Preparations and Template Cyclotetramerisations of 2,1,3-Benzothia(selena)diazole-5,6-dicarbonitriles

Eva H. Mørkved,[a,†] Siren M. Neset,[b] Olav Bjørlo,[a] Helge Kjøsen,[a] Georg Hvistendahl[b] and Frode Mo[c]

University of Trondheim-NTH, [a]Dept. of Organic Chemistry, [c]Dept. of Physics, N-7034 Trondheim-NTH, Norway and [b]University of Oslo, Dept. of Chemistry, P.O.Box 1033 Blindern, N-0315 Oslo, Norway

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2,1,3-Benzothiadiazole-5,6-dicarbonitrile **1b**, and the corresponding selena derivative **2b**, have been prepared in multistep syntheses. Template cyclotetramerisations with copper or magnesium powder in an inert atmosphere give the thiadiazole substituted phthalocyanines **4** in good yields and the selenadiazole analogues **5a** and **5b + 5c** (3:7 mixture) in fair yields. Compounds **5** are the first examples of phthalocyanines with a selenium-containing substituent.

Recently we reported[1] two template cyclotetramerisations of 1,2,5-thiadiazole-3,4-dicarbonitrile where the corresponding copper and magnesium porphyrazines were formed.

The present paper describes a study of cyclotetramerisations of 2,1,3-benzothiadiazole- and 2,1,3-benzoselenadiazole-5,6-dicarbonitriles. These reactions are expected to give phthalocyanines with a strong resemblance to the known thiadiazole substituted porphyrazines.[1] The characteristics of the N–S–N and N–Se–N bonds in the periphery of the macrocycles are of particular interest, and enhanced electron mobilities are expected in the molecular planes of these molecules either in the native, or in the oxidised states.
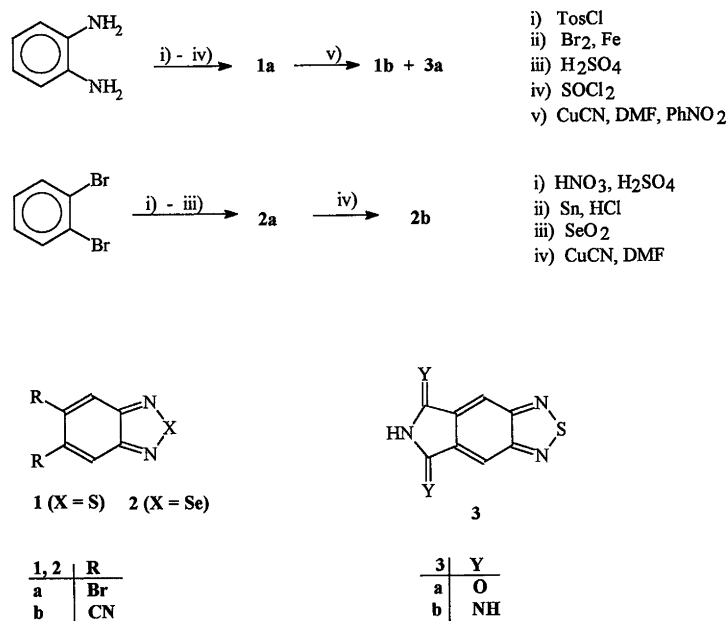
Results and discussion

The preparations of the target dinitriles **1b** and **2b** are shown in Scheme 1. Compound **1b** was prepared in a five-step reaction sequence from benzene-1,2-diamine. The conversion of the dibromide **1a** into **1b** has been reported and compound **1b** was obtained in 29% yield.[2] We were not able to reproduce those results, using the reported reaction conditions. However, our best results were obtained when **1a** was reacted with one mole equivalent of copper(I) iodide in addition to a large molar excess of copper(I) cyanide. A mixture of DMF and nitrobenzene was used as the solvent, and we obtained a mixture of **1b** (64%) and **3a** (16%). The diiminoimide **3b**,

an alternative synthon for phthalocyanines, was formed in 58% yield from **1b** by the method of Hopff.[3]

The selenium-substituted dinitrile **2b** was prepared in four steps from 1,2-dibromobenzene in 21% yield. The product-limiting step in this reaction sequence was the nitration of 1,2-dibromobenzene,[4] where 1,2-dibromo-5,6-dinitrobenzene was obtained in 35% yield. The subsequent steps gave satisfactory to quantitative yields.

Reactions of copper powder (copper bronze) or magnesium powder with **1b** gave excellent yields of the metal phthalocyanines **4a** and **4b**, shown in Scheme 2. Small amounts of unchanged **1b** were removed with dichloromethane, and the excess of metal was removed from the insoluble phthalocyanines with aqueous ammonium hydroxide or with acetic acid. Compounds **4** were identified by mass spectrometry, but owing to the very low volatility of these compounds, flash evaporation using DEI (desorption electron ionisation) was found necessary to obtain sufficient amount of the undecomposed sample in the gas phase for MS analysis. The mass spectra showed weak molecular ion peaks (1.4% for **4a** and 2.0% for **4b**) with the correct isotope distribution. The base peak for both compounds was at m/z 186, which corresponds to 25% of the mass of the macrocyclic ligand. Compounds **4** are insoluble in organic solvents and the UV spectra were therefore measured on 2×10^{-5} M solutions in concentrated sulfuric acid. A strong absorption was found at 830 nm ($\varepsilon = 76\,400$) for **4a** and at 822 nm ($\varepsilon = 81\,300$) for **4b**. The absorption maxima and the extinction coefficients are within the expected range for phthalocyanines, and thus support the assigned structures. Compound **4b** was found to be quite unstable in sulfuric acid and lost

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† To whom correspondence should be addressed.

i) TosCl
ii) Br$_2$, Fe
iii) H$_2$SO$_4$
iv) SOCl$_2$
v) CuCN, DMF, PhNO$_2$

i) HNO$_3$, H$_2$SO$_4$
ii) Sn, HCl
iii) SeO$_2$
iv) CuCN, DMF

1 (X = S)   2 (X = Se)

3

1,2	R
a	Br
b	CN

3	Y
a	O
b	NH

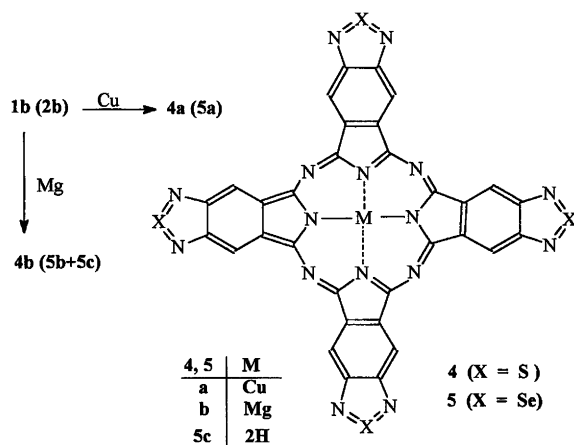*Scheme 1.* Preparations of 2,1,3-benzothia(selena)diazole-5,6-dicarbonitriles.

70% of its absorption at 822 nm within 24 h. The microanalyses of compounds **4** also support the assigned structures, and we note that **4b** is solvated with one mole each of acetic acid and water.

A reaction of benzoselenadiazole dinitrile **2b** with copper gave **5a** in 55% yield. A similar reaction of **2b** with magnesium powder gave, after removal of the excess of magnesium with acetic acid, a mixture of **5b** (30%) and the metal-free phthalocyanine **5c** (70%). These compounds were also solvated with acetic acid and water as shown by microanalysis. The molecular ion peaks of compounds **5** could not be detected by mass spectrometry. However, the compounds had strong ion peaks at m/z 234, which is the mass of 25% of the macrocyclic ligand. Both monomeric and dimeric selenium were detected in these mass spectra as well. The similarity of the

fragmentation patterns of these products with those for compounds **4**, gives a strong indication of the assigned structures **5**. Further indications for structures **5** are found in the striking similarity of the IR spectra of compounds **5** and **4**. UV absorptions of compounds **5** in sulfuric acid were found at 882 nm ($\varepsilon = 46\,200$) for **5a**, and at 880 nm ($\varepsilon = 49\,400$) for **5b** + **5c**. The sulfuric acid solution of **5b** + **5c** lost 20% of the absorption at 880 nm within one hour. Thus, the magnesium complex **5b** and the metal-free macrocycle **5c** are clearly the least stable of the phthalocyanines prepared.

Other workers have reported[5] unsuccessful attempts to prepare a metal-free phthalocyanine from 4-phenylselena-phthalonitrile, and further attempts to use copper bronze as a template for the cyclisation of the same dinitrile gave none of the expected copper phthalocyanine. The rationalisations given were either that selenium directly bound to the phthalonitrile lowered the electrophilicity of the aromatic dinitrile, or that selenide anions, produced by decomposition of the dinitrile, would react with the cyano groups.

The reactions of copper bronze with the dinitriles **1b** and **2b** clearly show the influence of selenium on these reactions. Whereas the benzothiadiazole **1b** gave a clean reaction and **4a** was isolated in excellent yields, the benzoselenadiazole **2b** gave a crude product which apparently was contaminated with a copper-complexed substance with a shorter chromophore (706 nm) than that of **5a**. This complex was removed with acetic acid, as seen from the UV absorptions. The extinction coefficient at 880 nm increased from 22 000 to 46 200, and the absorption at 706 nm disappeared upon treatment with acetic acid. An analogous interaction between copper and the selenadiazole moiety has been reported by Bezzubets

1b (2b) —Cu→ 4a (5a)

↓ Mg

4b (5b+5c)

4,5	M
a	Cu
b	Mg
5c	2H

4 (X = S)
5 (X = Se)

Scheme 2. Preparations of phthalocyanines **4** and **5**.

et al.[6] These workers studied the complexation of copper(II) chloride with various substituted 2,1,3-benzoselenadiazoles and found that coordination between the heterocyclic nitrogen and copper gave fairly stable complexes in ethanol.

The lower stability of the selenium-containing macrocycles **5** may also be rationalised by the preferred *o*-quinoid form of benzoselenadiazoles in the solid phase, i.e., these compounds have a more pronounced double bond character between carbon and nitrogen than the corresponding benzothiadiazoles.[7] The structures **4** and **5** require a high degree of double bond character between nitrogen and sulfur or selenium, and would consequently be more favourable for compounds **4**.

Various attempts to prepare compounds **4** from solutions of metal salts or metal alcoholates gave lower yields and less pure products. When the strong nitrogen base DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) was added to the reaction mixtures, extensive decomposition, presumably of the thiadiazole ring, occurred.

Conclusions

Good yields of the substituted metal phthalocyanines are obtained by fusion of 2,1,3-benzothiadiazole-5,6-dicarbonitrile **1b** with copper or magnesium in an inert atmosphere. The corresponding reaction between magnesium and 1,2,5-thiadiazole-3,4-dicarbonitrile has been shown to yield only triazine instead of the corresponding porphyrazine.[1] The benzoselenadiazole dinitrile **2b** also reacts with copper to give the corresponding metal phthalocyanine **5a** in fair yields. However, a side reaction between copper and the selenadiazole ring yields **5a** mixed with an unidentified copper complex which can be removed from **5a** with acetic acid. A similar reaction of **2b** with magnesium yields a mixture of the metallated and the metal-free macrocycles **5b** and **5c**. To our knowledge compounds **5** are the only known examples of phthalocyanines with selenium-containing substituents. Further studies of these and related compounds are in progress.

Experimental

General. Mass spectra of compounds **1–3** were obtained on an AEI MS-902 spectrometer at 70 eV electron energy, and of compounds **4** and **5** on a VG ProSpec-3000-Q mass spectrometer from Fisons Instruments, England. Samples of compounds **4** and **5** were flash evaporated using the DCI/DEI probe, and ionised by electron ionisation (EI). IR spectra were obtained on a Nicolet 20-SXC FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Jeol EX400 NMR spectrometer at 399.65 MHz and at 100.40 MHz, respectively, and with tetramethylsilane (TMS) as an internal standard. UV–VIS spectra were obtained on a Perkin Elmer 522 UV–VIS spectrophotometer. Microanalyses were per-

formed by *Analytische Laboratorien*, D-51647 Gummersbach, 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. Copper powder (copper bronze), 99% was obtained fro Aldrich, magnesium powder, 325 mesh from Johnson Matthey Alfa Products and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) from Aldrich.

Derivatives of 2,1,3-benzothiadiazole

5,6-Dibromo-2,1,3-benzothiadiazole, **1a**. Benzene-1,2-diamine and *p*-toluenesulfonyl chloride were reacted in pyridine to yield *N,N'*-(*o*-phenylene)bis(toluene-*p*-sulfonamide) (87%), m.p. 205–206.5°C, Lit.[8] 206.5–207.5°C. This compound was reacted with bromine in acetic acid and sodium acetate to yield 4,5-dibromo-*N,N'*-(*o*-phenylene)bis(toluene-*p*-sulfonamide) (89%), m.p. 219–221°C, Lit.[9] 221–224°C, which in turn was converted into 4,5-dibromobenzene-1,2-diamine (83.5%), m.p. 148–148.5°C (decomp.). Lit.[9] 150–151°C (decomp.) on treatment with sulfuric acid (93%). MS [m/z (% rel. int.)]: 268 (48), 266 (100), 264 (53, *M*). IR (KBr): 3385, 3312, 3232, 1628, 1487, 1389, 1273, 1216, 862, 730, 697, 640 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 3.17 (4 H, br s), 6.93 (2 H, s).

4,5-Dibromobenzene-1,2-diamine (3.0 g, 11.3 mmol) was added in portions to an ice-cold solution of thionyl chloride (23 ml) and pyridine (1.3 ml). The mixture was heated under reflux for 3 h, concentrated under reduced pressure and extracted with chloroform (50 ml). After counter-extraction with sodium hydrogen carbonate (5%, 2 × 25 ml), drying and evaporation, the crude product was recrystallised from acetone to yield compound **1a**, 2.5 g (76%), m.p. 131–135°C, Lit.[2,10] 132–134°C. MS [m/z (% rel. int.)]: 296 (53), 294 (100), 292 (51, *M*), 215 (27), 213 (27), 134 (17, *M* – 2Br). IR (KBr): 3077, 3061, 1765 (w), 1711 (w), 1577, 1478, 1414, 1347, 1229, 1062, 951, 887, 859, 823, 686, 532 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 8.39 (s). ^{13}C NMR (CDCl$_3$): δ 124.93 (C4, C7), 127.19 (C5, C6), 153.78 (C8, C9).

2,1,3-Benzothiadiazole-5,6-dicarbonitrile, **1b** *and 2,1,3-benzothiadiazole-5,6-dicarboximide,* **3a**. A mixture of nitrobenzene (40 ml) and dry DMF (120 ml) was added to a stirred mixture of **1a** (2.0 g, 6.8 mmol), copper(I) cyanide (2.5 g, 27.7 mmol) and copper(I) iodide (1.36 g, 7.2 mmol). The mixture was stirred under reflux for 4 h, cooled and poured into a mixture of hydrated ferric chloride (6.8 g), hydrochloric acid (1.7 ml) and water (10 ml). The suspension was heated at 70°C for 30 min, cooled, diluted with water and extracted with dichloromethane (2 × 50 ml). The combined organic phases were washed with hydrochloric acid (6 M, 5 × 40 ml), water, sodium hydrogen carbonate, water, and was finally dried and concentrated under reduced pressure to 20 ml. A yellow

solid precipitated, which was filtered and washed with diethyl ether to yield 0.23 g (16%) of **3a**, m.p. 272–275°C (decomp.). MS [m/z (% rel. int.)]: 207 (6), 206 (11), 205 (100, M), 162 (45), 161 (36), 134 (47). Found 204.9948, calc. for $C_8H_3N_3O_2S$ 204.9946. IR (KBr): 3318, 3089, 1780 (m), 1724 (s), 1621, 1564, 1476, 1439, 1314, 1152, 737 cm^{-1}. ^{1}H NMR [$(CD_3)_2SO$]: δ 8.53 (2 H, s), 11.9 (br). ^{13}C NMR [$(CD_3)_2SO$]: δ 117.32, 132.73, 156.09, 167.56.

The filtrate after removal of **3a** was chromatographed on silica. Dichloromethane eluted 0.81 g (64%) of **1b**, m.p. 205–207.5°C, Lit.[2] 201–203°C. MS [m/z (% rel. int.)]: 188 (5), 187 (11), 186 (100, M), 128 (16), 86 (11), 46 (31). Found 186.0002, calc. for $C_8H_2N_4S$ 186.0000. IR (KBr): 3091, 3015, 2237 (s), 1814 (m), 1492, 1452, 1351, 1149, 911, 875, 829, 741 cm^{-1}. ^{1}H NMR [$(CD_3)_2SO$]: δ 9.18 (s). ^{13}C NMR [$(CD_3)_2SO$]: δ 112.53 (CN), 115.62 (C5, C6), 130.38 (C4, C7), 153.62 (C8, C9).

2,1,3-Benzothiadiazole-5,6-dicarboximide diimine, **3b**. To sodium amide (50% in xylene, 0.35 g, 4.5 mmol) washed with hexane, was added formamide (10 ml) and **1b** (0.20 g, 1.1 mmol). The reaction mixture was heated at 70°C for 14 h and then poured into water after which the precipitate was filtered off and extracted with dichloromethane to remove **1b**. Compound **3b**, 0.13 g (58%), m.p. > 300°C was obtained as undissolved material. MS [m/z (% rel. int.)]: 205 (6), 204 (18), 203 (100, M), 187 (37), 186 (11), 161 (11), 134 (7), 43 (17). Found 203.0267, calc. for $C_8H_5N_5S$ 203.0266. IR (KBr): 3480–2700 (br), 1687 (m), 1639 (s), 1550, 1448, 1416, 1311, 865 cm^{-1}. ^{1}H NMR [$(CD_3)_2SO$]: δ 8.44 (s), 8–9 (br). ^{13}C NMR [$(CD_3)_2SO$]: δ 113.11, 137.51, 155.54, 169.33.

Derivatives of 2,1,3-benzoselenadiazole

5,6-Dibromo-2,1,3-benzoselenadiazole, **2a**. 1,2-Dibromo-benzene (70.8 g, 0.3 mol) was added over 15 min to an ice-cold, stirred mixture of nitric acid (100%, 200 ml, 4.8 mol) and sulfuric acid (98%, 150 ml, 27 mol). The solution was heated under reflux for 10 h, cooled and poured into water((4 l). The solid precipitate that slowly formed was filtered off after 48 h and washed on the filter with water (3 × 500 ml). The crude product, 90 g, was recrystallised from acetic acid and from ethanol to yield 34 g (35%) of 1,2-dibromo-4,5-dinitrobenzene, m.p. 113.5–114°C, Lit.[11] 114–115°C. ^{1}H NMR [$(CD_3)_2SO$]: δ 8.71 (s). ^{13}C NMR [$(CD_3)_2SO$]: δ 129.83, 130.50, 140.62.

This compound was reacted with tin and hydrochloric acid in ethanol to give quantitative yields of 4,5-dibromobenzene-1,2-diamine, m.p. 155°C, Lit.[12] 155°C (sintering at 140°C). ^{1}H NMR [$(CD_3)_2SO$]: δ 4.87 (4 H, s), 6.77 (2 H, s). ^{13}C NMR [$(CD_3)_2SO$]: δ 108.54, 117.02, 136.23.

A hot solution of selenium dioxide (8.3 g, 7.5 mmol) in ethanol (75 ml) was added to a hot solution of 4,5-di-

bromobenzene-1,2-diamine (18.6 g, 70 mmol) in ethanol (200 ml). The reaction mixture was cooled, the white precipitate was filtered off and washed with cold ethanol (2 × 50 ml) to give 23.8 g (100%) of **2a**. Recrystallisation of a small sample from *n*-propanol (0.12 g/10 ml) gave **2a** m.p. 208–210°C. MS [m/z (% rel. int.)]: 346 (6), 345 (6), 344 (52), 343 (6), 342 (100), 341 (14), 340 (80), 339 (12), 338 (36). Found 341.7721, calc. for $C_6H_2{}^{79}Br^{81}BrN_2{}^{80}Se$ 341.7729. IR (KBr): 3428, 3050, 2923, 1688, 1657, 1580, 1467, 1447, 1415, 1352, 1251, 1058, 943, 886, 862, 759, 735, 675, 625 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 8.23 (s). ^{13}C NMR (CDCl$_3$): δ 126.21, 127.69, 159.07.

2,1,3-Benzoselenadiazole-5,6-dicarbonitrile, **2b**. A mixture of **2a** (10.2 g, 30 mmol) and dry copper(I) cyanide (8.1 g, 90 mmol) in dry DMF (125 ml) was heated under nitrogen and reflux for 7 h. The reaction mixture was cooled, and a solution of hydrated ferric chloride (32.4 g, 120 mmol) in hydrochloric acid (50 ml) and water (250 ml) was added. The mixture was heated on a steam bath for 30 min, poured into water (2.5 l) and left for 15 h. The precipitate was filtered off, washed with water (5 × 50 ml) to yield 6.2 g (89%) of crude **2b**. This product was chromatographed on silica with dichloromethane, recrystallised from ethanol and 4.09 g (59%) of **2b** was obtained m.p. 218–219°C. MS [m/z (% rel. int.)]: 236 (17), 235 (10), 234 (100), 233 (5), 232 (50). Found 233.9441, calc. for $C_8H_2N_4{}^{80}Se$ 233.9445. IR (KBr): 3072, 3015, 2236, 1484, 1351, 1281, 1154, 902, 758, 742, 535 cm^{-1}. ^{1}H NMR [$(CD_3)_2SO$]: δ 8.91 (s). ^{13}C NMR [$(CD_3)_2SO$]: δ 111.14, 115.80, 132.37, 158.05.

Template assisted cyclisations of 1b and 2b

General procedure. A mixture of the dicarbonitrile and either copper or magnesium powder was stirred and heated under nitrogen in a sealed glass ampoule.[1] The reaction mixture was extracted three times with boiling dichloromethane, and unchanged **1b** or **2b** was obtained from these extracts. Undissolved material was stirred with aqueous ammonium hydroxide (25%) for 2 × 24 h to remove excess copper, or with acetic acid for 2 × 14 h to remove excess magnesium or copper. The dark solids were washed with large amounts of water, ethanol and acetone and were dried at 0.1 mmHg.

*{33H,35H-Tetrakis[2,1,3]benzothiadiazolo[5,6-b:5',6'-g:5",6"-l:5''',6'''-q]porphyrazin-2-*S^{IV}*-ato(2 −)-N^{33},N^{34},N^{35},N^{36}}copper,* **4a**. Compound **1b** (0.37 g, 2 mmol) and copper powder (0.10 g, 1.5 mmol) were heated at 200–205°C for 23 h. Unchanged **1b**, 0.03 g (8%) was recovered. Compound **4a**, 0.35 g (88%) m.p. > 300°C was obtained as a blue/black powder. MS [m/z (% rel. int.)]: 807 (1.4, M), 188 (6.4), 187 (10), 186 (100). IR (KBr): 3400 (w), 3060 (w), 1605, 1541, 1470, 1383 (s), 1348, 1149 (s), 1087 (s), 1044, 896, 882, 823 (s), 739 (s) cm^{-1}. UV [abs. H_2SO_4 (ε)]: 340 (65 200), 420

(10200), 580 (2800), 740 (16800), 830 (76400) nm. Anal. Found: C 44.62; H 1.14; N 26.19; S 14.69; Cu 9.98. Calc. for $C_{32}H_8N_{16}S_4Cu + 0.25Cu + 2H_2O$: C 44.68; H 1.41; N 26.05; S 14.91; Cu 9.23.

{33H,35H-Tetrakis[2,1,3]benzothiadiazolo[5,6-b:5', 6'-g:5",6"-l:5''',6'''-q]porphyrazin-2-S^{IV}*-ato(2 −)-*$N^{33},N^{34},N^{35},N^{36}$*}magnesium,* **4b**. Compound **1b** (0.30 g, 1.6 mmol) and magnesium powder (0.08 g, 3.2 mmol) were heated at 190–200°C for 21 h. Unchanged **1b** 0.01 g (3%) was recovered. Compound **4b**, 0.29 g (94%), m.p. > 300°C, was obtained as a dark blue/purple powder. MS [m/z (% rel. int.)]: 772 (0.35, $M + 4$), 771 (0.13, $M + 3$), 770 (0.74, $M + 2$), 769 (0.95, $M + 1$), 768 (2.0, M), 188 (5.5), 187 (12.1), 186 (100). IR (KBr): 1720, 1612, 1550, 1471, 1441, 1373 (s), 1231, 1138, 1082 (s), 1031, 877, 820, 741 cm^{-1}. UV [abs. H_2SO_4 (ε)]: 328 (96000), 426 (17000), 580 (6800), 822 (81300) nm. UV [abs. H_2SO_4 (ε)] after 24 h: 325 (52000), 822 (24700) nm. Anal. Found: C 48.18; H 1.50; N 26.26; S 14.91; Mg 2.96. Calc. for $C_{32}H_8N_{16}S_4Mg + CH_3COOH + H_2O$: C 48.21; H 1.67; N 26.45; S 15.14, Mg 2.87.

{33H,35H-Tetrakis[2,1,3]benzoselenadiazolo[5,6-b:5', 6'-g:5",6"-l:5''',6'''-q]porphyrazin-2-Se^{IV}*-ato(2 −)-*$N^{33}, N^{34},N^{35},N^{36}$*}copper,* **5a**. Copper powder (0.08 g, 1.2 mmol) and **2b** (0.28 g, 1.2 mmol) were heated at 200°C for 23 h. Unchanged **2b**, 0.035 g (12%) was recovered. Impure **5a**, 0.25 g (84%) was obtained after treatment with aqueous ammonium hydroxide. UV [abs. H_2SO_4 (ε)]: 358 (47000), 706 (7100), 876 (22000) nm. Anal. Found: C 34.33; H 0.76; N 20.23; Se 28.05; Cu 16.80. Calc. For $C_{32}H_8N_{16}Se_4Cu$: C 38.59; H 0.81; N 22.51; Se 31.71; Cu 6.38.

This product was treated with acetic acid, and compound **5a** 0.16 g (56%) was obtained as a dark blue/black powder, m.p. > 300°C. MS [m/z (% rel. int.)]: 237 (1.0), 236 (7.0), 235 (4.4), 234 (35.1), 233 (2.4), 232 (17.2), 160 (100), 80 (34.0). IR (KBr): 3422 (w), 1654 (w), 1560 (w), 1486, 1380, 1346 (w), 1319 (w), 1261 (w), 1145, 1093, 1042, 872, 737 cm^{-1}. UV [abs. H_2SO_4 (ε)]: 345 (91000), 462 (7800), 530 (700), 626 (5000), 882 (46200) nm.

{33H,35H-Tetrakis[2,1,3]benzoselenadiazolo[5,6-b:5', 6'-g:5",6"-l:5''',6'''-q]porphyrazin-2-Se^{IV}*-ato(2 −)-*

$N^{33},N^{34},N^{35},N^{36}$*}magnesium,* **5b** *and 33H,35H-tetrakis[2,1,3]benzoselenadiazolo[5,6-b:5',6'-g:5",6"-l:5''',6'''-q]prophyrazine-2-*Se^{IV}, **5c**. Magnesium powder (0.06 g, 2.4 mmol) and **2b** (0.19 g, 0.8 mmol) were heated at 200°C for 18 h. Unchanged **2b** 0.065 g (34%) was recovered. Compounds **5b + 5c**, 0.10 g (64%), were obtained as a blue/purple powder, m.p. > 300°C. MS [m/z (% rel. int.)]: 237 (2.7), 236 (18.2), 235 (10.5), 234 (94.7), 233 (5.6), 232 (48.4), 160 (84.6), 80 (100). IR (KBr): 3250 (w), 1709 (w), 1612, 1570, 1528, 1488, 1400, 1390, 1325, 1260 (w), 1170 (w), 1130, 1077, 1021, 872, 757, 739, 495 cm^{-1}. UV [abs. H_2SO_4 (ε)]: 345 (86300), 530 (1600), 620 (8600), 880 (49400) nm. UV [abs. H_2SO_4 (ε)] after 1 h: 345 (84700), 880 (39200) nm. Anal. Found: C 39.38; H 1.12; N 22.07; Se 31.30; Mg 0.73. Calc for [30% of $C_{32}H_8N_{16}Se_4Mg + 70\%$ of $C_{32}H_{10}N_{16}Se_4$] + $CH_3COOH + H_2O$: C 40.05; H 1.52; N 21.98; Se 30.97; Mg 0.71.

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