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Inducing asymmetry in free-base, Mn^{III}, Ni^{II} and Cu^{II} (ethylsulfanyl)-porphyrazines: synthetic aspects and spectro-electrochemical implications

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Treatment of 2,3,7,8,12,13,17,18-octakis(ethylsulfanyl)-5,10,15,20-porphyrazine (H_2OESPz) with $CrCl_2$ in a 1,2,4-trichlorobenzene–*n*-BuOH mixture resulted in one ethylsulfanyl branch at the pyrrolic β positions of the macrocycle being replaced by an hydrogen atom with >40% yield. The structure of the asymmetric pyrrolic subunit and of the nearest pyrrolic subunits have been determined by NMR spectroscopy. The reaction path leading to the asymmetric porphyrazine implies the formation of a two-electron reduced diprotonated porphyrazine, [H_2OESPz(-4)($2H^+$)], that, as a consequence of charge and structural intramolecular rearrangements at high temperature, undergoes nucleophilic substitution of an ethyl sulfide group by H^-. UV-Vis and near-IR results suggest that the asymmetric substitution modifies the (sulfanyl)porphyrazine π and n_{Sulfur} levels. On the contrary, ESR spectroscopy shows that the electronic properties of the coordinated Cu^{2+} ion are affected only marginally. The half-waves of the ligand first reductive processes sensibly shift towards cathodic potentials in the asymmetric metal porphyrazines, but not in the asymmetric free-base porphyrazine, probably due to conflicting electronic and structural effects induced by removal of an ethylsulfanyl tail.

Introduction

The synthesis of tetrapyrrole complexes in which the formally D_{4h} symmetry of the macrocyclic framework is reduced by a not uniform peripheral substitution is a topic of growing interest. Push-pull tetrapyrrolic systems lacking a symmetry center are indeed among the best performing non-linear optical (NLO) materials, as they show efficient Second Harmonic Generation (SHG) processes.[1] In turn, asymmetric tetrapyrroles of the (A_3; B) type (where A denotes pyrrolic (or indolic) subunits bearing long alkyl tails and B unsubstituted or differently substituted ones) give stable mesophases,[2a–e] whereas tetrapyrroles of the (A_3; B) type (where A denotes pyrrolic subunits with hydrophobic substituents and B a pyrrolic subunit with hydrophilic substituents) readily self-organize at the air–water interface and are useful building blocks to grow Langmuir–Blodgett (LB) films.[2f–k] Several synthetic methods have recently been developed to prepare porphyrazines, an important class of tetrapyrroles in which the pyrrolic subunits are held together by aza bridges, of the (A_3; B) type.[3–6]

In this paper we propose a new preparative strategy to obtain asymmetric (alkylsulfanyl)porphyrazines. According to this method, one ethylsulfanyl tail of a fully substituted porphyrazine, H_2OESPz 2,3,7,8,12,13,17,18-octakis(ethylsulfanyl)-5,10,15,20-porphyrazine) is replaced by an hydrogen atom, resulting in the asymmetrically substituted H_2HESPz 2,7,8,12,13,17,18-heptakis(ethylsulfanyl)-5,10,15,20-porphyrazine) (see Scheme 1). The method applies to the free base, as well as to redox inactive transition metal (ethylsulfanyl)porphyrazines, such as NiOESPz. The synthesis involves (i) a two-electron reduction of the porphyrazine ring by the one-electron donor $CrCl_2$, (ii) the formation of a two-electron reduced, diprotonated porphyrazine and (iii) its subsequent conversion into the unsymmetrically substituted porphyrazine through ejection of EtSH. This process is possible because the chromium(II) ion is a strong reductant[7] and the (alkylsulfanyl)porphyrazine is easily reduced due to electronic effects of peripheral sulfur atoms.[8] The present method has the advantage of giving the desired product in ≥40% yield, the only purification needed being the removal of unchanged starting materials. Furthermore, the key intermediate of the synthesis, *i.e.* the reduced diprotonated porphyrazine, can easily be isolated and may represent on its own an important material in view of its considerable reducing capability and appealing optical properties.[9,10] Therefore, as a part of the synthetic pathway leading to the mentioned asymmetric porphyrazine, we describe here the procedure used for the preparation and the characterization of the reduced diprotonated porphyrazine.

In order to understand the electronic and symmetry effects induced in (ethylsulfanyl)porphyrazine by replacing an ethylsulfanyl group by an hydrogen atom we compare here the spectroscopic and electrochemical properties of the asymmetric porphyrazine with those of its symmetrically substituted counterpart. An accurate spectroscopic and electrochemical investigation has also been carried out on the manganese(III), copper(II) and nickel(II) derivatives of both symmetric and asymmetric porphyrazines with the aim to gain insights on the possible effects of the above mentioned peripheral substitution on the metal–porphyrazine interaction.

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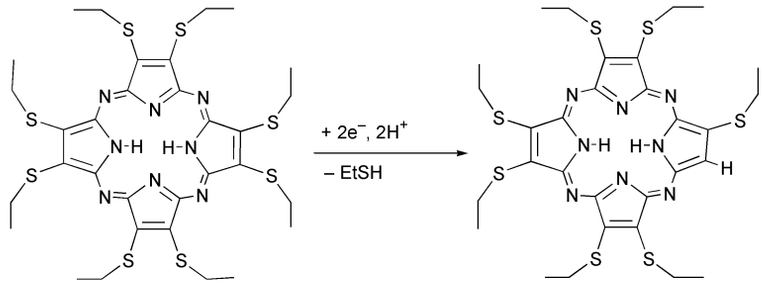


H_2OESPz H_2HESPz

Scheme 1

Experimental

General

All chemicals and solvents (Aldrich Chemicals Ltd.) were of reagent grade. Solvents were dried and distilled before use by standard methods. Solvents used in physical measurements were of spectroscopic or HPLC grade.

Microanalyses were performed by Butterworth Laboratories Ltd, Teddington, UK or at the University of Padova (Italy). Electronic spectra in the region 300–800 nm were recorded on a UV-vis-NIR 05E Cary spectrophotometer using 1 cm path length quartz cells, one- and two-dimensional ^{1}H NMR spectra on Bruker AM 300 and AMX R-300 spectrometers operating at 300.13 MHz. NMR samples were prepared by dissolving about 10 mg of compound in 0.5 cm^3 of $CDCl_3$, and at least five freezing and pumping cycles were performed under argon to degas the solutions. Chemical shifts are reported in ppm downfield of TMS, using the residual solvent peak as internal reference. Two dimensional phase sensitive ^{1}H COSY and ^{1}H NOESY experiments were done using the time proportional phase incrementation (TPPI) method. The mixing times ranged between 600 and 800 ms. MALDI MS spectra were obtained with a Perspective Biosystems/CISESMA instrument. Samples for mass spectrometric analysis were prepared by dissolving 3 μdm^3 of porphyrazine solution (<10^{-4} M in CH_2Cl_2) directly in a matrix of α-cyano-4-hydroxycinnammic acid. The matrix was deposited on the probe tip by placing 3 cm^3 of a solution of α-cyano-4-hydroxy-cinnammic acid in CH_2Cl_2–isopropyl alcohol (4 : 1) and allowing this solution to evaporate. Time-of-flight (TOF) mass spectra were obtained by irradiating the sample with 10 ns pulses of a Nd(YAG) laser operating at 335 nm. The spectra from 50 laser shots were added to obtain better statistics.

Cyclic voltammetric measurements were obtained with a double platinum electrode and an Ag–AgCl reference electrode equipped with a Luggin capillary under a purified N_2 atmosphere using an EG&G Princeton Applied Research (PAR) potentiostat/galvanostat, Model 273.[11]

Variable temperature EPR spectra were recorded at X band on polycrystalline powders with a Varian E9 spectrometer equipped with a continuous flow helium cryostat. No variation of the spin Hamiltonian parameters was observed with temperature.

Syntheses

H_2OESPz. The free-base porphyrazine was prepared according to ref. 11. The product was carefully purified by flash chromatography on silica gel (first band) using 1 : 1 CH_2Cl_2–*n*-hexane as eluent (Found: C, 48.70; H, 5.50; N, 13.88. $C_{16}H_{21}N_4S_4$ requires: C, 48.33; H, 5.32; N, 14.09%). ^{1}H NMR (300 MHz, $CDCl_3$, 297 K): δ 4.25 (q, J = 7.4, 16 H, SCH_2), 1.52 (t, J = 7.4 Hz, 24 H, CH_3) and −1.19 (2 H, $N_{pyrrolic}H$). UV-Vis (CH_2Cl_2): λ/nm (log ε): 354 (4.66) Soret; 498 (4.31); 637 (4.45), 714 (4.59) Q bands. MALDI-MS: m/z 796.42, MH^+ (calc. 796.13). IR (KBr, $\tilde{\nu}_{max}$/cm^{-1}): 3283s, 2958m, 2923m, 2865m, 1443s, 1307s, 1256s, 1003s, 792s, 741s and 683s.

H_2OESPz(−4)(2H$^+$). H_2OESPz (0.10 g, 0.12 mmol) and $CrCl_2$ (0.062 g, 0.50 mmol) were refluxed in dry EtOH (20 cm^3) under N_2, resulting in a change from dark blue to purple and formation of a red-purple precipitate. After 4 h the reaction was stopped and the precipitate filtered off, washed in sequence with cold EtOH (20 cm^3), *n*-hexane (10 cm^3) and Et_2O (10 cm^3) and air dried (Found: C, 48.34; H, 4.92; N, 13.23. $C_8H_{11}N_2S_2$ requires: C, 48.24; H, 5.50; N, 14.06%). ^{1}H NMR (300 MHz, $CDCl_3$, 297 K): δ 25.93 (s, 2 H, $N_{bridge}H$), 1.07 (t, J = 6.6, 12 H, CH_3), 4.79 (s, 2 H, $N_{pyrrolic}H$), 2.60 (bq, 8 H, SCH_2), 2.29 (q, J = 7.2, 8 H, SCH_2), 1.14 (t, J = 7.2, 12 H, CH_3) and 1.11 (t, J = 7.2 Hz, 12 H, CH_3). UV-Vis ($CHCl_3$): λ/nm (log ε) 354 (4.18) and 504 (4.38). IR (KBr, $\tilde{\nu}_{max}$/cm^{-1}): 3317s, 2960s, 2920s, 2863m, 1613s, 1562s, 1517s, 1255s, 998s, 796m and 711m.

H_2HESPz. H_2OESPz (0.30 g, 0.38 mmol) and $CrCl_2$ (0.120 g, 0.98 mmol) were refluxed in 5 : 1 (v/v) 1,2,4-trichlorobenzene (TCB)–*n*-BuOH (18 cm^3) under N_2. The mixture changed from dark blue to red and successively, after 2 h, to dark green. After 7 h the solvent was removed *in vacuo*, affording a dark solid that was purified by column chromatography on silica gel (Merck 60, 70–230 mesh) using a gradient technique. With an initial (1 : 1) CH_2Cl_2–*n*-hexane mixture as eluent a blue band was collected corresponding to unchanged H_2OESPz. The next slow moving green band, containing the desired compound, was collected using 7 : 3 CH_2Cl_2–*n*-hexane as eluent. Removal of the solvent and recrystallization from 9 : 1 CH_3OH–CH_2Cl_2 at *ca.* 0 °C gave 0.110 g (*ca.* 40%) of the desired pure product (Found: C, 48.97; H, 5.84; N, 14.99. $C_{30}H_{38}N_8S_7$ requires: C, 49.02; H, 5.21; N, 15.24%). ^{1}H NMR (300 MHz, $CDCl_3$, 297 K): δ 8.39 (s, 1H), 4.17 (q, J = 7.4, SCH_2), 4.15 (q, J = 7.4, SCH_2), 4.14 (q, J = 7.4, SCH_2), 4.06 (q, J = 7.4, SCH_2), 3.98 (q, J = 7.4, SCH_2), 3.91 (q, J = 7.4, SCH_2), 3.60 (q, J = 7.4, SCH_2), 1.80 (t, J = 7.4, CH_3), 1.60 (t, J = 7.4, CH_3), 1.58 (t, J = 7.4, CH_3), 1.57 (t, J = 7.4, CH_3), 1.55 (t, J = 7.4, CH_3), 1.52 (t, J = 7.4, CH_3), 1.51 (t, J = 7.4 Hz, CH_3) and −1.80 (br s, 2H). UV-Vis (CH_2Cl_2): λ/nm (log ε): 354 (4.42) Soret; 472 (3.97); 608 (4.09 sh); 636 (4.21), 704 (4.34) Q bands. MALDI-MS: m/z 734.85, MH^+ (calc. 735.13). IR (KBr, $\tilde{\nu}_{max}$/cm^{-1}): 3274m, 2962m, 2923m, 2864m, 1446s, 1313s, 1253s, 1017s and 783s, 740vs.

[Ni(OESPz)]. The complex was prepared according to the procedure reported in ref. 12 for the synthesis of similar nickel(II) (alkylsulfanyl)porphyrazines (Found: C, 45.35; H, 5.00; N, 13.75. $C_{32}H_{40}N_8NiS_8$ requires: C, 45.12; H, 4.73; N, 13.15%). ^{1}H NMR (300 MHz, $CDCl_3$, 297 K): δ 4.01 (q, J = 7.3, 16 H, SCH_2) and 1.52 (t, J = 7.3 Hz, 24 H, CH_3). UV-Vis (CH_2Cl_2): λ/nm (log ε) 325 (4.37) Soret; 344 (4.33 sh); 484 (4.05); 663 (4.40) Q bands. MALDI-MS: m/z 851.35, MH^+ (calc. 851.06).

[Ni(HESPz)]. *Method A.* [Ni(OESPz)] (0.10 g, 0.12 mmol) and anhydrous $CrCl_2$ (0.060 g, 0.48 mmol) were refluxed in 5 : 1 EtOH–TCB (20 cm^3) under N_2 for 3 h. The solvents were removed *in vacuo*. Purification of the resulting dark green solid by column chromatography on silica gel (Merck 60, 70–230 mesh) using 7 : 3 CH_2Cl_2–*n*-hexane as eluent afforded 0.45 g of the desired compound (Found: C, 45.37; H, 4.75; N, 14.25. $C_{30}H_{36}N_8NiS_7$ requires: C, 45.50; H, 4.58; N, 14.15%). UV-Vis (CH_2Cl_2): λ/nm (log ε) 327 (3.69) Soret; 467 (3.36); 588 (3.45 sh); 673 (3.68) Q bands. ^{1}H NMR (300 MHz, $CDCl_3$, 297 K): δ 8.51 (s, 1 H, pyrrole), 4.15 (q, J = 7.3, 2 H, SCH_2), 4.07 (q, J = 7.3, 2 H, SCH_2), 4.04 (q, J = 7.3, 2 H, SCH_2), 4.00 (q, J = 7.3, 2 H, SCH_2), 3.97 (q, J = 7.3, 2 H, SCH_2), 3.84 (q, J = 7.3, 2 H, SCH_2), 3.55 (q, J = 7.3, 2 H, SCH_2), 1.78 (t, J = 7.3, 3 H, CH_3), 1.58 (t, J = 7.3, 3 H, CH_3), 1.57 (t, J = 7.3, 3 H, CH_3), 1.56 (t, J = 7.3, 3 H, CH_3), 1.53 (t, J = 7.3, 3 H, CH_3), 1.50 (t, J = 7.3, 3 H, CH_3) and 1.47 (t, J = 7.3 Hz, 3 H, CH_3). MALDI-MS: *m*/*z* 791.04, MH^+ (calc. 791.14).

Method B. The complex was prepared according to the procedure reported for the preparation of [Ni(OESPz)] and using H_2HESPz as starting porphyrazine.

[Cu(OESPz)]. The complex was prepared according to the procedure reported in ref. 12 for similar copper(II) (alkylsulfanyl)porphyrazines and using H_2OESPz as starting porphyrazine (Found: C, 45.15; H, 5.07; N, 13.67. $C_{32}H_{40}CuN_8S_8$ requires: C, 44.86; H, 4.71; N, 13.08%). UV-Vis (CH_2Cl_2): λ/nm (log ε) 339 (4.56 sh); 355 (4.58) Soret; 492 (4.17); 619 (4.28 sh), 669 (4.66) Q bands. MALDI-MS: *m*/*z* 856.79, MH^+ (calc. 856.04).

[Cu(HESPz)]. The complex was prepared using the same procedure as for the preparation of [Cu(OESPz)] (Found: C, 46.23; H, 5.30; N, 13.57. $C_{30}H_{36}CuN_8S_7$ requires: C, 45.23; H, 4.56; N, 14.07%). UV-Vis (CH_2Cl_2): λ/nm (log ε) 342 (4.49 sh); 355 (4.51) Soret; 471 (4.07); 624 (4.26 sh), 665 (5.52) Q bands. MALDI-MS: *m*/*z* 798.56, MH^+ (calc. 797.49).

[Mn(Cl)(OESPz)]. The complex was prepared according to ref. 12 (Found: C, 43.25; H, 4.50; N, 12.75. $C_{32}H_{40}ClMnN_8S_8$ requires: C, 43.50; H, 4.55; N, 12.70%). UV-Vis (CH_2Cl_2): λ/nm (log ε) 328 (3.99 sh); 368 (3.90) Soret; 432 (3.53 sh); 512 (3.96), 590 (3.60 sh) Q bands; 714 (3.95); 800 (3.00); 931 (2.87); 1104 (2.95). MALDI-MS: *m*/*z* 847.05, $(M - Cl)^+$ (calc. 847.05).

[Mn(Cl)(HESPz)]. In an inert-atmosphere glove-box, H_2HESPz (0.10 g, 0.12 mmol) and manganese(II) acetate, $C_4H_6MnO_4$ (0.03 g, 0.17 mmol), were added to dry EtOH (10 cm^3) and the mixture refluxed. After 6 h it was dried *in vacuo* and the resulting dark solid added to CH_2Cl_2 (10 cm^3) under stirring. The solution slowly changed from blue to red. After 3 h the solvent was removed *in vacuo* and the resulting red solid passed through a silica gel (Merck 60, 70–230 mesh) column (45 × 2 cm) using 1 : 1 CH_2Cl_2–$CHCl_3$. The second red band was collected. This solution, after solvent removal, afforded 0.70 g of the desired compound (Found: C, 44.05; H, 4.39; N, 13.65. $C_{30}H_{36}MnClN_8S_7$ requires: C, 43.76; H, 4.41; N, 13.61%). UV-Vis (CH_2Cl_2): λ/nm (log ε) 335 (4.17) Soret; 446 (4.03); 505 (4.04); 585 (4.00); 720 (4.22) Q bands; 825 (2.85 sh); 956 (2.63); 970 (2.55); 1137 (2.83). MALDI-MS: *m*/*z* 787.69, $(M - Cl)^+$ (calc. 787.04).

Results and discussion

Synthesis of H_2ESPz

(a) General. Chromium(II) chloride is, in general, unsuited for the synthesis of tetrapyrrole complexes. Its tendency to exhibit a strong reducing power and scarce lability in organic solvents prevent an easy accommodation of the metal into the tetrapyrrolic cavity. Examples of porphyrin-like chromium complexes prepared by direct reaction of $CrCl_2$ and the appropriate macrocycle mostly concern the mono- and di-nuclear chromium complexes of the highly flexible tmtaa^{2-} tetraazamacrocycle (5,7,12,14-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecine).[13] The reaction between H_2OESPz and $CrCl_2$ in dry ethanol, under strictly anaerobic conditions, resulted in formation of the purely two-electron reduced porphyrazine, $[H_2OESPz(-4)]^{2-}$. This species was isolated and characterized as air stable purple microcrystals of the diprotonated adduct, $H_2OESPz(-4)(2H^+)$. This compound readily converted into the asymmetric porphyrazine, H_2HESPz, upon heating in dry TCB. The conversion of the fully substituted porphyrazine into H_2HESPz could also be achieved by treating the former directly with 4 equivalents of $CrCl_2$ in a TCB–*n*-BuOH mixture. UV-visible spectroscopic changes observed during the course of this reaction gave a hint for the two-electron reduced porphyrazine formation also in this case, confirming its key role in the $H_2OESPz \longrightarrow H_2HESPz$ conversion. For this reason, we will first describe in some detail the relevant physico-chemical properties of this species.

(b) Identification and stability of the two-electron reduced diprotonated porphyrazine. The $[H_2OESPz(-4)]^{2-}$ dianion was primarily identified through UV-visible spectroscopy. The optical spectrum of this species was found to be substantially identical to that of the $[H_2OMSPz(-4)]^{2-}$ dianion (H_2OMSPz = octa(methylsulfanyl)porphyrazine), generated by Bottomley and Chiou[8] through controlled potential electrolysis of a H_2OMSPz solution in pyridine, at −1.0 V (*vs.* SCE), a slightly cathodic potential of the second one-electron reduction of this porphyrazine. The optical spectra of both free base dinegative ions, $[H_2OESPz(-4)]^{2-}$ and $[H_2OMSPz(-4)]^{2-}$, show indeed very little absorption in the near-infrared region, but an intense band in the visible region at 504 nm. It is worth mentioning that also the spectra of dinegative ions of free base as well as Mg^{II}, Cu^{II} and Ni^{II} phthalocyanines are characterized by very weak absorptions in the near-infrared and by a prominent absorption in the visible region between 520 and 540 nm.[10,14] Theoretical studies of these dianions[14] have suggested that the two additional electrons populate the lowest unoccupied Pc-e_g orbitals, accounting for the diamagnetism of these species. Our results seem to indicate that the addition of two electrons to the (sulfanyl)porphyrazine ring has the same electronic effect. Actually, the two-electron reduced porphyrazine shows ^{1}H NMR spectra typical of a diamagnetic species. This observation is consistent not only with the just mentioned spectroscopic results but also with recent theoretical investigations on (alkylsulfanyl)porphyrazines.[15]

Upon conversion from H_2OESPz into the reduced form the ^{1}H NMR signal of the two inner pyrrolic protons (N_p) changes from δ −1.20 for the former to 4.79 for the latter, a value very close to the resonance of the aza-pyrrolic proton in the isolated pyrrole. The ^{1}H NMR spectrum of the reduced porphyrazine shows a rather *sharp* singlet at δ 25.93, associated, on integration, to two protons. The considerable downfield chemical shift of this resonance indicates that the two protons bind two bridge nitrogen atoms (N_b). Bridge-protonated neutral porphyrazines show indeed similarly downfield shifted signals of the aza bridge protons.[16] Two different structural arrangements of the $H_2OESPz(-4)(2H^+)$ species can be predicted, consistent with the protonated aza bridges assuming a "*cis*" or "*trans*" position with respect to the center of the tetrapyrrolic cavity (see Scheme 2). The ^{1}H NMR features seem to indicate that (i) either one of the two structures is particularly stable in solution and, hence, is by far dominant, or (ii) some interchange between them occurs *via* protonation/deprotonation equilibria not resolved in the actual NMR timescale. The analysis of the ^{1}H NMR signals of the peripheral ethylsulfanyl tails points to the same conclusions. The resonances of both the CH_2S and CH_3 groups shift, although not homogeneously, upfield,

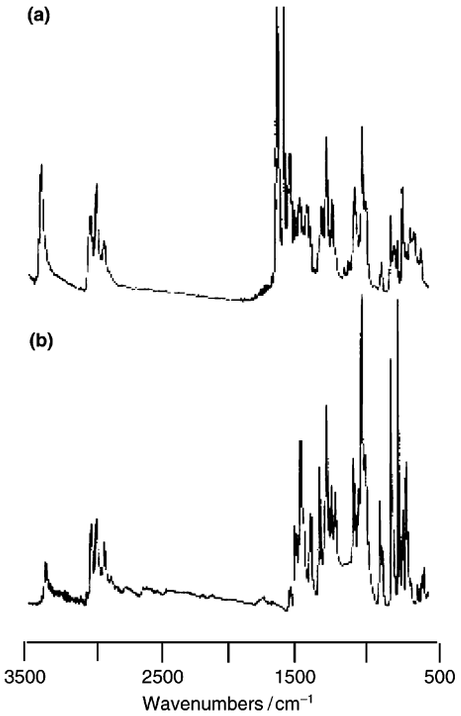
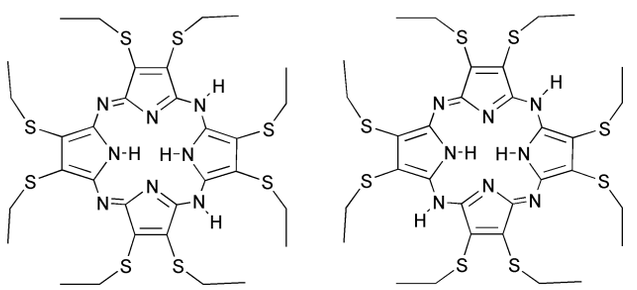


Fig. 1 IR spectra of (a) $H_2OESPz(-4)(2H^+)$ and (b) H_2OESPz from 500 to 3500 cm^{-1} taken as KBr disks.



[$H_2OESPz(-4)(2H^+)$]

Scheme 2

compared to the corresponding signals of the free-base porphyrazine and split due to lowering of the molecular symmetry. Two quartets at δ 2.60 and 2.29 each accounts for four CH_2S groups, and two severely overlapped triplets at δ 1.14 and 1.11, each accounting for four CH_3 groups, are present in the spectrum.

Analysis of the infrared (IR) spectral changes on going from pure H_2OESPz to the reduced porphyrazine (see Fig. 1) supports the salient structural features of the two-electron reduced species deduced from optical and ^1H NMR spectra. The IR spectrum of the latter does not show in fact the characteristic bands of H_2OESPz, namely the $\nu_{sym,asym}(N_p–H)$ at 3253 and 3283 cm^{-1}, respectively, and the numerous and intense bands in the range 500–1350 cm^{-1}, usually attributed to vibrations of the aromatic porphyrazine skeleton. Rather it is characterized by (i) a very intense band at 3317 cm^{-1} accounting for overlapping absorptions due to stretching of N–H groups belonging to pyrroles and protonated aza bridges and (ii) three very intense features at 1613, 1562 and 1517 cm^{-1}, assigned to deformation vibrations of the $C_a–N_b(H)–C_a$ groups.

Thus, all the experimental results support the two-electron reduction causing a pronounced disruption of the conjugation along the inner 16-atom polyene ring and, possibly, deformation of the porphyrazine ring from planarity.

The diprotonated adduct of $[H_2OESPz(-4)]^{2-}$ is slowly

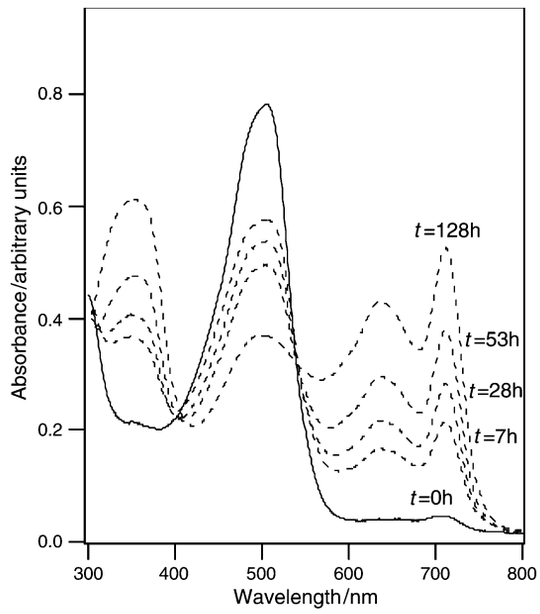


Fig. 2 Optical spectra of $H_2OESPz(-4)(2H^+)$ in the presence of dioxygen as a function of time. Spectra were recorded at 293.0 K in $CHCl_3$ solvent at the indicated time intervals.

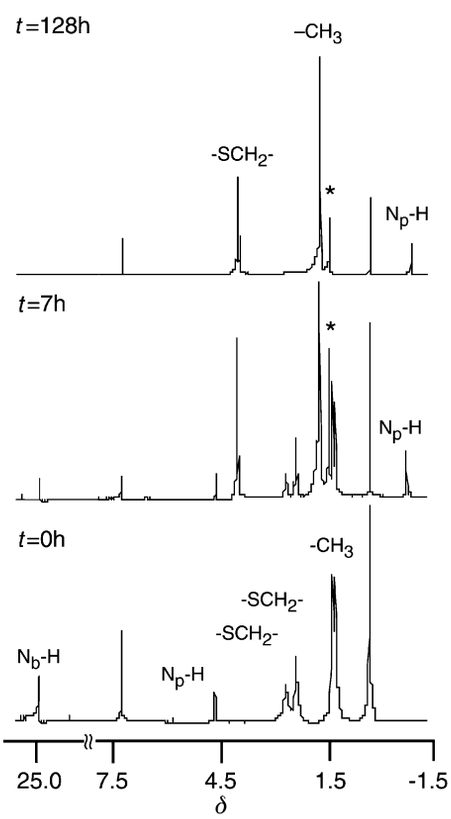


Fig. 3 ^1H NMR spectra of the reaction mixture containing $H_2OESPz(-4)(2H^+)$ and dioxygen as a function of time. Spectra were recorded at 293.0 K in $CDCl_3$ at the indicated time intervals. Chemical shifts are relative to TMS. Starred peaks refer to reaction water.

reoxidized by dioxygen to the initial free-base porphyrazine. Fig. 2 reports the optical spectrum of the diprotonated adduct of $[H_2OESPz(-4)]^{2-}$ in $CHCl_3$ as a function of time. The presence of isosbestic points at 535 and 405 nm seems to exclude the formation of spectroscopically detectable amounts of the one-electron reduced porphyrazine, the $[H_2OESPz(-3)]^{-\bullet}$ radical anion, and, hence, a multipath dioxygen reduction process, at least on the porphyrazine side. When the course of the reaction between $(H_2OESPz)(-4)(2H^+)$ and dioxygen is followed by ^1H NMR (see Fig. 3) similar conclusions can be drawn from the

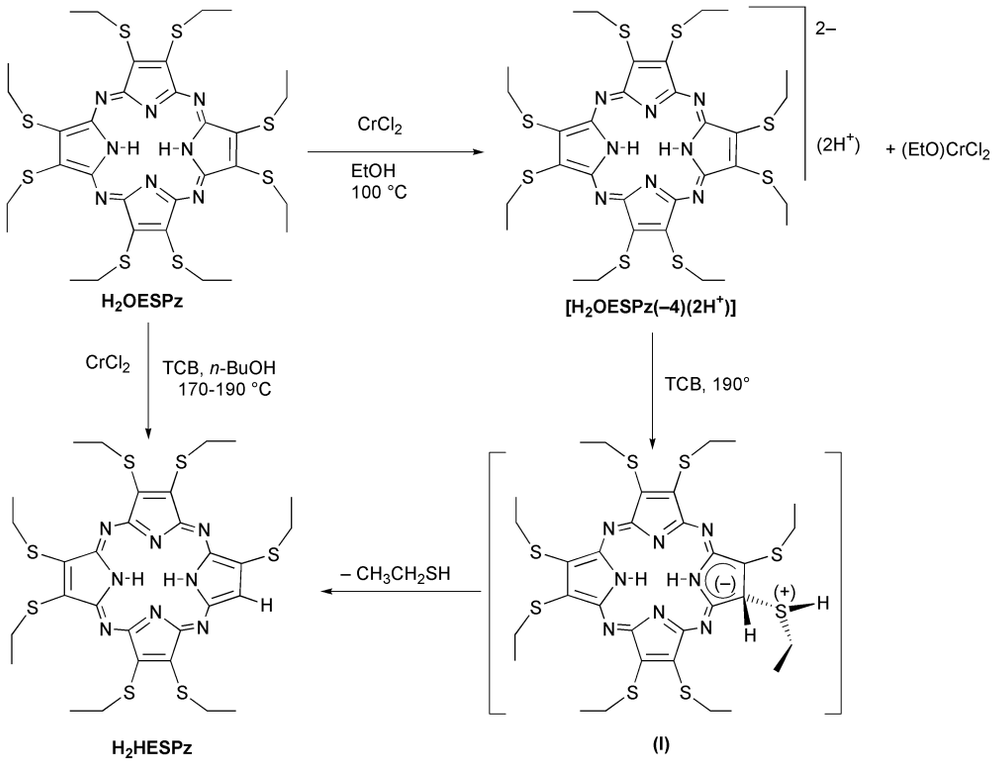


Fig. 4 Summary of the one-pot and two stage conversion of H_2OESPz into the asymmetric porphyrazine, H_2HESPz.

observed spectral changes. A slow decrease of the signals due to the reduced porphyrazine corresponds indeed to a simultaneous and matching increase of the free-base porphyrazine signals, suggesting, in agreement with UV-Vis data, a single-path reaction between the reduced porphyrazine and dioxygen.

(c) Mechanistic aspects related to the $H_2OESPz \longrightarrow H_2HESPz$ conversion. As mentioned above, two consecutive steps are clearly discernible in the reaction pathway leading to the asymmetric porphyrazine: the first involves formation of the two-electron reduced diprotonated $H_2OESPz(-4)(2H^+)$ porphyrazine, and the second implies rearrangement of this species to the final product. These processes can occur in the same reaction flask. In this case, optical spectroscopy is helpful to discriminate between the two stages. UV-Vis spectra recorded on aliquots of the TCB–*n*-BuOH mixture containing the H_2OESPz and $CrCl_2$ reactants at different times indicated, in line with the observed color changes from blue to deep purple, progressive conversion of the free-base porphyrazine into the two-electron reduced species. Once formed, this species disappeared in 3–4 h as indicated by optical spectra showing, again, the typical features of a free-base porphyrazine. It is also possible to separate the two reaction stages, by preparing first the $H_2OESPz(-4)(2H^+)$ species at low temperature, in boiling EtOH, and subsequently converting it into the asymmetric porphyrazine in dry TCB, at 190 °C. This procedure supports the previous observations and helps to gain further insights in the separate steps. Both the one-pot and the "separate" step methods are illustrated in Fig. 4. The stoichiometry of the first reaction step in EtOH can be described by eqn. (1). Formation

$$H_2OESPz + 2Cr^{II}Cl_2 + 2EtOH \longrightarrow H_2OESPz(-4)(2H^+) + 2Cr^{III}Cl_2(EtO) \quad (1)$$

of the mixed ligand chromium(III) species, $Cr^{III}Cl_2(EtO)$, was confirmed by X-ray photoelectron spectroscopy (XPS) studies.[17] The alcohol is the proton source for protonation of the dinegative porphyrazine ion as demonstrated by conducting the synthesis of $H_2OESPz(-4)(2H^+)$ in deuteriated ethanol. Actually we found that deuterium was introduced on the porphyrazine bridges with a content of >50%. We notice that, when *n*-BuOD was used instead of *n*-BuOH in the one-flask synthesis, deuterium was introduced on the β position of the asymmetric porphyrazine with a content of 97% in perfect agreement with the above results.

In the second step, which requires higher temperature (≈190 °C) and dry TCB as solvent, the conversion of the reduced porphyrazine $H_2OESPz(-4)(2H^+)$ into the asymmetric porphyrazine (eqn. 2) implies the ejection of CH_3CH_2SH.

$$H_2OESPz(-4)(2H^+) \longrightarrow H_2HESPz + CH_3CH_2SH \quad (2)$$

Formation of ethanethiol was easily detected by ^1H NMR spectroscopy on the reaction vapors captured by a cold trap. The $H_2OESPz(-4)(2H^+) \longrightarrow H_2HESPz$ conversion is caused by concerted intramolecular charge and structural rearrangements occurring in the reduced porphyrazine. These rearrangements can be rationalized in terms of a net hydride transfer at the pyrrolic β position and by concomitant protonation of the sulfur atom of the attached ethylsulfanyl group (see structure **I** of Fig. 4). The formation of H^-, as well as its nucleophilic attack on the pyrrolic β position, is effective by virtue of (i) the high reaction temperature, (ii) the appreciable electron-drawing capability of ethylsulfanyl tails and (iii) the stability and propensity of ethanethiol to behave as a good leaving group. The observation that $H_2OESPz(-4)(2H^+)$ transforms in the asymmetric species also in the absence of $CrCl_2$ rules out that a chromium hydride equivalent generated by $CrCl_2$ and the alcohol could be in principle the H^- source, at least in the one-flask synthesis.

It is interesting that treatment of [Ni(OESPz)] with $CrCl_2$ in TCB–*n*-BuOH leads to recovery of the metallated asymmetric porphyrazine, [Ni(HESPz)], in ≈40% yield in a much shorter time (2 h). This is probably due to a more pronounced reactivity of the [Ni{$OESPz(-4)(2H^+)$}] intermediate (see Experimental section). Spectroscopic changes observed during the course of the reaction clearly indicate in fact that a mechanism similar to the above described is operative also in this case.

(d) Structure of H_2HESPz. The MALDI-MS spectrum of the asymmetric free-base porphyrazine exhibits only a peak

Table 1 ^{1}H COSY connection scheme between methylene and methyl groups in the EtS substituents on H_2HESPz (see also Fig. 5 for a partial attribution of resonances on the basis of the observable cross peaks in the ^{1}H NOESY spectrum)

$\delta(CH_2)$	$\delta(CH_3)$
4.17	1.60
4.15	1.58
4.14	1.57
4.06	1.55
3.98	1.51
3.91	1.52
3.60	1.80

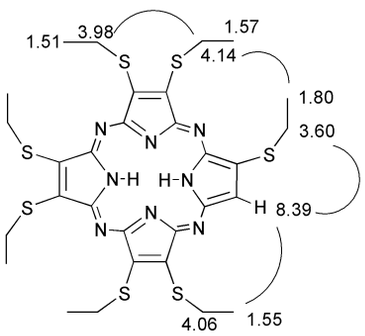


Fig. 5 Correlation from ^{1}H NMR NOESY spectrum of H_2HESPz.

corresponding to the singly charged intact molecular ion at m/z = 734.85. The absence of peaks of appreciable intensity in the lower mass region indicates that concomitant, even partial S-dealkylation of the (alkylsulfanyl)porphyrazine has to be excluded.

The structure of the asymmetric pyrrolic unit and of the nearest pyrrolic units in H_2HESPz has been elucidated by NMR spectroscopy. The ^{1}H NMR spectrum of H_2HESPz exhibits four distinct regions of signals: (i) a single resonance at δ 8.39 which is easily attributable to the hydrogen atom of the pyrrole asymmetric unit, (ii) seven quartets in the region δ 4.17–3.60, corresponding to the methylene groups, (iii) seven triplets in the region 1.80–1.51 for the methyl groups, and (iv) a broad signal at δ −1.80 assigned to the NH of the macrocycle. The scalar coupling pattern between the methylene and the methyl groups has been established through a ^{1}H COSY experiment, and the connection scheme is reported in Table 1. The ^{1}H NOESY spectra show low intensity cross peaks between the pyrrole-hydrogen atom and the signal at δ 3.60, allowing the assignment of the asymmetric pyrrole unit. A partial attribution of resonances is reported in Fig. 5, on the basis of the observable cross peaks. A complete resolution of the NMR spectrum was prevented by severe overlap of the signals and by the very weak intensities of the cross peaks, maybe due to partial aggregation of the porphyrazine or, possibly, to the presence of paramagnetic impurities, *i.e.* chromium(III) compounds from the synthetic work-up procedure. Benzene-d_6 as solvent leads to a better spreading of the signals, but the intensities of the NOEs are even lower, suggesting an even more pronounced aggregation in this solvent.

Physico-chemical properties of free-base and metallated symmetric and asymmetric porphyrazines: a comparative analysis

(a) Optical spectra. The asymmetric free-base porphyrazine, like its symmetrically substituted counterpart, shows an intense $\pi \longrightarrow \pi^*$ band at ≈354 nm (the B or Soret band), an almost equally intense $\pi \longrightarrow \pi^*$ band with main absorption at 704 nm (the Q band), and an additional, rather intense absorption due to $n_{Sulfur} \longrightarrow \pi^*$ transitions, in between. The most conspicuous change in the optical spectra on going from the symmetric to the asymmetric porphyrazine results in a generalized, although not homogeneous, blue shift in the range 400–700 nm. Actually, for H_2HESPz, the Q-band main peak lies 10 nm higher than for H_2OESPz, and the broad band due to $n_{Sulfur} \longrightarrow \pi^*$ transitions is blue shifted 26 nm with respect to the corresponding band of H_2OESPz. This spectral behavior is not surprising. It is known indeed that the Q band is located, for peripherally not substituted free-base porphyrazines, about 90 nm higher than for fully substituted (alkylsulfanyl)porphyrazines.[16] Thus, the observed blue shift on going from H_2OESPz to H_2HESPz is related to perturbation of the porphyrazine π levels caused by the diminished number of peripheral ethylsulfanyl tails.

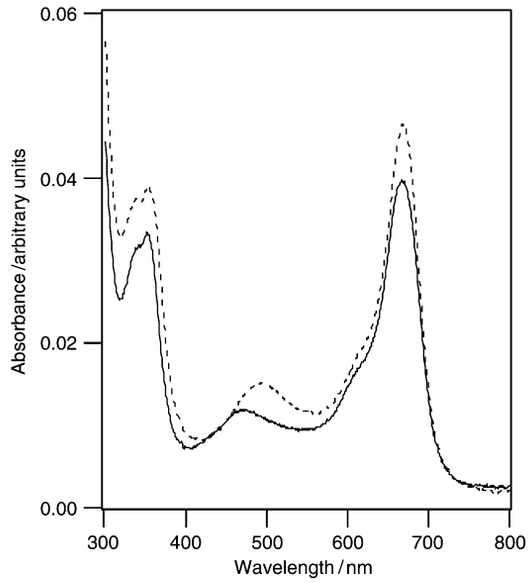


Fig. 6 Optical spectra of [Cu(OESPz)] (dashed line) and [Cu(HESPz)] (full line) in $CHCl_3$. [Complex] = 1.5×10^{-6} M.

Contrary to expectations that an asymmetric tetraazamacrocycle should present a sensible splitting of the main bands, it is interesting that this effect is not visible in the H_2HESPz spectrum. The reduced symmetry seems indeed to be effective only in inducing a marked asymmetry of the $n_{Sulfur} \longrightarrow \pi^*$ band at 472 nm. However, it is reasonable to assume that the effects of asymmetry are not visible in view of the breadth of the bands in (alkylsulfanyl)porphyrazines caused by the considerable crowding of the excited states.[15c,d]

The spectroscopic changes in the $n_{Sulfur} \longrightarrow \pi^*$ and Q bands observed on going from the symmetric to the asymmetric free-base porphyrazine are nearly reproduced in the corresponding copper(II) and nickel(II) complexes (see Fig. 6). This effect is understandable considering that, in the optical spectra of these transition metal complexes, the main bands involve also intraligand transitions of the type $\pi \longrightarrow \pi^*$ or $n_{Sulfur} \longrightarrow \pi^*$. The molecular asymmetry and the reduced number of peripheral ethylsulfanyl tails seem to induce more complicated spectral changes in manganese(III) porphyrazine. In particular, most of the severely crowded metal to ligand charge transfer (MLCT) bands occurring between 350 and 550 nm for [Mn(Cl)(OESPz)][14] change in energy and intensity for the asymmetric complex, whereas ligand to metal charge transfer (LMCT) bands shown in the near-IR by the symmetric manganese(III) porphyrazine[14] undergo a red shift up to 33 nm and split for [Mn(Cl)(HESPz)].

(b) ESR spectra of copper(II) porphyrazines. ESR spectra of magnetically diluted samples of symmetric and asymmetric copper(II) porphyrazines have been recorded to gain insights on the effects of peripheral asymmetry on the metal porphyrazine. The simulation of the spectrum of [Cu(HESPz)] was performed

Table 2 Summary of redox potentials, $E_{1/2}$/V (ΔE_p/mV), for symmetrically and asymmetrically substituted (ethylsulfanyl)porphyrazines and the corresponding nickel(II), copper(II) and manganese(III) complexes in dichloromethane (*vs.* Ag–AgCl)[a]

Compound	Ligand oxidation (I)	Metal M^{III}–M^{II}	Ligand reduction (I)	(II)	(III)
Symmetrically substituted (ethylsulfanyl)porphyrazines					
H_2OESPz	1.22(96)		−0.42(106)	−0.75(118)	−1.77(E_{pc})
[Ni(OESPz)]			−0.45(62)	−0.81(64)	−1.73(150)
[Cu(OESPz)]	—		−0.46(66)	−0.79(78)	−1.78(E_{pc})
[Mn(Cl)(OESPz)]	—	0.05(120)	−0.49(94)	−1.16(190)[b]	−1.45(E_{pc})
Unsymmetrically substituted (ethylsulfanyl)porphyrazines					
H_2HESPz	1.12(129)		−0.42(100)	−0.73(98)	−1.74(126)
[Ni(HESPz)]	1.24(E_{pa})		−0.52(64)	−0.87(66)	—
[Cu(HESPz)]	1.05(E_{pa})		−0.52(84)	−0.84(84)	—
[Mn(Cl)(HESPz)]	—	0.08(142)	−0.61(140)	−1.16(190)[b]	−1.48(E_{pc})

[a] Measured in 10^{-3} M solutions ([$N(C_4H_9$-*n*)$_4BF_4$] = 0.15 M) using a platinum working electrode with a scan rate of 200 mV s^{-1}. [b] Possibly metal centered redox process.

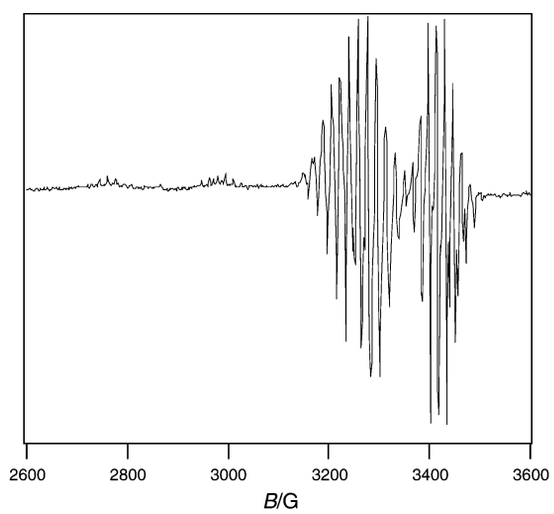


Fig. 7 Room temperature X-band ESR spectrum of [Cu(HESPz)] magnetically diluted (1 : 100) in the H_2HESPz diamagnetic host.

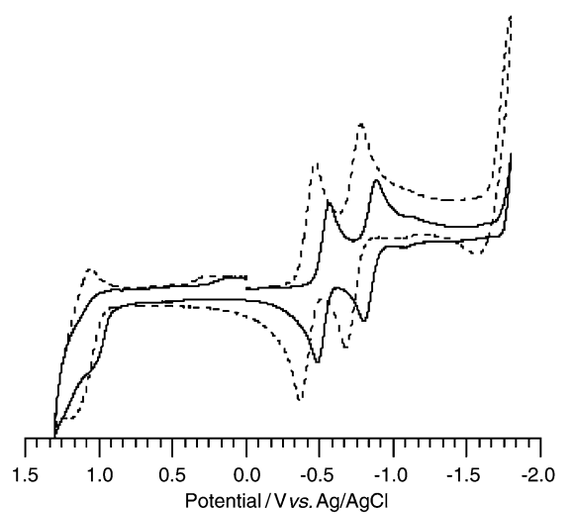


Fig. 8 Cyclic voltammograms of [Cu(OESPz)] (dashed line) and [Cu(HESPz)] (full line). Conditions: [Complex] = 1.5 mM; [$N(C_4H_9$-*n*)$_4$-BF_4] = 0.15 M; solvent = CH_2Cl_2; v = 0.2 V s^{-1}.

using WIN-EPR SimFonia,[18] a program based on a second-order perturbative solution of the spin Hamiltonian. The spectrum of [Cu(HESPz)] is reported in Fig. 7. The simulated spectrum (not shown) was computed with $g_{\|} = 2.148$, $g_{\perp} = 2.034$, $^{63}A_{\|} = 219.5$, $^{63}A_{\perp} = 37.5$, $^{N}A_{\|} = 16.8$, $^{N}A_{\perp} = 16.5$ G, with an isotropic linewidth of 6 G. The observed spin Hamiltonian parameters agree well with those reported for porphyrin-like systems,[19] showing that the unpaired electron resides in a σ* orbital mainly localized on a copper $3d_{x^2-y^2}$ orbital. The spectra of [Cu(OESPz)] could be reproduced with nearly the same spin Hamiltonian parameters, $g_{\|} = 2.20$, $g_{\perp} = 2.07$, $A_{\|} = 217$, $A_{\perp} = 30$, $^{N}A_{\|} = 19$, $^{N}A_{\perp} = 16$ G, indicating that the type and strength of copper–macrocycle interaction change only marginally on going from [Cu(OESPz)] to [Cu(HESPz)].

(c) Redox properties. The redox properties of symmetric and asymmetric free-base and manganese(III), nickel(II) and copper(II) derivatives were studied by cyclic voltammetry in dichloromethane, because of their high solubility in this solvent. A summary of half-wave and peak potentials in CH_2Cl_2 containing 0.1 M $N(C_4H_9$-*n*)$_4BF_4$ is given in Table 2, whereas representative cyclic voltammograms are illustrated in Fig. 8 for copper(II) porphyrazines. The voltammograms of the asymmetric porphyrazines exhibit shapes similar to those of the corresponding symmetric counterparts. The four electrode reactions of each compound can be unambiguously assigned to formation of a porphyrazine π-cation radical upon oxidation and π-anion radicals, dianions and π-anion radicals upon reduction.[8,10]

The voltammograms of H_2HESPz and H_2OESPz are practically identical in the cathodic region. However, formation of the π-cation radical upon oxidation is easier in H_2HESPz than in H_2OESPz by ≈100 mV. Introducing nickel(II), copper(II) and manganese(III) ions into the macrocyclic cavity induces a remarkable, although not homogeneous cathodic shift of the half-waves of the reductive processes. The shift is only ≈40 mV in the case of the symmetric porphyrazine, whereas it is up to 110 mV in the case of the asymmetric counterpart. The cathodic shift of the half-waves for the reductive processes in the studied asymmetric metal porphyrazines is in line with expectations. (Alkylsulfanyl)porphyrazine complexes are electroreduced at potentials ≈340 mV more positive with respect to the porphyrazine complexes not containing peripheral sulfur atoms.[8,10] Thus, removal of an alkylsulfanyl tail in the former should cause a shift of the reductive potentials towards more negative values, in line with the experimental observations. The apparently anomalous cathodic behavior of the free-base porphyrazine could be ascribed, probably, to conflicting electronic and structural effects induced by removal of an ethylsulfanyl tail, not operating in metallated porphyrazines. From the electrochemical data of Table 2, it is seen that a not negligible cathodic shift is experienced by the Mn^{III}–Mn^{II} redox couple on going from [Mn(Cl)(OESPz)] to [Mn(Cl)(HESPz)].

Conclusion

We have shown that reaction of the free-base octakis(ethylsulfanyl)porphyrazine with $CrCl_2$ at 190 °C in a TCB–*n*-BuOH mixture results in one ethylsulfanyl branch being replaced by an hydrogen atom with >40% yield. The whole process consists in the formation of the two-electron reduced diprotonated porphyrazine, $H_2OESPz(-4)(2H^+)$. This species undergoes, as a consequence of high temperature, charge and structural intramolecular rearrangements, a nucleophilic substitution of an ethyl sulfide by H^-.

Electronic effects of the asymmetric pattern of the peripheral substituents in the free-base porphyrazine and in complexes of Mn^{III}, Cu^{II} and Ni^{III} were investigated by UV-Vis spectroscopy, ESR (in the case of copper(II) porphyrazines) and cyclic voltammetry. It is found that asymmetry modifies significantly the (sulfanyl)porphyrazine π and n_{Sulfur} levels, but has little effect on the electronic properties of the coordinated metal ions.

It is worth mentioning that the hydrogen atom at the β position of H_2HESPz can easily be replaced by a bromine atom, whereas the 2,7,8,12,13,17,18-heptakis(octylsulfanyl)-5,10,15,20-porphyrazine exhibits, unlike its symmetric counterpart, discotic mesomorphism. These results will be reported and discussed in forthcoming papers.[20,21]

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