the calculated values.

The crude magnesium complex **5a** was heated at 140 °C for 15 h with copper(II) chloride in formamide. A TOF-SIMS analysis showed that the product was a mixture of unreacted **5a** and the copper complex **5c**. Both molecular ions, each with the calculated isotopic pattern, were observed.

Treatment of crude **5a** with cold trifluoroacetic acid (TFA) gave the metal free AzaPc **5b**. This product had satisfactory element analyses.

A reaction of **3a** with magnesium propoxide in propanol gave a dark blue powder with $\varepsilon = 129\,000$ at 624 nm, but with C, H, N and Mg element analyses much closer to the calculated values for the octa(propoxy)AzaPc **5e** than for **5a**, thus indicating exchange of the methoxy side chains during the cyclotetramerisation.

Octa(ethoxy) MgAzaPc (**5d**) was obtained in 75% yield from **3b** and magnesium ethoxide. The electronic spectra of **5d** are distinctly different in dichloromethane (DCM) and pyridine, indicating that these solvents may influence aggregation of **5d** to various degrees. Three absorptions are observed in DCM, at 670, 625 and 604 nm, all with ε in the range 28 000–30 000. However, the pyridine solution shows one strong absorption at 626 nm with $\varepsilon = 81\,000$. Whereas the pyridine solution of **5d** has a strong red fluorescence in 365 nm light, the DCM solution has practically no fluorescence.

Propoxy-substituted **5e** was obtained from **3c** and magnesium propoxide in propanol. Compound **5e** had satisfactory elemental analyses and was obtained in 75% yield. The variation of the electronic spectra of **5e** with solvent was similar to that described for **5d**. MgAzaPc (**5e**) was reacted with cold TFA, and the metal-free compound **5f** was obtained in 87% yield. Both **5e** and **5f** are easily soluble in most organic solvents.

An attempt to prepare **5e** directly from **1** and magnesium propoxide in propanol gave a dark blue solid, which has a strong absorption at 630 nm in pyridine, but the element analyses of the product showed a considerably lower content of carbon than calculated for **5e**.

The phenoxy substituents of **3d** are too labile for AzaPc formation from this compound. Thus, a reaction mixture of **3d** and magnesium propoxide produced a strong odor of phenol, and the AzaPc which was obtained had C, H, N and Mg analyses close to the calculated values for **5e**, i.e. the phenoxy side chains had been replaced with propoxy groups. An attempt to prepare the metal-free AzaPc from **3d** and hydroquinone also produced free phenol and a dark blue powder which was not investigated further.

Conclusions

The labile alkoxy and phenoxy side chains of pyrazines **3** complicate their cyclotetramerisation reactions. However, MgAzaPc's **5a**, **5d** and **5e** can be obtained, provided the reactant magnesium alkoxide corresponds to the alkoxide substituents of compound **3**. No practical cyclotetramerisation reaction was found for phenoxy-substituted **3d**.

Propoxy-substituted MgAzaPc (**5c**) and 2HAzaPc (**5f**) are readily soluble in organic solvents, and are of potential interest for a variety of applications.

The methyl carboximidate **4** was established as an intermediate between pyrazine **3a** and MgAzaPc (**5a**). Similar alkyl carboximidates were observed for the first time from reactions of dialkylamino-substituted pyrazine-dicarbonitriles,[6] and represent an unusual type

of intermediate in cyclotetramerisations of aromatic dicarbonitriles.

Experimental

General. EI mass spectra of compounds **1**–**3** were obtained on an AEI MS-902 spectrometer at 70 eV electron energy. The TOF-SIMS (Ar^+) mass spectra of **5a** and **5c** were obtained by *Institut Fresenius Angewandte Festkörperanalytik GmbH,* Germany. IR spectra were obtained on a Nicolet 20-SXC FT-IR spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX 400 NMR spectrometer at 399.65 MHz and at 100.40 MHz, respectively, and with tetramethylsilane (TMS) as internal standard. UV–VIS spectra were obtained on a Perkin Elmer 522 UV–VIS spectrophotometer. Microanalyses were performed by *Analytische Laboratorien*, Lindlar, Germany. Melting points were obtained on a Büchi 530 melting-point apparatus and are uncorrected.

Merck Kieselgel 60F 254 was used for TLC, and Merck silica 63–200 μm was used for column chromatography. Cellulose, Merck 2331 Avicel, was used for column chromatography of compound **5e**. Diaminomaleonitrile was obtained from Janssen, 1-propanol was dried over potassium carbonate, distilled and stored over 3 Å molecular sieves.

5,6-Dichloropyrazine-2,3-dicarbonitrile (**1**) was prepared in two steps from diaminomaleonitrile,[5,10] but with the following modification: Compound **1** was extracted with dichloromethane (DCM) instead of toluene, and purified by chromatography on silica with DCM to give **1** as a yellow powder, m.p. 179–181 °C in 55% overall yield. ^{13}C NMR ($CDCl_3$): δ 111.21 (CN), 129.94, 151.91.

Compounds **3a**–**c**.

General. A solution of triethylamine (11 mmol, 1.1 g) in ROH (10 ml) was added to a stirred suspension of **1** (5 mmol, 1.0 g) in ROH (25 ml) at ambient temperature. The solutions, which formed upon addition of the base, were monitored with TLC (silica, benzene). Complete reactions were observed: in methanol after 2 h and in ethanol after 44 h at ambient temperature, in propanol after 2 h at 80 °C. The solvent was removed under reduced pressure. The residue was extracted with benzene, filtered, and the organic phase was chromatographed on silica with benzene.

5,6-Bis(methoxy)pyrazine-2,3-dicarbonitrile, **3a**. Yield 0.80 g (84%), m.p. 164–166 °C. MS [*m/z* (%rel. int.)]: 191 (10.8), 190 (*M*,100), 161 (81.0), 160 (18.8), 131 (8.32), 130 (39.1). Found 190.0493, calc. for $C_8H_6N_4O_2$ 190.0491. IR (KBr): 3042 (CH), 2964 (CH), 2237 (CN), 1561,1500, 1484,1253 (C–O stretch) cm.$^{-1}$. ^1H NMR ($CDCl_3$): δ 4.15 (3 H, s). ^{13}C NMR ($CDCl_3$): δ 56.48, 113.67 (CN), 123.41 (C-5, C-6), 152.53.

5,6-Bis(ethoxy)pyrazine-2,3-dicarbonitrile, **3b**. Yield 0.61 g (56%), m.p. 117–118 °C. MS [*m/z* (%rel. int.)]: 219 (4.1), 218 (*M*, 31.5) 190 (14.1), 162 (100). Found 218.0801, calc. for $C_{10}H_{10}N_4O_2$ 218.0804. IR (KBr): 2995, 2238 (CN), 1554, 1465, 1340, 1247, 1016, 882 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.50 (3 H, t, J=7 Hz), 4.57 (2 H, q, J=7 Hz). ^{13}C NMR ($CDCl_3$): δ 13.95, 65.51, 113.49 (CN), 122.67 (C-5, C-6), 151.80.

A small amount, 0.08 g (7%) of *5,6-dichloro-3-ethoxy-2-pyrazinecarbonitrile*, m.p. 48–51 °C, was eluted from the column ahead of compound **3b**. MS [*m/z* (%rel. int.)]: 219 (17.2), 217 (*M*, 28.0), 191 (64.98), 189 (100). IR (KBr): 2991, 2237 (CN), 1548, 1431, 1345, 1201, 1159, 998 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.51 (3 H, t, J=7 Hz), 4.55 (2 H, q, J=7 Hz). ^{13}C NMR ($CDCl_3$): δ 14.11, 66.08, 112.48, 115.09, 137.98, 148.25, 159.11.

In another experiment, the reaction products were isolated after two hours at ambient temperature, and *6-chloro-5-ethoxypyrazine-2,3-dicarbonitrile* (**2a**), 0.54 g (52%), m.p. 60–62 °C, was obtained as the first chromatographic fractions. MS [*m/z* (%rel. int.)]: 210 (8.40), 208 (*M*, 26.59), 182 (32.31), 180 (100). IR (KBr): 2990, 2241 (w), 1545, 1450, 1347, 1147 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.52 (3 H, m), 4.62 (2 H, m).
^{13}C NMR ($CDCl_3$): δ 13.89, 67.14, 112.25, 112.35, 123.70, 129.15, 142.88, 157.32.

Compound **3b** 0.16 g (14%), m.p. 117–118 °C was then eluted from the column.

5,6-Bis(1-propoxy)pyrazine-2,3-dicarbonitrile, **3c**. Yield 0.75 g (61%), m.p. 55–60 °C, R_f (benzene)=0.59. MS [*m/z* (%rel. int.)]: 246 (*M*, 12.7), 163 (37.2), 162 (39.9), 43 (100). Found 246.1121, calc. for $C_{12}H_{14}N_4O_2$ 246.1117. IR (KBr): 2972, 2237 (CN), 1551, 1498, 1458, 1360, 1338, 1240, 942 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.04 (3 H, t, J=7 Hz), 1.87 (2 H, q, J=7 Hz), 4.31 (2 H, t, J=6 Hz). ^{13}C NMR ($CDCl_3$): δ 10.26, 21.69, 70.85, 113.52, 122.62, 152.03.

The second product, R_f (benzene)=0.41, was eluted after **3c**. Yield 0.15 g (14%), m.p. 77–78 °C. MS [*m/z* (%rel. int.)]: 247 (3.75), 246 (20.85), 205 (7.86), 204 (12.37), 163 (88.85), 162 (46.68), 43 (100). IR (KBr): 2971, 2235 (CN), 1548, 1489, 1425, 1333, 1205, 1174, 943 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.08 (3 H, m), 1.91 (2 H, m), 4.46 (2 H, m). ^{13}C NMR ($CDCl_3$): δ 10.30, 21.85, 71.10, 110.72, 112.91, (125.92), 162.06. This product, apparently an isomer of **3c**, was not investigated further.

In another experiment a mixture of triethylamine (4 mmol, 0.4 g) and **1** (2 mmol, 0.2 g) in propanol (15 ml) was stirred at ambient temperature for 2 h. The reaction products were separated by chromatography with benzene on silica, and *6-chloro-5-propoxypyrazine-2,3-dicarbonitrile* (**2b**), 0.35 g (70%), liq., was obtained. R_f (benzene)=0.69. MS [*m/z* (%rel. int.)]: 225 (0.32), 224 (1.68), 222 (*M*, 5.18), 181 (7.75), 180 (2.79). ^1H NMR ($CDCl_3$): δ 1.10 (3 H, m), 1.91 (2 H, m), 4.50 (2 H, m). ^{13}C NMR ($CDCl_3$): δ 10.23, 21.71, 72.49, 112.24, 112.33, 123.70, 129.16, 142.90, 157.44.

5,6-Bis(phenoxy)pyrazine-2,3-dicarbonitrile (**3d**), was prepared from **1** (5 mmol, 1.0 g), triethyl amine (11 mmol, 1 g) and phenol (10 mmol, 0.94 g), in THF (50 ml) at 65 °C for 30 min, then purified by chromatography with benzene on silica. Yield 8.2 g (65%), m.p. 187–188 °C. MS [*m/z* (%rel. int.)]: 315 (20.2), 314 (*M*, 100), 313 (8.0), 286 (48.0), 269 (22.5). Found 314.0810, calc. for $C_{18}H_{10}N_4O_2$ 314.0804. IR (KBr) : 3736, 2232 (CN, w), 1540, 1486, 1454, 1353, 1254, 1242, 1151, 748 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.25 (2 H, m), 7.37 (1 H, m), 7.50 (2 H, m). ^{13}C NMR ($CDCl_3$): δ 112.72, 121.16, 123.91, 127.00, 130.08, 151.18, 151.37.

Methyl 2,3-di(methoxy)-6-cyano-pyrazine-5-carboximidate (**4**). A solution of sodium methoxide (3.0 mmol, 6 ml of 0.5 M) was added to a solution of **1** (1.5 mmol, 0.30 g) in methanol (12 ml). The solution was stirred at ambient temperature for 23 h, evaporated, and water (15 ml) was added. The solid precipitate was filtered off, washed with methanol, and 0.19 g (57%) m.p. 172–181 °C dec. was obtained. MS [*m/z* (%rel. int.)]: 223 (10.6), 222 (*M*, 100), 208 (11.1), 207 (76.6). Found 222.0751, calc. for $C_9H_{10}N_4O_3$ 222.0753. IR (KBr): 3301 (s), 2954, 2232 (CN, s), 1648, 1550, 1500, 1440, 1405, 1318, 1232, 1073, 976 cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.07 (3 H, s), 4.12 (3 H, s), 4.16 (3 H, s), 8.84 (1 H, s, broad). ^{13}C NMR ($CDCl_3$): δ 54.04, 55.23, 55.59, 115.64, 125.91, 136.11, 150.82, 150.96, 163.34.

Reaction of **3a** *with ammonia in methanol and propanol.* Compound **3a** (1 mmol, 0.20 g) was added to a mixture of sodium hydride (0.1 mmol, 5 mg) and methanol (30 ml). A rapid stream of ammonia was led through the solution, which was slowly heated and kept under reflux for 2 h. Compound **3a** was converted into **4**, as shown by TLC, R_f (acetone) = 0.85. Propanol (20 ml) was added, the temperature of the oil bath was raised to 110 °C, methanol was evaporated through the condenser, and ammonia was led through the reaction mixture for 3 h. At this time compound **4** had been replaced by a product of R_f(acetone) = 0. The solvent was removed, and the residue filtered with diethyl ether and hexane. Yield 0.09 g, m.p. 160–170 °C (dec.) MS [*m/z* (%rel. int.)]: 263 (7.74), 235 (31.86), 207 (74.33). These radical ions correspond to diiminoimides with respecively two propoxy; one propoxy and one methoxy; and two methoxy side chains on the pyrazine ring. ^1H NMR (CD_3OD): δ 0.83, 0.85, 1.02, 1.84, 3.96, 4.43, 8.5 (w).

Compounds **5a–c**.

General. Magnesium alkoxide was prepared, by heating under reflux, a nitrogen flushed mixture of magnesium (7 mmol, 0.18 g), iodine (one crystal) and either methanol (10 ml) for 2 h, ethanol (10 ml) for 4 h, or 1-propanol (10 ml) for 8 h. Compound **3** (2.0 mmol) was added and dissolved at once in the magnesium alkoxide slurry. The reaction mixture changed color from light green to dark blue during the heating under reflux for 24 h. The solvent was removed, water (60 ml) and glacial acetic acid (15 ml) were added, and the mixture was stirred at ambient temperature for 2 h. The dark solid was filtered off, and washed on the filter with large amounts of water, several portions of methanol, diethyl ether or acetone, depending on the product solubility.

{29H,31H-[2,3,9,10,16,17,23,24-Octakis(methoxy)-1,4,8,11,15,18,22,25-(octaza)phthalocyaninato](2-)-N^{29},N^{30},N^{31},N^{32}}magnesium, **5a**. Yield 0.27 g (69%). IR (KBr): 2949, 1839, 1546, 1478, 1317, 1250, 1008 cm^{-1}. UV [abs. pyridine (ε)]: 370 (27 000), 570 (16 000), 624 (33 200), 676 (8 800) nm. Anal. Found: C 50.26; H 4.76; N 24.92; Mg 1.40, calc. for $C_{32}H_{24}N_{16}O_8Mg$ C 48.96; H 3.08; N 28.55; Mg 3.10. Calc. for $C_{32}H_{24}N_{16}O_8Mg + 2\,CH_3COCH_3$ 50.65; H 4.03; N 24.87; Mg 2.70.

Compound **5a** *from* **4** *and magnesium methoxide in methanol.* Magnesium propoxide was prepared from magnesium (180 mg) and methanol (15 ml). Compound **4** (1 mmol, 0.22 g) was added, and the suspension was heated under reflux for 92 h. Water (60 ml) and acetic acid (15 ml) were added, the mixture was left at ambient temperature for 24 h, and the solid was filtered and washed with water, methanol and acetone. Yield 0.11 g (56%) of a dark powder. UV [abs. pyridine (ε)]: 370 (26 900), 570 (16 000), 624 (33 000), 676 (8 800) nm.

In another experiment **3a** was reacted with magnesium propoxide in propanol. A dark blue powder (ca. 60%) was obtained after the same work-up procedure as above. IR (KBr): 2986, 2876, 1543, 1438 (s), 1377, 1298, 1250 cm^{-1}. UV [abs. pyridine (ε)]: 366 (77 000), 566 (20 400), 624 (129 000) nm. Found: C 53.47; H 5.46; N 21.60; Mg 2.03, calc. for $C_{32}H_{24}N_{16}O_8Mg$ (**5a**): C 48.96; H 3.08, N 28.55; Mg 3.10.

{29H,31H-[2,3,9,10,16,17,23,24-Octakis(methoxy)-1,4,8,11,15,18,22,25-(octaza)phthalocyaninato](2-)-N^{29},N^{30},N^{31},N^{32}}2H, **5b**. A suspension of **5a** (100 mg) in trifluoroacetic acid (1 ml) was left at ambient temperature for 24 h. Water (20 ml) was added slowly with cooling, and the solid was filtered off and washed with water to yield a dark powder (70 mg). IR (KBr): 2922, 1941, 1543, 1479, 1389, 1330, 1250, 1135, 998 cm^{-1}. UV [abs. pyridine (ε)]: 300 (22 700), 440 (11 000, sh), 564 (21 000), 606 (21 000) nm. Anal. Found: C 44.44; H 3.54; N 24.58; calc. for $C_{32}H_{26}N_{16}O_8 + 2\,H_2O + CF_3COOH$: C 44.74; H 3.42, N 24.55.

{29H,31H-[2,3,9,10,16,17,23,24-Octakis(methoxy)-1,4,8,11,15,18,22,25-(octaza)phthalocyaninato](2-)-N^{29},N^{30},N^{31},N^{32}}copper(II), **5c**. A solution of copper(II) chloride (0.29 mmol, 50 mg) in formamide (5 ml) was heated to 140 °C. Compound **5a** (0.12 mmol, 0.10 g) was added, and the suspension was heated at 140 °C for 15 h. Water (30 ml) was added, and the dark precipitate was filtered and washed with water, triturated with ammonium hydroxide (aq), filtered and washed with water, methanol and acetone. Yield 0.10 g. IR (KBr): 3088, 1548, 1482, 1389, 1319, 1254, 1175, 1009, 898 cm^{-1}. UV [abs. pyridine (ε)]: 365 (25 300), 567 (6000), 624 (28 800) nm. TOF-SIMS analyses. Found. One high intensity cluster centered around 785 u, Mg

$C_{32}H_{25}N_{16}O_8^+ = (M+H)^+$, and another cluster of comparable strength, centered around 824 u, $CuC_{32}H_{25}N_{16}O_8 = (M+H)^+$. Both clusters showed the expected isotopic patterns for, respectively, **5a** and **5c**. The fragmentation pattern was very similar to the copper (octapyrrolidinyl) AzaPc, which has been analysed previously.[6]

{29H,31H-[2,3,9,10,16,17,23,24-Octakis(ethoxy)-1,4,-8,11,15,18,22,25-(octaza)phthalocyaninato](2-)-N^{29},N^{30}, N^{31},N^{32}}magnesium, **5d**. Yield 0.36 g (82%), IR (KBr): 2980, 2931, 1542, 1436, 1386, 1304, 1251, 1028, 941 cm^{-1}. UV [abs. CH_2Cl_2 (e)]: 360 (65 000), 604 (32 300), 625 (30 700), 670 (29 000) nm. UV [abs. pyridine (ε)]: 368 (62 700), 570 (16 000, sh), 626 (81 000) nm.

{29H,31H-[2,3,9,10,16,17,23,24-Octakis(propoxy)-1,4,8,11,15,18,22,25-(octaza)phthalocyaninato](2-)-N^{29}, N^{30},N^{31},N^{32}}magnesium, **5e**. Yield 0.38 g (75%), IR (KBr): 2967, 1647, 1534, 1438, 1372, 1288, 1245 cm^{-1}. UV [abs. CH_2Cl_2 (ε)]: 348 (100 800), 602 (50 000), 620 (42 000, sh), 666 (45 100) nm. UV [abs. pyridine(e)]: 362 (78 000), 568 (20 100, sh), 624 (118 500), 656 (20 100, sh) nm. The crude product was chromatographed on cellulose with DCM, and 0.30 g (60%) of a dark blue–purple powder was obtained. IR (KBr): 2965, 2935, 2876, 1542, 1437, 1375, 1294, 1249, 1058, 974, 750 cm^{-1}. UV [abs. CH_2Cl_2 (ε)]: 358 (118 300), 604 (58 000), 622 (48 000, sh), 670 (53 000) nm. Anal. Found: C 54.80; H 5.77; N 21.11; Mg 2.15, calc. for $C_{48}H_{56}N_{16}O_8Mg + 2\,H_2O$: C 55.15; H 5.78; N 21.44; Mg 2.32.

{29H,31H-[2,3,9,10,16,17,23,24-Octakis(propoxy)-1,4,8,11,15,18,22,25-(octaza)phthalocyaninato](2-)-N^{29}, N^{30},N^{31},N^{32})2H, **5f**. A mixture of **5e** (0.1 mmol,100 mg) and TFA (2 ml) was left at ambient temperature for 17 h. Water (10 ml) was added dropwise with cooling, and the dark blue solid was filtered off and washed thoroughly with water and a small amount of diethyl ether. Yield 85 mg (87%) of a dark blue–green powder. IR (KBr): 2966, 2944, 1707, 1607, 1443 (s), 1381, 1320, 1244, 1212, 1126, 1020 cm^{-1}. UV [abs. CH_2Cl_2 (ε)]: 344 (140 500), 420 (49 000), 554 (28 000, sh), 596 (80 000, sh), 605 (97 600), 646 (142 000) nm. ^1H NMR (CD_2Cl_2): δ 1.44 (3 H, t, $J=7$ Hz), 2.32 (2 H, m), 5.09 (2 H, t, $J=7$ Hz).

In another experiment, compound **1** was reacted with magnesium propoxide, and after the usual work-up procedure, a dark blue powder was obtained in approx. 36% yield.

UV [abs. pyridine (ε)]: 364 (100 800), 570 (22 700, sh), 630 (121 000) nm. Anal. Found: C 51.00; H 4.74; N 22.66; Mg 2.13, calc. for $C_{48}H_{56}N_{16}O_8Mg$ C 57.12; H 5.59; N 22.20; Mg 2.41.

Reaction of **3d** *with magnesium propoxide in propanol.* A dark blue powder was obtained in ca. 50% yield after the usual work-up procedure. IR (KBr): 2967, 2875, 1542, 1434, 1372, 1296, 1250, 1058, 990, 752 cm^{-1}. UV [abs. pyridine (ε)]: 368 (126 000), 570 (32 000, sh), 600 (126 000), 626 (192 000) nm. Anal. Found: C 56.04; H 5.66; N 20.04; Mg 1.74, calc. for $C_{72}H_{40}N_{16}O_8Mg$ C 67.48; H 3.15; N 17.49; Mg 1.90.

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Received March 11, 1999.