

# Octakis (9-anthracenylmethylthio) iron porphyrazine derivatives

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Chloro[octakis(9-anthracenylmethylthio)porphyrazinato]iron(III), ([FePzCl]), was prepared by the reaction of metal-free porphyrazine with iron(II) acetate and further treatment with HCl solution. The monomeric bisaxial complex [FePz(py)<sub>2</sub>] as well as the bridged complex [FePz(py<sub>2</sub>)<sub>n</sub>] were formed as stable complexes by reacting [FePzCl] with pyridine or pyrazine, respectively. These novel complexes were characterised by elemental analysis, together with FT-IR, <sup>1</sup>H NMR, UV-Vis and mass spectral data.

**Keywords:** anthracene, pyridine, pyrazine, shishkebab type oligomer; bisaxial complex

Metal complexes with various tetrapyrrole ligands, namely, porphyrins (Ps), porphyrazines (Pzs, also called tetraazaporphyrins) and phthalocyanines (Pcs), modified by the attachment of peripheral substituents, have found wide applications in diverse areas such as liquid crystals, chemical sensors, electrophotography, optic data collection, laser technology catalysis, electron transfer and the photodynamic therapy of tumours, as well as in their classical fields as pigments and dyes.<sup>1-5</sup>

Peripheral heteroatom functionalisation of the macrocycle results in significant modulation of their physical and electronic properties. In contrast, the structurally related porphyrazines have been less well studied. However, due to the easy and multi-purpose synthetic route for the preparation of porphyrazines, namely the metal-templated cyclisation of the maleonitrile precursors, these macrocyclic compounds are now subject to enhanced interest. While the alkyl chains make the products readily soluble in common organic solvents, the presence of eight electron-donating thioether groups on the periphery certainly alter the electronic properties of this interesting ligand, thus providing high electron density of the same order as in Pcs.<sup>6-10</sup>

During the last two decades, we have studied the preparation of novel porphyrazine and phthalocyanine derivatives. Among these are phthalocyanines, which are fused to, or attached through bridges to macrocyclic structures<sup>11</sup> and porphyrazines with peripheral functional groups such as quaternizable amino groups,<sup>12</sup> crown ethers,<sup>13</sup> ferrocenes,<sup>14</sup> triphenylphosphine<sup>15</sup> and 4-*tert*-butylphenylthio-<sup>16</sup> and tosylaminoethylthio-<sup>17</sup> groups.

Recently, we have synthesised novel *seco*-porphyrazines substituted with 1-naphthyl<sup>18</sup>, *p*-tolyl, *o*-tolyl, or 4-biphenyl groups<sup>19</sup> on the peripheral positions as encountered by Barrett, Hoffman and coworkers, with peripheral amino-derivatives.<sup>20</sup> We have also synthesised porphyrazines with bulky electron rich substituents such as 1-naphthylmethylthio- or 9-anthracenylmethylthio-units.<sup>21-24</sup> These additional donor sites lead to multinuclear complexes and, at the same time, enhance the solubility of the new compounds.

In this paper, we report novel soluble iron porphyrazine derivatives with eight (9-anthracenylmethylthio-) substituents appended to the peripheral positions. Chloro [octakis (9-anthracenylmethylthio)porphyrazinato]iron(III) ([FePzCl]) was prepared by the reaction of metal-free porphyrazine with iron(II) acetate and further treatment with HCl solution. The monomeric bisaxial complex [FePz(py)<sub>2</sub>] as well as the bridged complex [FePz(py<sub>2</sub>)<sub>n</sub>] were formed as stable complexes by reacting [FePzCl] with pyridine or pyrazine, respectively. These novel complexes were characterised by elemental analysis, together with FT-IR, <sup>1</sup>H NMR, UV-Vis and mass spectral data.

## Experimental

IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR (ATR sampling accessory) spectrophotometer, electronic spectra on a Unicam UV2 spectrophotometer. Elemental analyses were recorded on a Thermo Finnigan Flash EA 1112 instrument. Proton NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer using TMS and *d*-chloroform as the reference and solvent, respectively. Mass spectra were recorded on a Bruker Daltonics MicroTOF LC-MS spectrometer using the electrospray ionisation (ESI) method. The instrument was operated in positive ion mode. All starting materials were purchased from major suppliers and used without any further purification. The homogeneity of the products was tested in each step by TLC.

[2,3,7,8,12,13,17,18-octakis(9-anthracenylmethylthio) H<sup>20</sup>, H<sup>22</sup> porphyrazine] (1) was prepared according to the previously reported procedure.<sup>24</sup>

Chloro[octakis(9-anthracenylmethylthio)porphyrazinato]iron(III) ([FePzCl] (2): A mixture of 1 (100 mg, 0.0478 mmol) and Fe(OAc)<sub>2</sub> (416 mg, 2.39 mmol) in acetic acid (20 ml) was heated at 120 °C for 24 h under N<sub>2</sub>. The reaction was monitored continuously for the presence of metal-free porphyrazine by UV-Vis spectroscopy. After completion of the reaction, the mixture was filtered and HOAc was evaporated under reduced pressure. The residue was dissolved in CHCl<sub>3</sub> (50 ml) and then extracted several times with 1 M, 100 ml HCl until no yellowish colour of ferric salts was present in the aqueous phase. The chloroform solution was washed twice with water and dried over Na<sub>2</sub>SO<sub>4</sub>. When the solvent was evaporated, a green product was obtained. Finally, the pure porphyrazine was obtained by chromatography on silica gel using methanol/chloroform (1:50) mixture as eluent. The product was soluble in chloroform, dichloromethane and acetone, but insoluble in *n*-hexane. Yield: 44 mg (42%). FT-IR,  $\nu_{\max}$ (cm<sup>-1</sup>): 3048 (CH, aromatic), 2922–2885 (CH, aliphatic), 1668 (C=C, aromatic), 1444, 1260, 1087, 1018, 881, 735 cm<sup>-1</sup>. UV-Vis (CHCl<sub>3</sub>)  $\lambda_{\max}$  (nm) (log  $\epsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 352 (4.72), 540 (4.20), 584 (4.30), 676 (3.99). MS (ESI): (*m/z*): 2182.81 [M]<sup>+</sup>. Calcd. for C<sub>136</sub>H<sub>88</sub>N<sub>8</sub>S<sub>8</sub>ClFe: C 74.86; H 4.06; N 5.14. Found: C 74.71; H 4.18; N 5.27.

Bis(pyridine)[octakis(9-anthracenylmethylthio)porphyrazinato]iron(II) [FePz(py)<sub>2</sub>] (3): [FePzCl] (50 mg, 0.023 mmol) was dissolved in benzene (10 ml) and 0.1 ml of pyridine was added. The mixture was refluxed for 5 h under N<sub>2</sub>. After the solvent was removed under reduced pressure, the residue was dissolved in diethyl ether and added dropwise to DMF (10 ml). The precipitate formed was filtered and dried *in vacuo*. The pure porphyrazine was obtained by chromatography on silica gel using methanol/chloroform (1:20) mixture as eluent. The product was soluble in chloroform, dichloromethane and acetone, but insoluble in *n*-hexane. Yield: 34 mg (65%). FT-IR,  $\nu_{\max}$ (cm<sup>-1</sup>): 3050 (CH, aromatic), 2951–2853 (CH, aliphatic), 1680 (C=C, aromatic), 1590, 1440, 1259, 1017, 882, 732 cm<sup>-1</sup>. UV-Vis (CHCl<sub>3</sub>)  $\lambda_{\max}$  (nm) (log  $\epsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>): 348 (5.11), 592 (4.66). MS (ESI): (*m/z*): 2304.33 [M]<sup>+</sup>. Calcd. for C<sub>146</sub>H<sub>98</sub>N<sub>10</sub>S<sub>8</sub>Fe: C 76.08; H 4.29; N 6.08. Found: C 76.20; H 4.18; N 6.17. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$ , ppm 8.90–7.45 (m, 9H, aromatic H), 6.88 (m, py-H<sub>c</sub>), 5.44 (br s, 2H, S–CH<sub>2</sub>), 4.73 (m, py-H<sub>b</sub>), 2.33 (m, py-H<sub>a</sub>).

$\mu$ -Pyrazine[octakis(9-anthracenylmethylthio)porphyrazinato]iron(II) [FePz(py<sub>2</sub>)<sub>n</sub>] (4): [FePzCl] (100 mg, 0.046 mmol) and pyrazine (344 mg, 4.6 mmol) were mixed and melted at 80 °C under N<sub>2</sub> and the mixture was kept at 60 °C for 3 h. The excess pyrazine was sublimed under high vacuum during 5 h. Yield: 0.059 g (53.1%). Calcd. for (C<sub>140</sub>H<sub>92</sub>N<sub>10</sub>S<sub>8</sub>Fe)<sub>n</sub> (2226.71)<sub>n</sub>: C 75.52; H 4.16; N 6.29. Found: C 75.66; H 4.05; N 6.39. FT-IR,  $\nu_{\max}$ (cm<sup>-1</sup>): 3055 (CH, aromatic),

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2960–2880 (CH, aliphatic), 1685 (C=C, aromatic), 1440, 1265, 1020, 884, 730  $\text{cm}^{-1}$ . UV-Vis ( $\text{CHCl}_3$ )  $\lambda_{\text{max}}$  (nm) ( $\log \epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ): 376 (4.83), 620 (4.62), 712 (4.15).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$ , ppm 8.84–7.50 (m, 9H, aromatic H), 5.48 (br s, 2H, S–CH<sub>2</sub>), 2.24 (s, pyz-H).

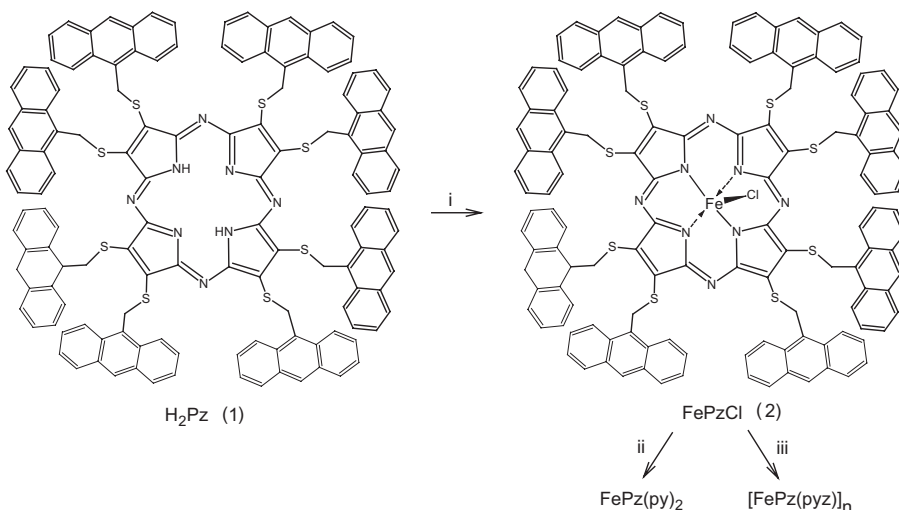
## Results and discussion

The starting point for a new porphyrazine structure with eight (9-anthracenylmethylthio-) groups bound to the periphery through flexible methylthio-chains is 1,2-bis(9-anthracenylmethylthio)dinitrile, which was obtained from the disodium salt of dithiomaleonitrile and 9-(chloromethyl)anthracene. It was a mixture of maleo- and fumaro-nitriles and the latter was present in higher ratio as expected from the presence of bulky anthracenylmethylthio-substituents. The presence of bulky electron-donating S-groups is expected to enhance the chemical stability and optical properties of porphyrazines.<sup>22</sup> Its reluctance to turn into porphyrazine under the usual conditions (*i.e.*  $\text{Mg}(\text{OR})_2$  in refluxing butanol) exposes the lower ratio of the maleonitrile component. This problem was solved by the activation of the fumaronitrile derivative to the corresponding pyrroline derivative, which cyclises quite easily to porphyrazine at the reflux temperature of butanol.<sup>23</sup> Conversion of 3,4-(9-anthracenylmethylthio)pyrroline-2,5-dimine into porphyrazine[octakis(9-anthracenylmethylthio)porphyrazinato]magnesium was achieved by the template effect of magnesium butanolate.<sup>24</sup> Anthracenylmethylthio-groups are comparable with naphthylmethylthio-groups as electron donors to the 18- $\pi$  electron system of the inner core.<sup>18</sup> The metal-free derivative (**1**) was obtained by its treatment with trifluoroacetic acid.<sup>24</sup> Iron insertion into **1** was carried out in acetic acid using anhydrous iron(II)

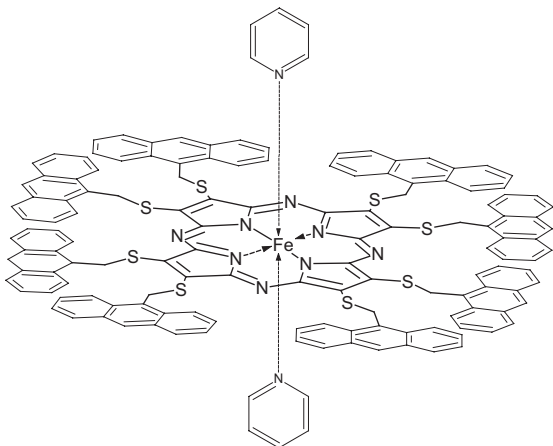
acetate as the metal salt<sup>25,26</sup> (Scheme 1). Although the reaction was carried out under an inert atmosphere, trace amounts of oxygen led to Fe(III) derivatives. Further exposure to air was almost inevitable during the work-up procedures, so the product was treated with dilute HCl solution in order to convert all of the trivalent iron products into  $[\text{FePzCl}]$ . The band at 1087  $\text{cm}^{-1}$  in the FT-IR spectrum of **2** can be assigned to the contribution of axial ligands to CN-skeleton vibrations as encountered in octaphenyltetraazaporphyrins.<sup>28</sup> Another consequence of the presence of the axial chloride ligand is the changes occurring in the Q-band absorption from an MPz derivative of  $D_{4h}$  symmetry (*e.g.*  $\text{MgPz}$ , where the Q band is at 648 nm as a single intense absorption<sup>25</sup>) to  $C_{4v}$  symmetry, resulting in an intense band at 584 nm together with two others at 540 and 676 nm. This Q band absorption appeared as two peaks at 624 and 680 nm in the case of the metal-free porphyrazine with  $D_{2h}$  symmetry.<sup>24</sup> Elemental analyses correspond closely with the values calculated for (**2–4**).

As in the case of phthalocyanines, it is not practical to reduce  $[\text{FePzCl}]$  to the divalent state in non-donating solvents, but treatment of  $[\text{FePzCl}]$  with pyridine at reflux temperature results in the octahedrally-coordinated  $[\text{Fe}^{\text{II}}\text{Pz}(\text{py})_2]$  complex<sup>25</sup> (Fig. 1). Its formation may be easily followed by the changes in the colour of the solution and also confirmed by the visible spectrum, which contains a single, intense Q band absorption at 592 nm, typical of  $D_{4h}$  symmetry. UV-Vis spectrum of **3** in chloroform is shown in Fig. 3.

In the FT-IR spectrum of **1** the N–H stretching absorption of the inner core was observed around 3320  $\text{cm}^{-1}$ . FT-IR spectra of all porphyrazines derivatives (**1–4**) showed that the aromatic and aliphatic C–H peaks are around 2853–3055  $\text{cm}^{-1}$ , aromatic C=C peaks are around 1655–1685  $\text{cm}^{-1}$  and a characteristic substituted anthracene peak is at 730–735  $\text{cm}^{-1}$ . In the FT-IR spectrum of **3**,



**Scheme 1** Synthesis route to new compounds: (i)  $\text{Fe}(\text{OAc})_2$ , acetic acid, HCl; (ii) pyridine; (iii) pyrazine.



**Fig. 1** Bis(pyridine)[octakis(9-anthracenylmethylthio)porphyrazinato]iron(II)  $[\text{FePz}(\text{py})_2]$  (**3**).

the newly-appearing band at 1590  $\text{cm}^{-1}$  is likely to be due to the breathing mode of the axial pyridine groups.

When a bidentate ligand such as pyrazine is used instead of pyridine, similar changes occur in the oxidation state of the metal ion. In addition, bidentate ligands form a bridge between the metal centres and form a shishkebab-type oligomer<sup>28,29</sup> (Fig. 2). In the visible spectrum the Q band absorption at 620 nm has been shifted to longer wavelength (*ca* 28 nm) when compared with the monomeric structure obtained with pyridine. There is also a shoulder around 712 nm in the visible spectra after oligomer formation. A penta-coordinated 1:1  $\text{FePz}/\text{pyz}$  complex can be easily ruled out by the diamagnetic property of the product.

The  $^1\text{H}$  NMR spectrum indicates an octahedrally-coordinated Fe(II) complex. The chemical shift values of the axially coordinated ligands have been extensively affected by the 18- $\pi$  electrons of the porphyrazine core, *i.e.* the peaks at 8.60, 7.68 and 7.30 ppm in free pyridine have been shifted to 6.88, 4.73 and 2.33 ppm, respectively, after binding axially to form  $[\text{FePz}(\text{py})_2]$ . Similarly, there is only a single peak at 2.24 ppm for pyrazine protons in the bridged structure  $[\text{FePz}(\text{pyz})]_n$ .<sup>30,31</sup> When taken together with NMR and IR data, the Q bands, appearing at 592 and 620 nm in the UV-Vis spectrum of  $[\text{FePz}(\text{py})_2]$  or  $[\text{FePz}(\text{pyz})]_n$  confirm the coordination of the

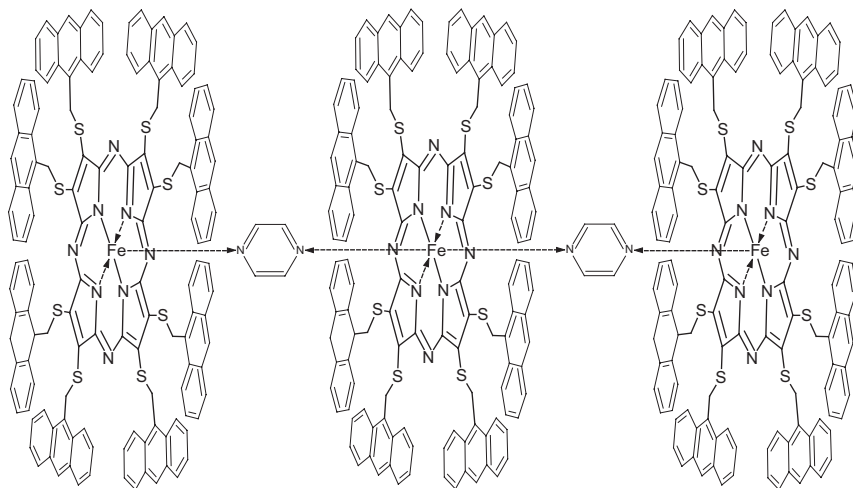


Fig. 2  $\mu$ -Pyrazine[octakis(9-anthracenylmethylthio)porphyrinato]iron(II) [FePz(pyz)]<sub>n</sub> (4).

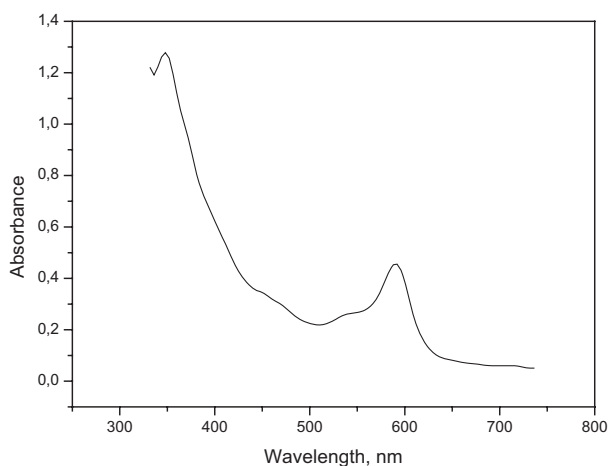


Fig. 3 UV-Vis spectrum of **3** in chloroform.

pyridine and pyrazine ligands to the metal ion. Consequently, we might conclude that the Fe(II)Pz macro-cycle reacts in excess liquid pyrazine to form exclusively a polymeric compound as is the case for most tetraaza-annulenes.

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