The first structural studies of nitrosoarene binding to iron-(II) and -(III) porphyrins

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The nitrosoarene ligands in ferrous [Fe^{II}(tpp)(PhNO)$_2$] are bound through their nitrogen atoms, whereas they are bound through their oxygen atoms in ferric [Fe^{III}(tpp)(Et$_2$NC$_6$H$_4$NO)$_2$]SbF$_6$.

It has been known for a long time that PhNO and some of its substituted analogues bind to haemoglobin (Hb).[1,2] Indeed, PhNO binding to Hb has long been associated with PhNO$_2$ poisoning.[1c] It has also been proposed that nitrosoalkane monomers bind to cytochrome P450 during the oxidative metabolism of amphetamine, phenylalkylamines, and *N*-hydroxyamphetamine, or during the reduction of nitroamphetamine.[3,4]

Furthermore, primary and secondary aliphatic nitro compounds react with Mb, Hb and cytochrome P450 under reducing conditions to produce iron(II)–nitrosoalkane complexes.[5] Although there is ample precedent for the existence of nitrosoalkane and nitrosoarene complexes of haems, there were no structurally characterized nitrosoarene complexes of metalloporphyrins prior to this study. We now wish to report the first isolation and structural characterization of nitrosoarene complexes of iron porphyrins. In addition, our structural studies show distinct η^1 nitroso-N binding to Fe^{II} and unprecedented η^1 nitroso-O binding to Fe^{III}.

Reaction of [Fe^{II}(tpp)] with an excess of PhNO in CH$_2$Cl$_2$ generates diamagnetic [Fe^{II}(tpp)(PhNO)$_2$] **1** which was isolated in 50% yield by precipitation with hexane.†‡ The $\nu_{N=O}$ of the coordinated PhNO is at 1353 cm^{-1} (KBr) in a region that is commonly associated with η^1 nitroso-N binding.[6] Interestingly, **1** is also obtained in 91% yield from the reaction of [Fe^{III}(tpp)(SC$_6$F$_4$H)]·0.5PhMe with excess PhNO in CH$_2$Cl$_2$ followed by precipitation with hexane. Our attempts to obtain the *ferric* [Fe^{III}(tpp)(PhNO)$_2$]$^+$ analogue were unsuccessful. However, the use of *para*-dialkylamino substituted nitrosoarenes provided a convenient entry into the desired ferric compounds. Thus, reaction of [Fe^{III}(tpp)(thf)$_2$]SbF$_6$·thf with an excess of R$_2$NC$_6$H$_4$NO in CH$_2$Cl$_2$ generates the [Fe^{III}(tpp)(R$_2$NC$_6$H$_4$NO)$_2$]SbF$_6$ compounds (R = Me **2** or Et **3**) in 66 and 83% yields, respectively.§¶ The IR spectrum of paramagnetic **2** reveals medium bands at 1364 and 1336 cm^{-1} (KBr) that are characteristic of the nitrosoaniline and are usually assigned as NO and C–N stretches, respectively.[7] Employing O^{15}NC$_6$H$_4$NMe$_2$ in the above reaction resulted in these bands being shifted to lower wavenumbers (1359 and 1323 cm^{-1}). The IR spectrum also shows a strong band at 657 cm^{-1} due to uncoordinated SbF$_6^-$.

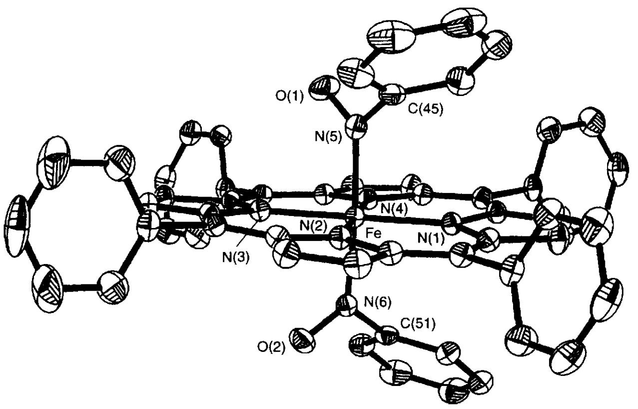


Fig. 1 Molecular structure of **1**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Fe–N(1) 2.003(2), Fe–N(2) 1.994(2), Fe–N(3) 1.995(2), Fe–N(4) 1.998(2), Fe–N(5) 1.874(2), N(5)–O(1) 1.237(3), Fe–N(6) 1.899(2), N(6)–O(2) 1.227(3); Fe–N(5)–O(1) 123.6(2), Fe–N(6)–O(2) 123.4(2).

The molecular structures of ferrous **1** and the ferric cation of **3** are shown in Fig. 1 and 2,‖ respectively. As can be seen in Fig. 1, the PhNO ligands in **1** are distinctly η^1 nitroso-N bound,** and the PhN–O–Fe–O–NPh torsion angle of *ca.* 90° suggests an orientation of the PhNO ligands in which the overlap of the HOMO of the d^6 low-spin Fe^{II}(tpp) fragment (namely the filled degenerate d$_{xz}$ and d$_{yz}$ orbitals)[8] and the π^* orbitals of the PhNO ligands are maximized. The average Fe–N(porphyrin) bond length of 1.998(2) Å is consistent with that expected for a low-

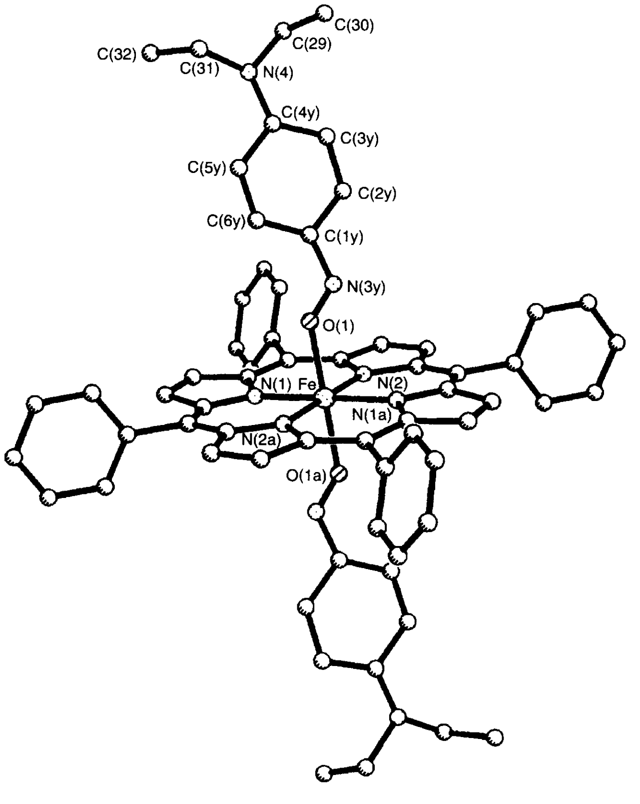
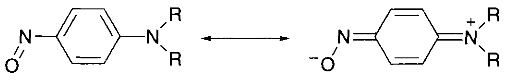


Fig. 2 Molecular structure of the cation of **3**. Hydrogen atoms have been omitted for clarity. Only one of the two disordered positions of the phenyl ring and the N(3) atom is shown (see text). Selected bond distances (Å) and angles (°): Fe–N(1) 2.010(3), Fe–N(2) 2.006(3), Fe–O(1) 1.950(3), O(1)–N(3y) 1.157(6), N(3y)–C(1y) 1.323(11), C(4y)–N(4) 1.35(2); N(3y)–O(1)–Fe 127.7(3), O(1)–N(3y)–C(1y) 118.7(7), C(4y)–N(4)–C(31) 134.5(7), C(4y)–N(4)–C(29) 109.5(8), C(31)–N(4)–C(29) 116.0(4).

spin d^6 Fe^{II} centre.[8] In contrast, the structure of **3** reveals a distinct η^1 nitroso-O binding of the nitrosoarene ligands to the cationic Fe^{III} centre (Fig. 2). Importantly, this is the *first* time that sole η^1 nitroso-O binding of RNO ligands has ever been observed in non-d^{10} transition-metal chemistry.[6,7] In the cation, the phenyl ring and the N(3) atom of the *N,N*-diethyl-4-nitrosoaniline are disordered at two sites. Due to the nature of this disorder we are cautious not to over-interpret specific bond lengths and angles in **3**.†† The average Fe–N(porphyrin) bond length of 2.008(3) Å is shorter than that normally associated with a high-spin Fe^{III} centre [2.045(8)], but is longer than that for an intermediate spin state [1.995(3)].[8] The nitrosoaniline moiety is essentially planar with a O(1)–N(3y)–C(1y)–C(2y) torsion angle of 176.8°, and the amido nitrogen N(4) is also essentially planar with the sum of angles around it being 360°.

We recently reported[9] the structure of the bis(diethylnitrosamine) complex $[Fe^{III}(tpp)(Et_2NNO)_2]ClO_4$ in which the nitrosamine ligands appear to have a contribution from a dipolar structure that places a substantial negative charge on the nitroso oxygens. Indeed, a similar dipolar structure may be a determining factor in the case of **3**, where the resonance form on the right plays a role in stabilizing η^1 nitroso-O binding to the cationic iron(III) porphyrin. The planarity of the amido nitrogen in the complex is consistent with this view.



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Footnotes

† All three compounds give satisfactory elemental analyses for C, H, N and Cl.

‡ *Spectroscopic data* for **1**: ^1H NMR (C_6D_6): δ 8.91 (s, 8 H, pyr-H), 8.11 (m, 8 H, *o*-H of tpp), 7.48 (m, 12 H, *m*/*p*-H of tpp), 6.49 (m, 2 H, *p*-H of PhNO), 6.19 (m, 4 H, *m*-H of PhNO), 4.98 (m, 4 H, *o*-H of PhNO). Low-resolution mass spectrum (FAB+): *m*/*z* 668 $[Fe(tpp)]^+$ 100%. EI mass spectrum (DIP, 70 eV): *m*/*z* 107 $[C_6H_5NO]^+$ 47%; 77 $[C_6H_5]^+$ 100%.

§ *Spectroscopic data* for **2**: Low-resolution mass spectrum (FAB+): *m*/*z* 668 $[Fe(tpp)]^+$ 100%, 151 $[ONC_6H_4NMe_2 + H]^+$ 70%. μ_{eff} (C_6D_6) = 6.1 μ_B. IR of coordinated $ONC_6H_4NMe_2$ ligand: 1606s, 1557w, 1441w, 1397w, 1364m, 1336m, 1304m, 1226w(sh), 1151s, 1120s, 1073m, 939w(sh), 836m, 723m, 634m(sh), 605w(sh) cm^{-1}.

¶ *Spectroscopic data* for **3**·$0.3CH_2Cl_2$: Low-resolution mass spectrum (FAB+): *m*/*z* 668 $[Fe(tpp)]^+$ 100%; 179 $[ONC_6H_4NEt_2 + H]^+$ 86%; 178 $[ONC_6H_4NEt_2]^+$ 47%. μ_{eff} (C_6D_6) = 6.0 μ_B. IR of coordinated $ONC_6H_4NEt_2$ ligand: 1614(sh), 1602s, 1548m, 1441m, 1421m, 1381w, 1370vw, 1331s, 1304s, 1281m(sh), 1189s, 1148vs, 1121m, 1072s, 1005m, 835m, 716m, 632m, 606m, 497w cm^{-1}.

‖ Crystal data for the two compounds were collected on a Siemens P4 diffractometer with Mo-Kα radiation (λ = 0.71073 Å). The structures were solved using the SHELXTL (Siemens) system and refined by full-matrix least squares on F^2 using all reflections (SHELXL-93). The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied.

Crystal data for **1**·$2CH_2Cl_2$: $C_{58}H_{42}Cl_4FeN_6O_2$, M = 1052.63, triclinic, space group $P\bar{1}$, a = 13.113(4), b = 14.584(2), c = 15.614(2) Å, α = 65.050(10), β = 68.05(2), γ = 73.410(10)°, U = 2481.9(9) $Å^3$, Z = 2, D_c = 1.409 g cm^{-3}, T = 173(2) K. Final $R1$ = 0.0469 ($wR2$ = 0.1164, GOF = 1.034) for 8470 'observed' reflections with $I \geqslant 2\sigma(I)$.

For **3**·$2CH_2Cl_2$: $C_{66}H_{60}Cl_4F_6FeN_8O_2Sb$, M = 1430.62, monoclinic, space group $C2/c$, a = 19.916(4), b = 15.021(3), c = 22.899(5) Å, β = 108.43(3)°, U = 6499(2) $Å^3$, Z = 4, D_c = 1.462 g cm^{-3}, T = 213(2) K. Final $R1$ = 0.0572 ($wR2$ = 0.1518, GOF = 1.021) for 6665 'observed' reflections with $I \geqslant 2\sigma(I)$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

** The structure of the nitrosoalkane complex $[Fe^{II}(tpp)(Pr^iNO)(Pr^iNM_2)]$ also reveals N-binding of the nitrosoalkane (ref. 10); ArNO complexes of iron phthalocyanine (ref. 11) and ruthenium porphyrins (ref. 12) have been reported.

†† For example, both the O(1)–N(3y) and N(3y)–C(1y) measured bond lengths in **3** are shorter than those previously determined for the free ligand (which was also disordered), and the N(4)–C(4y) bond length appears essentially unaffected by coordination of the ligand: H. J. Talberg, *Acta Chem. Scand. Ser. A*, 1977, **31**, 743.

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