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The first unambiguous determination of a nitrosyl-to-nitrite conversion in an iron nitrosyl porphyrin

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The picket fence porphyrin complex [Fe(tpivpp)(NO)] undergoes complete conversion to the isolable *N*-bound nitrite derivative [Fe(tpivpp)(NO_2)(py)] in air in the presence of pyridine: reconversion to the starting nitrosyl complex is achieved using triphenylphosphine as reductant.

The study of the reactions of nitric oxide ligands in iron nitrosyl porphyrins is receiving increased attention in bioinorganic chemistry.[1] This is due, in part, to a need to understand the fate of the NO group after it binds to the metal center in heme biomolecules and related model complexes, and to elucidate the chemical processes involved in the conversion of the coordinated NO group to nitrite. There are very interesting results in the literature regarding the formation of coordinated NO_2 groups in iron porphyrins.† For example, Scheidt and coworkers have prepared and structurally characterized a series of [Fe(por)(NO)(NO_2)] complexes by the reaction of $[Fe(por)]_2O$ or [Fe(tpivpp)(NO)] with an excess of NO,[2] and they have proposed the intermediacy of reactive nitrite compounds during the formation of nitrate [Fe(por)(NO_3)] products (por = tpivpp, oep, tpp, ttp) from their nitrosyl precursors.[3,4] Ford and Lorkovic have demonstrated that NO_2 (N_2O_3; derived from reaction of NO gas with trace oxygen) reacts with [Fe(tpp)(NO)] to give [Fe(tpp)(NO)(NO_2)].[5]

Surprisingly, and although it is of fundamental interest in heme–NO chemistry, no direct chemical evidence has been reported on the straightforward conversion of the coordinated NO group in an iron nitrosyl porphyrin to an isolable nitrite complex.‡ We now produce the first unambiguous experimental evidence that the [Fe(tpivpp)(NO)] compound converts to the [Fe(tpivpp)(NO_2)(py)] derivative in air and in the absence of added NO.

The X-ray structure of [Fe(tpivpp)(NO)] is shown in Fig. 1.§¶ Reaction of this compound in $CHCl_3$ with air in the presence of pyridine results in its complete conversion to [Fe(tpivpp)(NO_2)(py)]‖** within 1 h as judged by IR spectroscopy of KBr pellets of dried aliquots.†† When the reaction of [Fe(tpivpp)(NO)] (20–50 mg, 0.018–0.040 mmol) with air and pyridine is performed in a $CHCl_3$–heptane mixture, and the solvent allowed to evaporate over a 3 d period, needle-shaped crystals of the [Fe(tpivpp)(NO_2)(py)]·py product were obtained in 70–80% isolated yields. The observed Fe–NO_2 distances of 1.92–1.97 Å in the [Fe(tpivpp)(NO_2)(py)] products are longer than the axial Fe–NO distance in the precursor [Fe(tpivpp)(NO)] complex (1.65–1.74 Å), and the nitrite O-atoms point towards the HN groups of the picket fence (O···N distances of 3.7–3.8 Å) suggesting possible stabilization of the bound nitrite through weak H-bonding interactions.

The added base is essential for the generation of the stable ferric nitrite derivative, since the reaction of [Fe(tpivpp)(NO)] with air in $CHCl_3$ solution (without added pyridine) results in its quantitative conversion to the known ferric chloro [Fe(tpivpp)(Cl)] complex (λ_{max} = 417 nm).[12,13] We have found that this latter reaction is also enhanced by UV–VIS light (*e.g.* when monitoring the reaction by UV–VIS spectroscopy). We have also confirmed an earlier observation that air oxidation of the non-picket fence [Fe(por)(NO)] compounds (por = tpp, ttp, oep) results in the isolation of the $[Fe(por)]_2O$ oxo dimers,[4] suggesting that the picket fence pocket is indeed crucial for the stabilization of the singly-oxidized nitrite product.

Deoxygenation of the coordinated nitrite to nitrosyl in this picket fence [Fe(tpivpp)(NO_2)(py)] complex in $CHCl_3$ (under a nitrogen atmosphere) is achieved by the addition of triphenylphosphine. The reaction is complete within 15 min, and the five-coordinate nitrosyl [Fe(tpivpp)(NO)] complex is obtained in 80% isolated yield, with triphenylphosphine oxide as the oxidized product. The overall reaction is shown in eqn. (1):

$$[\mathrm{Fe(tpivpp)(NO)}] \underset{\substack{\mathrm{PPh_3} \\ (-\,\mathrm{OPPh_3})}}{\overset{\text{air, py}}{\rightleftarrows}} [\mathrm{Fe(tpivpp)(NO_2)(py)}] \tag{1}$$

The conversion of coordinated nitrite to nitrosyl has precedent in iron porphyrin chemistry. For example, (i) the anionic bisnitro $[Fe(tpivpp)(NO_2)_2]^-$ complex undergoes rearrangement in the presence of boron trifluoride to [Fe(tpivpp)(ONO_2)] and [Fe(tpivpp)(NO)] in some organic solvents,[3] and (ii) oxygen-atom transfer to organic compounds by the [Fe(oep)Cl]/nitrite mixture is believed to occur *via* the intermediacy of '[Fe(oep)(NO_2)]', although this intermediate was not unambiguously identified.[14]

The observation of this base-assisted stabilization of an iron-bound nitrite product derived from its nitrosyl precursor has implications for the reactivity of the bound NO group in nitrosyl heme proteins containing *trans* axial N-bases, and suggests that

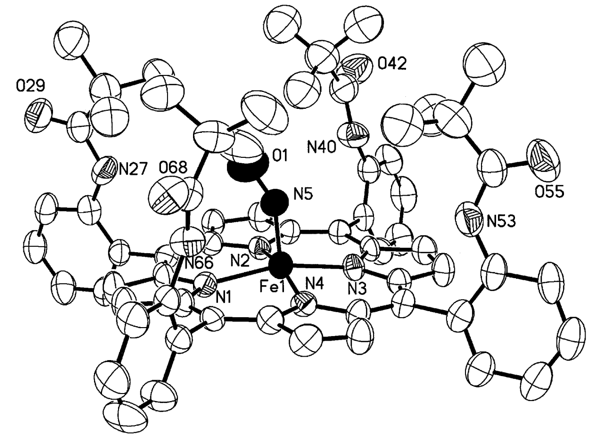

Fig. 1 Molecular structure of [Fe(tpivpp)(NO)]. The nitrosyl group is disordered over two positions, and only one of these positions is shown. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Fe(1)–N(por) 1.991(5)–2.007(5), Fe(1)–N(5) 1.65(5), Fe(1)–N(5′) 1.74(6), N(5)–O(1) 1.17(5), N(5′)–O(1′) 1.20(7); Fe(1)–N(5)–O(1) 149(4), Fe(1)–N(5′)–O(1′) 137(4).

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iron-bound nitrite could be one of several products or intermediates in some heme–NO ligand oxidations.

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Notes and references

† *Abbreviations*: por = porphyrinato dianion, tpivpp = 'picket fence' tetra(α,α,α,α-*o*-pivalamidophenyl)porphyrinato dianion, oep = octaethylporphyrinato dianion, tpp = tetraphenylporphyrinato dianion, ttp = tetratolylporphyrinato dianion.

‡ Related conversions of cobalt[6] and rhodium[7] nitrosyl porphyrins to nitrite derivatives have been reported.

§ Crystal data for [Fe(tpivpp)(NO)] were collected on a Bruker (Siemens) SMART/CCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods using the SHELXTL system and refined by full-matrix least squares on F^2. *Crystal data*: $C_{64}H_{64}FeN_9O_5$, M = 1095.09, monoclinic, space group $P2_1/n$, a = 17.7905(14), b = 17.6238(13), c = 20.2731(16) Å, β = 99.390(2)°, V = 5913.3(8) Å^3, Z = 4, D_c = 1.230 g cm^{-3}, T = 158(2) K, absorption coefficient = 0.311 mm^{-1}, 7705 independent reflections (R_{int} = 0.0758). Final R (F obs. data) = 0.0709 for 4338 'observed' reflections with [$I > 4\sigma(I)$].

CCDC 182/1820. See http://www.rsc.org/suppdata/cc/b0/b006775j/ for crystallographic files in .cif format.

¶ The X-ray structure of the related [Fe(tpivpp)(NO)][K(NO_2)(18-crown-6)] has been reported.[8] The [Fe(por)(NO)] compounds are commonly referred to as ferrous nitrosyls.[1]

‖ This compound was initially prepared from the reaction of the anionic bis-nitro [Fe(tpivpp)$(NO_2)_2$]$^-$ complex with pyridine.[9]

** We have obtained three solid-state X-ray structures of this [Fe(tpivpp)(NO_2)(py)]·solvate product from these reactions that differ in the nature of the solvate (pyridine, chloroform or dichloromethane). These structures are available in the above .cif file, and are similar to the previously reported structure of [Fe(tpivpp)(NO_2)(py)]·PhCl.[9] The structure of the anionic five-coordinate [Fe(tpivpp)(NO_2)]$^-$ compound is known.[10] Anionic iron porphyrin nitrites also have rich electrochemistry.[11]

†† KBr pellets were used to observe the ν_{NO} (1675 cm^{-1}) and $\nu_{\mathrm{NO_2}}$ (1307 cm^{-1}) bands. These bands were confirmed by the use of the ^{15}N-labeled [Fe(tpivpp)(^{15}NO)] ($\lambda_{\max}$ = 409 nm) precursor: $\nu_{^{15}\mathrm{NO}}$ of 1641 cm^{-1} for the nitrosyl complex, and $\nu_{^{15}\mathrm{NO_2}}$ 1289 cm^{-1} for the nitrite derivative. We have not been able to determine the position of the second $\nu_{\mathrm{NO_2}}$ band owing to extensive overlap with the porphyrin bands. Also, the UV–VIS spectrum of [Fe(tpivpp)(NO_2)(py)] ($\lambda_{\max}$ = 419 nm) is very similar to that of the six-coordinate nitrosyl [Fe(tpivpp)(NO)(py)] complex ($\lambda_{\max}$ = 419 nm), making the monitoring of the reaction by UV-VIS spectroscopy very difficult.

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