Bull Soc Chim Fr (1997) 134, 689-696
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Elemental sulfur–porphyrin interactions

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(Received 5 March 1997; accepted 2 July 1997)

Summary — To mimic geochemical processes, several alkylporphyrins were heated in the presence of elemental sulfur above 200 °C. A variety of products were observed, and thiopyrano- and thienylporphyrins as well as dealkylated, homologated and dehydrogenated porphyrins were characterized.

porphyrin / geochemistry / sulfur / thermal reaction / thiopyranoporphyrin

Résumé — **Interactions soufre élémentaire–porphyrines.** Pour modéliser certains processus géochimiques, plusieurs alkylporphyrines ont été chauffées en présence de soufre élémentaire à des températures supérieures à 200 °C. On observe de nombreux produits parmi lesquels des thiopyrano- et thiénylporphyrines, de même que des composés désalkylés, homologués et déshydrogénés, ont été caractérisés.

porphyrine / géochimie / soufre / réaction thermique / thiopyranoporphyrine

Introduction

Sulfur is present in most sediments containing organic matter and is involved in the transformation of organic molecules. These transformations include sulfur incorporation, dehydrogenation, reticulation, and lead to macromolecular entities. Sulfur-containing compounds may represent as much as 75–80% of the total organic matter. Depending on the substrate and the conditions (deposition, diagenesis), the sulfur-containing products observed (free as well as bound compounds) are thiols, thioethers, thiophenes, etc. The study of these compounds has been very useful in organic geochemistry, especially in paleoenvironment reconstruction [1–17]. The presence of porphyrins bound to macromolecules via carbon–sulfur bonds was demonstrated in oil shales, although the precise nature of the bonding still awaits further investigation [6–8].

In order to mimic the interaction of sulfur or sulfur compounds with porphyrins we decided to react porphyrins, natural or synthetic, with elemental sulfur. In this article we will describe the reaction of sulfur with simple synthetic alkylporphyrins as well as with a moderately functionalized natural porphyrin, protoporphyrin [18].

Results

Model compounds

Our first choice was to use nickel complexes of the selected porphyrins: nickel may protect the central part of the molecules, in order to simplify the resulting mixtures, but it is also a metal often present in the natural porphyrins [19], in particular during the late stages of their transformation, when defunctionalization has occurred to a large extent. In addition nickel porphyrins are diamagnetic, while the complexes of the other metal often present in porphyrins from sediments, vanadium (IV), are paramagnetic.

Since the simplest synthetic porphyrins, *meso*-tetraarylporphyrins [20], proved to be inert in the presence of excess sulfur up to 200 °C, we turned to more reactive compounds, first tetraalkylporphyrins **2–5**, then octaethylporphyrin **6**, these being accessible via pyrrole–aldehyde condensations [21, 22]. These substrates are shown in figure 1. The tetraalkyl series was extended up to tetrabutylporphyrin in order to facilitate the formation of a thiophene ring, as in various terpenoid series [1]. In addition, one porphyrin from the natural series, nickel protoporphyrin IX dimethyl ester **7**, was chosen to test the reactivity of the vinyl group under sulfuration conditions.

Reaction conditions and isolation of the products

All reactions were run in sealed tubes under vacuum. A high-boiling solvent, benzyl acetate (bp 213 °C), was chosen. Although it had been used earlier in reactions involving elemental sulfur [23] – and accordingly we supposed that it was moderately reactive – benzyl acetate participated to a large extent in the formation of the products, as shown by mass spectrometry. However, the nuisance due to the higher complexity of the reaction

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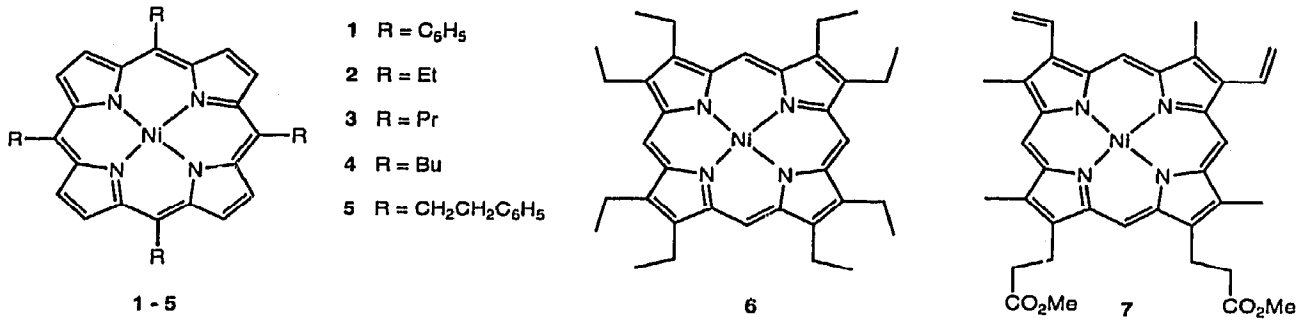


Fig 1. Starting porphyrins.

mixtures was compensated by the observation of various unexpected C–C bond-forming reactions.

A temperature of ca 200 °C was necessary to bring into reaction the nickel porphyrins used in this study. The reaction period had to be chosen carefully to keep the conversion and the complexity of the mixture at levels compatible with the isolation of pure products (see experimental section).

After opening of the sealed tube (H_2S evolution) the crude reaction mixtures were separated using TLC, then reverse-phase HPLC. Only the major peaks were selected and no attempt was made to quantify the amount of individual porphyrins. The composition of each peak was monitored by mass spectrometry and, if possible, the fractions further purified using analytical HPLC columns. Finally the products were cleaned from solvent residues on short silica gel columns under 'geochemical' conditions (all equipment rinsed and chromatography run with redistilled solvents). The structural assignments resulted from the recording of UV–visible, NMR and mass spectra (including HRMS).

In parallel, some reaction mixtures (from octaethyl- and protoporphyrin) were treated with nickel boride [24, 25] in order to cleave carbon–sulfur bonds and to simplify the reaction mixtures [6, 7]. It is known that the porphyrin nucleus survives under these conditions while it is often destroyed by Raney nickel treatment [6]. The resulting desulfurized mixtures showed an increase of the low-polarity fractions, which were separated into individual components as described above.

Due to the complexity of the reaction mixtures, as well as the multiple separation and purification steps, the following remarks must be kept in mind:

– only small amounts of a few pure porphyrins could be isolated and these are the only ones that will be presented;

– a large number of products [26] were detected and sometimes partially characterized, but will not be discussed further;

– it is thus clear that the discussion will be limited to the structural data, any quantitative interpretation being obviously meaningless.

Structure of the products

• *Products from meso-tetraalkylporphyrins (fig 2)*

Most low-polarity fractions (eluent: hexane/dichloromethane, 1:1) were red, as are the starting nickel complexes, but each reaction mixture from tetraalkylporphyrins showed at least one green band. Structures of green compounds **8–11** are in agreement with the presence of only 7 pyrrolic protons and 3 intact side-chains, one olefinic proton at low field vicinal to a residue from the fourth side-chain (H, Me, Et, C_6H_5) and an additional sulfur atom. A bathochromic shift of the UV–visible spectrum (of magnitude 22 to 62 nm for the tetraalkyl series) is indicative of an extended conjugated system and a strong involvement of the additional thiopyran ring. Attempts to obtain crystals for X-ray structural determination were unsuccessful, precluding the measurements of the corresponding bond lengths. An additional compound **12** was isolated in the tetrapropylporphyrin series. Its NMR data are compatible with that of the dihydro counterpart of compound **9**.

Two thiophene-containing products **13** and **14** were also isolated from the tetrabutylporphyrin–sulfur reaction. The NMR data for thiophene **13** are unequivocal and the structure assignment was confirmed by comparison with a synthetic sample obtained by condensation of 2-formylthiophene, benzaldehyde and pyrrole. The symmetry elements for compound **14** are identical, but the NMR spectrum indicated the presence of an additional phenyl group attached to a polar functional group. High-resolution mass spectrometry data confirmed the presence of an oxygen atom. Accordingly, we suggest the structure of a benzoylated thiophene for compound **14**.

Nickel tetraphenethylporphyrin yielded a product of low polarity which did not show sulfur incorporation. Structure **15** is in agreement with its NMR data, in particular the signals typical for the protons of an *E*-olefin (J = 16 Hz).

• *Products from octaethylporphyrin (fig 3)*

The complexity of the mixture obtained from nickel octaethylporphyrin was even greater than in the case of the tetraalkylporphyrins. As a consequence, the isolation and structure determination of pure compounds was more difficult, and this is why the desulfurization sequence was applied in this series. Some products were present in both desulfurized (DP) and non-desulfurized porphyrin mixtures (SP), while others were only present in the desulfurized mixture, implying that in this last case we will only be allowed to take into account the carbon framework for the discussion. Due to the numerous compounds whose peaks overlap in the HPLC

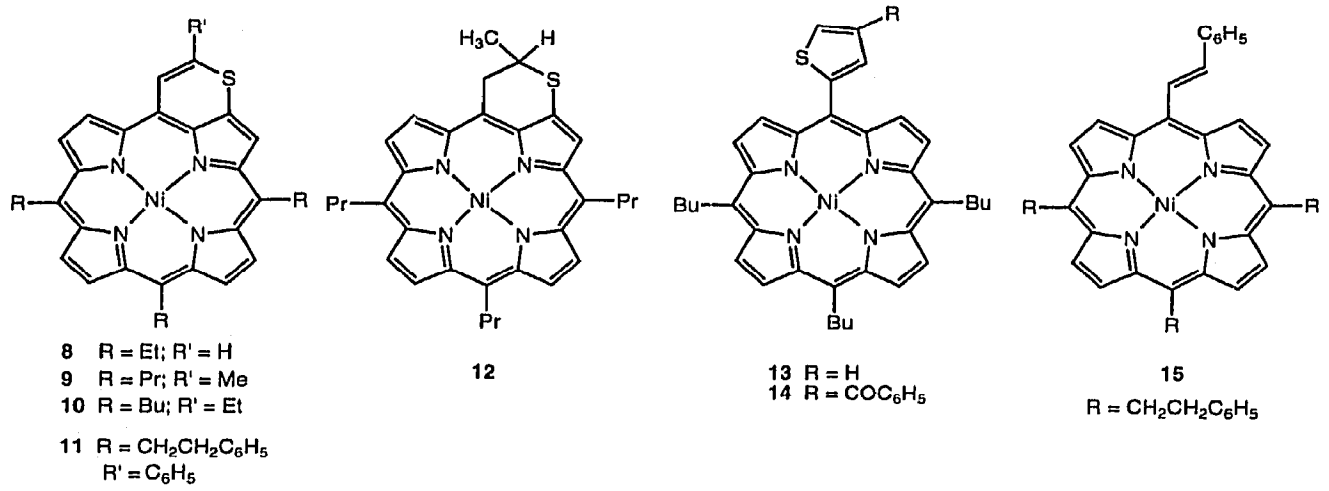


Fig 2. Products from the reaction of nickel tetraalkylporphyrins and elemental sulfur.

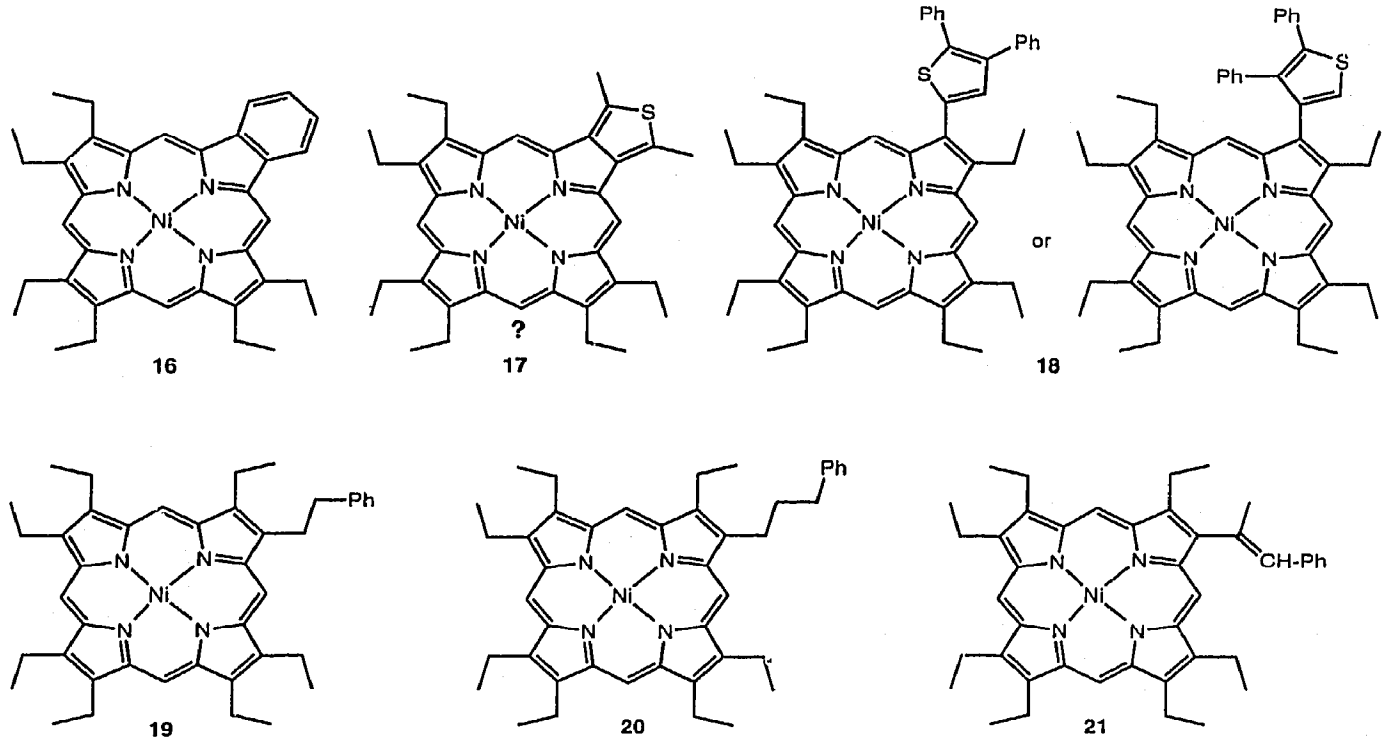
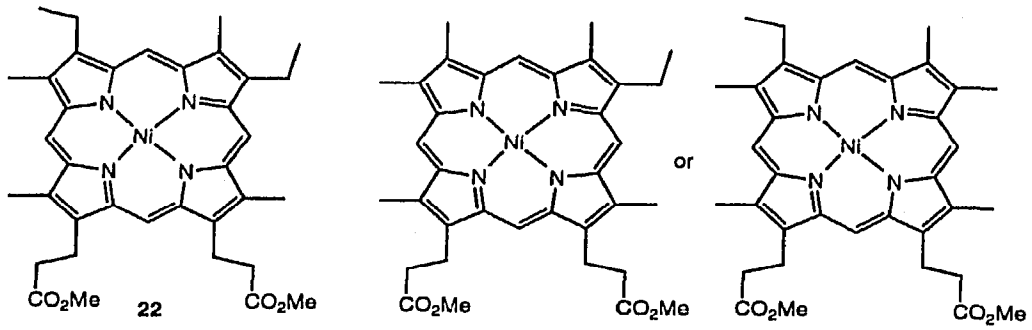


Fig 3. Products from the reaction of nickel octaethylporphyrin and elemental sulfur.

chromatograms, it is clear that, for minor compounds, detection may be a consequence of the efficacy of preparative isolation. Thus the presence of minor compounds may not always have been detected in the SP and DP mixtures.

The spectral data for two compounds suggested an additional aromatic ring fused to the porphyrin macrocycle. The first one was formulated as **16** (SP + DP), the *meso* protons appearing as 2 singlets and a AA′BB′ system being observed at δ 8.11 and 9.36 ppm. These last data are in agreement with the chemical shifts recorded for the known benzoporphyrins [27–29]. A blue compound possessing the same symmetry elements (*meso* protons as 2 singlets) but containing a sulfur atom (HRMS) was tentatively formulated as **17** (SP). However, the instability of this compound precluded its retention in a pure state and the high-field NMR signals remained obscured by impurities.

A thiophene-containing porphyrin **18** (SP) showed, in addition to 7 ethyl groups and 4 different *meso* protons, an aromatic singlet at 7.79 and the signal of two phenyl groups attached to a π system (low-field shift of *ortho* vs *meta* and *para* proton signals). The two structures shown are compatible with these data.



22 23

Fig 4. Products from the reaction of nickel protoporphyrin dimethyl ester and elemental sulfur.

Two groups of porphyrins showed little difference with the starting material, except for the incorporation of a phenyl group, and were only detected, and in some cases isolated, from the desulfurized fractions. The simplest members of the series, **19** (DP) and **20** (SP + DP), are homologous. In addition to NMR data typical for the proposed structures their mass spectra show respectively an expected loss of 91 ($-CH_2Ph$) and 105 ($-CH_2CH_2Ph$). Both **19** and **20**, when isolated from the desulfurized fractions, were accompanied by a minor homolog in which one ethyl group was replaced by a methyl group. In both cases, the typical −91 and −105 fragments were observed as well as the modified side-chain NMR signals. The methyl group appears as a group of peaks (isomer mixture). A higher homolog of 20, also from a desulfurized fraction, in which two phenylpropyl chains replaced two ethyl groups, was also isolated, the two singlets (2 + 2 H) of the *meso* protons still leaving the possibility of 4 isomers.

A last compound was purified from the desulfurized octaethylporphyrin series. Signals typical for a phenyl group close to a porphyrin (*ortho* and *meta* + *para* H appearing as two multiplets), and a methyl and an olefinic H in allylic relationship, strongly suggest structure **21** (DP).

• *Products from protoporphyrin IX (fig 4)*

Nickel mesoporphyrin dimethyl ester **22** was isolated as a major component from both the sulfurized and desulfurized mixtures from protoporphyrin **7** and was easily characterized by comparison with a sample prepared by hydrogenation of the same starting material. In addition, a lower homolog was isolated in low amount from the desulfurized mixture and proved to be diester **23** (one of two possible isomers).

Discussion

The products observed arise from different reaction sequences, involving both side-chains and porphyrin nucleus, but also additional fragments produced by the fragmentation of the solvent. We do not know by which mechanism benzyl acetate is transformed, but it is clear that at some stage benzyl radicals are produced and are able to recombine with porphyrinic moieties.

The initial step must involve sulfur radicals: a significant reactivity was not observed below 200 °C, a temperature necessary for the homolytic cleavage of S–S bonds [30]. Abstraction of hydrogen atoms from the benzylic positions of a porphyrin is a known reaction [31, 32].

The discussion will be presented in the following order: hydrogenation–dehydrogenation, thiophenes, thiopyranoporphyrins and related compounds, phenethyl- and phenylpropylporphyrins.

Hydrogenation–dehydrogenation

The least modified compounds, **15** and **22**, correspond respectively to a dehydrogenation of two benzylic positions within the porphyrin and to the hydrogenation of a vinyl group. Hydrogen abstraction by sulfur-centered radicals as well as hydrogen transfer via thiols are both well documented [30, 33, 34]. Benzoporphyrin **16** may arise from successive dehydrogenation of two adjacent ethyl groups. Radical or electrocyclic cyclization can form the 6-membered ring, followed by irreversible dehydrogenation into the benzene ring.

Thiophenes

Numerous compounds containing thiophene units have been isolated from geological sources [3, 35–38]. Most are derived from terpenic or linear structures. It was postulated that they originate from the reaction of functionalized substrates, olefins for example, with sulfur or thiols, followed by cyclization and dehydrogenation [9, 38]. However, a direct reaction of sulfur with saturated hydrocarbon chains may also occur, as shown by simulation experiments [1]. In our case an initial attack, H abstraction, at the benzylic *meso*-CH_2 is expected, followed by either olefin formation or H transfer. In any case, successive H abstractions, S addition, and final dehydrogenation must end at the stable thiophene stage, viz compound **13** when a side-chain of appropriate length (butyl) is present. Thiophene **14** obviously derives from **13**. We propose the following sequence: benzylation by a solvent fragment, thioketone formation at the reactive bibenzylic position [30, 39] and subsequent transformation into the ketone during the isolation procedure. The influence of the mechanism

on the substitution pattern of the thiophene is not considered in detail because of the lack of an exhaustive product inventory. Thiophene **18** (OEP series) may also arise from the addition of benzyl radicals to an activated porphyrin such as vinylporphyrin, produced by dehydrogenation of an ethyl side-chain. Similarly, addition of a sulfur-centered radical to such a vinylporphyrin, followed by H abstraction from the neighboring ethyl group, may initiate the formation of **17**.

Thiopyranoporphyrins

The formation of thiopyranoporphyrins is best described following the preceding sequence for the first steps. After the addition of H_2S to an olefinic intermediate, a ring closure to a pyrrolic position takes place and results in the formation of the 6-membered ring. Dehydrogenation of this ring and of the macrocycle lead to the fully unsaturated compounds **8–11**. The sequence might involve compound **12** and its homologs as intermediates.

Phenethyl- and phenylpropylporphyrins

Compound **20**, and its homologs bearing one or more phenylpropyl side-chains, did not lose any carbon of the starting material but clearly incorporated a benzyl fragment from the solvent. It is likely formed by the addition of a benzyl radical to a vinyl group, itself produced by hydrogen abstraction from an ethyl group. The resulting radical could then abstract another H to give the phenylpropyl side-chain. Olefin **21** is best described as the product of the recombination of a benzyl radical with a benzylic radical from the porphyrin, followed by dehydrogenation at both benzylic positions.

The phenethylporphyrins, **19** and homologs, as well as methylporphyrin **23**, were only isolated from desulfurized fractions. The structures of both series imply at some stage a C–C bond cleavage (by analogy with **20**, one would expect the phenethyl group to arise from the reaction of a benzyl radical with a porphyrinyl–CH_2 radical). The cleavage of such an ethyl C–C bond is classical under mass spectrometry conditions, but not during radical reactions [31, 32]. However, successive substitutions of H˙ by S–R˙ would favor a radical: a sequence of H abstractions followed by recombinations with an HS or RS radical (or addition on a vinylic substituent) would weaken the C–C bond by increasing the steric stress and the S atoms would stabilize a radical. Recombination (H˙ or $PhCH_2$˙) followed by desulfurization would lead to the observed products.

Conclusion

Although it is clear that (1) quantitative conclusions could not be drawn, and (2) the laboratory conditions may differ significantly from that in the sediments, this study shows that the reaction of elemental sulfur with various porphyrins illustrates the processes observed during the transformations of sedimentary organic matter. In particular the incorporation of sulfur was observed to yield thiophenes, frequently observed in sediments, but also a new series of modified porphyrins, the thiopyranoporphyrins. Side-chain C–C bond cleavage is often observed in porphyrins extracted from sediments, formation of benzoporphyrins less frequently; although sulfur may not be the only factor responsible for these transformations, our study suggests that it is a good candidate.

Experimental section

NMR spectra were run on Bruker AM 400 and ARX 500 spectrometers in $CDCl_3$, unless otherwise indicated. Chemical shifts are expressed in ppm (δ). UV–visible spectra were recorded on a Hewlett-Packard 8452A spectrophotometer in CH_2Cl_2. Mass spectra (low resolution) were recorded on a Finnigan MAT TSQ 70 spectrometer (direct inlet; 12 eV; 12 and 70 eV for **19** and **20**). HRMS analyses were performed by the Laboratoire de Spectrométrie de Masse du Service Central d'Analyses du CNRS (Vernaison). Microanalyses were performed by the Service de Microanalyse du Centre de Recherche Chimie, Université Louis Pasteur, Strasbourg.

Mixtures were first separated on silica gel or alumina column (Merck 70–230 Mesh) and TLC plates (Merck Kieselgel 60 F_{254}). HPLC separations were performed on Waters 6000A and Waters 600MS equipment (respectively M440 detector set at 405 and 546 nm or 996 diode-array detector; DuPont RP-18 Zorbax ODS 8μ columns; eluent: pure methanol to methanol/CH_2Cl_2, 9:1). The last purification steps were run under 'geochemical' conditions: redistilled solvents, and preliminary washing of all equipment (glassware, silica gel, etc) with redistilled solvents. Before NMR measurements all fractions were first checked by mass spectrometry, then run through a short silica gel column under geochemical conditions.

Starting porphyrins **1** [20], **2–4** [21], **6** [22], **7** [40] were prepared according to literature procedures. Metallation proceeded quantitatively on refluxing overnight the free base with excess $Ni(acac)_2$ in benzene. The complex was percolated through a short silica gel column (hexane/CH_2Cl_2, 1:1), crystallized from CH_2Cl_2–methanol, dried and used as such.

Nickel-m-tetraphenethylporphyrin **5**

To a stirred suspension of K10 montmorillonite (1 g; Aldrich) in CH_2Cl_2 was added 3-phenylpropanal (1.32 mL) and pyrrole (0.7 mL). After 1 h at 20 °C, chloranil (1.85 g) was added and the suspension brought to reflux for 1 h. Filtration (Celite; eluent AcOEt + 1% NEt_3) and purification (alumina column, CH_2Cl_2) gave the porphyrin-free base (55 mg), which was quantitatively metallated ($Ni(acac)_2$) to give **5**.

UV–vis (nm; rel int): 420 (0.1), 538 (0.07).

NMR (CD_2Cl_2): 9.35 (s, 8H, pyrrole); 7.37 (m, 20H, phenyl); 4.80 and 3.64 (2m, 8 + 8H, CH_2CH_2).

Anal calc for $C_{52}H_{44}N_4Ni$: C, 79.70; H, 5.66; N, 7.15. Found: C, 78.8; H, 5.7; N, 7.0.

Thermal reactions and product isolation

Nickel–porphyrin (20 mg), elemental sulfur (20 mg), and benzyl acetate (0.7 mL) were placed in a glass tube which was sealed under vacuum. The tube was heated (200 °C) in an oven, then cooled and opened (strong H_2S smell). Excess solvent was eliminated under vacuum (80 °C; 0.1 Torr).

Depending on the complexity of the reaction mixtures the isolation procedures varied slightly. The products from tetraalkylporphyrins were cleaned by successive TLC runs (eluent hexane + decreasing % CH_2Cl_2), followed by HPLC separation. In the case of octaethylporphyrin two sequences

were followed. Either the crude mixture was fractioned on silicagel TLC, then each individual band purified by HPLC (methanol/CH_2Cl_2, 9:1, then pure methanol), or the total fraction of low polarity was purified by HPLC (same conditions) for comparison with the corresponding desulfurized mixture (see below). The products from protoporphyrin appeared as 3 bands of low polarity on a silicagel column. Each band was isolated and purified individually (TLC, then HPLC).

Desulfurization reaction

The crude thermal reaction mixture from 20 mg porphyrin was dissolved in methanol–THF (1:1; 10 mL), cooled to 0 °C, and stirred under argon for 30 min. Nickel chloride (1.04 g) followed by sodium borohydride (0.5 g) were added slowly, and the solution stirred for a further 45 min at 0 °C, then 3 h at 20 °C. The resulting mixture was filtered through a short Celite® column (25 mL, eluent: CH_2Cl_2) and the red fraction collected.

Thiopyranoporphyrin **8**

UV–vis (nm; rel int): 420 (0.99), 438 (1), 540 (0.06), 576 (0.07), 610 (0.16).

HRMS: calc for $C_{28}H_{24}N_4NiS$: 506.107. Found: 506.107.

NMR: 9.2–9.3 (m, 7H, pyrrole); 9.00 (d, 1H, J = 8 Hz, thiopyrane 5′-H); 7.66 (d, 1H, J = 8 Hz, thiopyrane 5″-H); 4.49 (q, 6H, $EtCH_2$); 1.94 (t, 9H, $EtCH_3$).

Thiopyranoporphyrin **9**

UV–vis (nm; rel int): 424 (0.92), 440 (1), 540 (0.08), 576 (0.08), 612 (0.17).

HRMS calc for $C_{32}H_{32}N_4NiS$: 562.170. Found: 562.172.

NMR: 9.15–9.25 (m, 6H, pyrrole); 9.10 (s, 1H, pyrrole 2-H); 8.62 (q, 1H, J = 1 Hz, thiopyrane 5′-H); 4.40 (m, 6H, propyl CH_2); 2.87 (d, 3H, thiopyrane methyl); 2.26 (m, 6H, propyl CH_2); 1.13 (t, 9H, propyl CH_3).

Thiopyranoporphyrin **10**

UV–vis (nm; rel int): 420 (1), 438 (0.83), 538 (0.07), 574 (0.06), 614 (0.13).

HRMS calc for $C_{36}H_{40}N_4NiS$: 618.232. Found: 618.231.

NMR: 9.2–9.3 (m, 6H, pyrrole); 9.15 (s, 1H, pyrrole 2-H); 8.75 (t, 1H, J = 1 Hz, thiopyrane 5′-H); 4.43 (m, 6H, butyl CH_2); 3.20 (dq, 2H, thiopyrane CH_2); 2.21 (m, 6H, butyl CH_2); 1.65 (t, 3H, thiopyrane CH_3); 1.56 (m, 6H, butyl CH_2); 1.00 (t, 9H, butyl CH_3).

Thiopyranoporphyrin **11**

UV–vis (nm; rel int): 415 (sh), 450 (1), 534 (0.05), 574 (0.07), 622 (0.22).

HRMS calc for $C_{52}H_{40}N_4NiS$: 810.232. Found: 810.232.

NMR: 9.44, 9.35, 9.34, 9.33, 9.30, 9.27 (6d, 6H, pyrrole); 9.33 (s, 1H, pyrrole 2-H); 9.25 (s, 1H, thiopyrane 5′-H); 8.09, 7.66, 7.58 (d + m + m, 2 + 2 + 1H, 5″-phenyl); 7.46, 7.38, 7.28 (3m, 6 + 6 + 3H, 10″, 15″, 20″ phenyl); 4.75, 3.63 (2m, 6 + 6H, CH_2–CH_2).

5′,5″-Dihydrothiopyranoporphyrin **12**

UV–vis (nm; rel int): 422 (1), 542 (0.08).

HRMS calc for $C_{32}H_{34}N_4NiS$: 564.185. Found: 564.184.

NMR: 9.24–9.29 (m, 5H, pyrrole); 9.17 (d, 1H, J = 5 Hz, pyrrole 7-H); 8.88 (s, 1H, pyrrole 2-H); 4.88 (dd, 1H, J = 3.5, 16.5, 5′-CH_2), 4.80 (dd, 1H, J = 10.5, 16.5 Hz, 5′-CH_2); 4.45 (m, 6H, propyl CH_2); 3.87 (m, 1H, 5″-H); 2.26 (m, 6H, propyl CH_2); 1.75 (d, 3H, 5‴-CH_3); 1.12 (3t, 9H, propyl CH_3).

Thienylporphyrin **13**

UV–vis (nm; rel int): 420 (1), 538 (0.047).

HRMS calc for $C_{36}H_{38}N_4NiS$: 616.217. Found: 616.214.

NMR: 9.29 (s, 4H, pyrrole); 9.20, 8.90 (2d, AB, 2 + 2H, pyrrole); 7.72 (dd, 1H, J = 5 and 1 Hz, thiophene); 7.66 (dd, 1H, J = 3.5 and 1 Hz, thiophene); 7.40 (dd, 1H, J = 5 and 3.5 Hz, thiophene); 4.52, 2.19, 1.51 (3m, 6 + 6 + 6H, butyl CH_2); 1.00 (t, 9H, butyl CH_3).

The same product was prepared in CH_2Cl_2 from 2-formylthiophene (1.43×10^{-3} M), pentanal (8.6×10^{-3} M), pyrrole (10^{-2} M), and trifluoroacetic acid (5×10^{-3} M). After 2 h at 20 °C, chloranil (7×10^{-3} M) was added and the mixture refluxed for 1.5 h. After evaporation of the solvent, the crude residue was metallated with $Ni(acac)_2$ and chromatographed on silica gel (eluent: CH_2Cl_2/hexane, 1:2). Purification of the fractions was completed by HPLC (RP-18/MeOH), followed by preparative TLC. One product proved to be identical to thienylporphyrin **13** (UV–vis; MS; NMR; HPLC). Due to the purification steps the yield is very low (< 1%).

Thienylporphyrin **14**

UV–vis (nm; rel int): 420 (1), 538 (0.07).

HRMS calc for $C_{43}H_{42}N_4NiOS$: 720.243. Found: 720.250.

NMR (CD_2Cl_2): 9.37 and 9.34 (2d AB, 2 + 2H, pyrrole); 9.32 and 9.04 (2d AB, 2 + 2H, pyrrole); 7.76 (m, 2H, phenyl *o*-H); 7.69 and 7.52 (2d AB, 1 + 1H, thiophene); 7.50 (m, 3H, phenyl *m* + *p* − H); 4.53 (broad q, 6H, butyl CH_2); 2.26 (m, 6H, butyl CH_2); 1.57 (m, 6H, butyl CH_2); 1.03 (t, 9H, butyl CH_3).

Styrylporphyrin **15**

UV–vis (nm; rel int): 434 (1), 552 (0.08), 598 (0.06).

HRMS calc for $C_{52}H_{42}N_4NiS$: 780.276. Found: 780.276.

NMR (CD_2Cl_2): 9.34 (d, 2H, pyrrole); 9.27 (m, 6H, pyrrole); 9.20 and 6.78 (2d, 1 + 1H, olefin, J = 15.9 Hz); 7.80, 7.51 and 7.38 (d + t + t, 2 + 2 + 1H, conjugated phenyl *o*-, *m*- and *p*-H); 7.45 (broad d, 6H, phenyl *o*-H); 7.37 (t, 6H, phenyl *m*-H); 7.26 (t, 3H, phenyl *p*-H); 4.75 and 3.59 (2m, 6 + 6H, CH_2–CH_2).

Benzoporphyrin **16**

UV–vis (nm; rel int): 398 (1), 526 (0.06), 562 (0.18), 570 (0.19).

HRMS calc for $C_{36}H_{38}N_4Ni$: 584.244. Found: 584.243.

NMR (CD_2Cl_2): 10.24 and 9.87 (2s, 2 + 2H, *meso*); 9.36 and 8.11 (2m, 2 + 2H, benzo); 4.0 and 1.8 (2m, obscured by impurities).

Compound **17**

Fractions containing the blue compound **17** showed a specific absorption at 610 nm and additional peaks at 406, 522 and 552 nm. The NMR spectra also showed two specific singlets in the *meso* region at 9.48 and 9.60 ppm. High-resolution mass spectral analysis allowed us to measure a composition corresponding to a thienylporphyrin: calc for $C_{36}H_{38}N_4Ni$: 618.232. Found: 618.230.

Thienylporphyrin 18

UV–vis (nm; rel int): 392 (1), 520 (0.06), 560 (0.15).

HRMS calc for $C_{50}H_{50}N_4NiS$: 796.311. Found: 796.310.

NMR (CD_2Cl_2): 10.20, 9.99, 9.86 and 9.85 (4s, 1 + 1 + 1 + 1H, *meso*); 7.79 (s, 1H, thiophene); 7.62 and 7.60 (2dd, 2 + 2H, phenyl *o*-H); 7.43 and 7.42 (2t, 2 + 2H, phenyl *m*-H); 7.36 (broad t, 2H, phenyl *p*-H); 4.21 and 3.97 (q + m, 2 + 12H, ethyl CH_2); 1.94 and 1.82–1.86 (t + m, 3 + 18H, ethyl CH_3).

Heptaethyl(phenethyl)porphyrin 19

The fraction described here contains ca 65–70% **19**, the remaining being the homolog in which one ethyl group is replaced by a methyl (mixture of isomers, signal for the methyl groups as an m at ca 3.25–3.30 ppm).

UV–vis (nm; rel int): 392 (1), 516 (0.05), 552 (0.16).

HRMS calc for $C_{42}H_{48}N_4Ni$: 666.323. Found: 666.320.

NMR (CD_2Cl_2): 9.85, 9.84, 9.83 (3s, 2 + 1 + 1, *meso*); 7.40 (d, 2H, phenyl *o*-H); 7.32 (t, 2H, phenyl *m*-H); 7.20 (t, 1H, phenyl *p*-H); 4.23 (t, 2H, 2′-CH_2); 3.95–3.85 (m, ethyl CH_2); 3.54 (t, 2H, 2″-CH_2); 1.85–1.75 (m, ethyl CH_3).

Heptaethyl(phenylpropyl)porphyrin 20

This fraction contains ca 75% **20**, the remaining being a lower homolog. This homolog corresponds to an ethyl group being replaced by a methyl group, not being **19**, as shown by the absence of any signal between 4.1 and 4.5 ppm.

UV–vis (nm; rel int): 392 (1), 516 (0.06), 552 (0.15).

HRMS calc for $C_{43}H_{50}N_4Ni$: 680.339. Found: 680.340.

NMR (CD_2Cl_2): 9.84, 9.69 (2s, 3 + 1H, *meso*); 7.38, 7.26 (2m, 4 + 1H, phenyl); 4.01 (t, 2H, 2′-CH_2); 3.96–3.94 (m, 12H, ethyl CH_2); 3.86 (q, 2H, ethyl CH_2); 3.08 (t, 2H, 2‴-CH_2); 2.57 (q, 2H, 2″-CH_2); 1.78–1.81 (m, 21H, ethyl CH_3).

Heptaethyl(β-methylstyryl)porphyrin 21

UV–vis (nm; rel int): 394 (1), 516 (0.06), 552 (0.16).

HRMS calc for $C_{43}H_{48}N_4Ni$: 678.320. Found: 678.323.

NMR (CD_2Cl_2): 9.88, 9.86, 9.83, 9.74 (4s, 1 + 1 + 1 + 1, *meso*); 7.37 (q, 1H, J = 1 Hz, vinyl H); 6.96 (d, 2H, phenyl *o*-H), 6.71–6.69 (m, 3H, phenyl *m*- and *p*-H); 4.0–3.8 (m, 14H, ethyl CH_2); 2.80 (d, 3H, J = 1 Hz, 2″-methyl); 1.86, 1.81, 1.71, 1.63 (m + 3t, 12 + 3 + 3 + 3H, ethyl CH_3).

3-(or 8-)Desethyl-3-(or 8-)methylmesoporphyrin 23

UV–vis (nm; rel int): 392 (1), 516 (0.06), 552 (0.17).

HRMS calc for $C_{35}H_{38}N_4NiO_4$: 636.225. Found: 636.225.

NMR (CD_2Cl_2; due to the presence of isomers, all signals appear as multiplets whose chemical shift for the highest peak is indicated): 9.87 (*meso*); 4.27 (13′ and 17′ CH_2); 3.95 (ethyl CH_2); 3.65 (ester CH_3); 3.52 (porphyrin CH_3); 3.18 (13″ and 17″ CH_2); 1.78 (ethyl CH_3).

Acknowledgments

Thanks are due to P Wehrung, MC Schweigert, E Krempp and R Graff for MS and NMR measurements, and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

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