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Reactions of nitrogen oxides with heme models. Low temperature spectral characterization of the unstable nitrato-nitrosyl complex $Fe^{III}(TPP)(ONO_2)(NO)$†

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Reaction of NO gas with low temperature films of the η^2-nitrato model heme $Fe^{III}(TPP)(O_2NO)$ (TPP = *meso*-tetraphenylporphyrinato^{2-}) leads to formation of the previously unknown η^1-nitrato nitrosyl species $Fe^{III}(TPP)(ONO_2)(NO)$ as characterized by IR and optical spectroscopy with isotopically substituted nitrogen oxides.

The interaction of the nitrogen oxides NO_x with metalloporphyrins, especially with heme models, has drawn considerable attention owing to the potential relevance of such reactions to mammalian biochemistry.[1,2] Numerous ferro- and ferri-heme complexes with NO and NO_2 have been characterized, but nitrato complexes are quite rare.[3] In this context, we report the use of low temperature spectroscopy of sublimed layers to characterize the previously unknown nitrato nitrosyl complex $Fe(TPP)(ONO_2)(NO)$ and to study the subsequent reactions of this unstable species.

Low temperature sublimates of Fe(TPP) on KBr or CaF_2 substrate were prepared from $Fe(TPP)(B)_2$ (B = pyridine or piperidine) as previously described.[4] Such M(TPP) layers obtained by sublimation onto a low-temperature (77 K) surface are sponge-like and have high microporosity.[5] Potential reactants easily diffuse across these layers, and adducts thus formed can be studied spectroscopically without solvent interference.

A Fe(TPP) sublimed layer was heated to room temperature under dynamic vacuum, then NO_2 gas[6] was introduced, and the sample was cooled to 80 K to record the spectra. As shown previously,[7] this procedure leads to the formation of the η^2-nitrato complex $Fe(TPP)(O_2NO)$ (eqn. 1)

$$Fe(TPP) + 2\ NO_2 \rightarrow Fe(TPP)(O_2NO) + NO \qquad (1)$$

which was characterized by its known IR spectrum displaying coordinated NO_3^- bands at 1531 and 1275 cm^{-1} (Fig. 1, dashed line). Gaseous ^{15}NO was introduced and the system was warmed to 160 K then cooled to 80 K. The resulting product displayed new bands at 1863, 1505, 1266, 978 and 542 cm^{-1}. If instead, ^{14}NO was used, these appeared at 1901, 1505, 1266, 978 and 548 cm^{-1} (Figs. 1 and 2). Reaction of ^{15}NO with a film containing $Fe(TPP)(^{15}NO_3)$ gives the analogous bands at 1863, 1470, 1248, 963 and 542 cm^{-1} (see Table 1 and ESI, Fig. S1†). The intensities of these bands correlate and clearly indicate the formation of a new nitrato nitrosyl complex from the reaction of NO with $Fe(TPP)(O_2NO)$.

The isotopic shifts in the bands summarized in Table 1 demonstrate that the 1901 and 548 cm^{-1} bands for the product of $Fe(TPP)(O_2{}^{14}NO)$ plus ^{14}NO are associated with the nitrosyl while those at 1505, 1266 and 978 cm^{-1} are associated with the nitrato ligand. The 1901 cm^{-1} band with a ^{15}N isotopic shift of about -40 cm^{-1} can be assigned to NO stretching vibration of coordinated nitrosyl in analogy to linear FeNO units of other $\{FeNO\}^6$ complexes[8] (using the notation of Enemark and Feltham).[9] The band at 548 cm^{-1} that is shifted to 542 cm^{-1} with ^{15}NO can be assigned to the iron–nitrogen stretch $\nu\{Fe–N(NO)\}$.

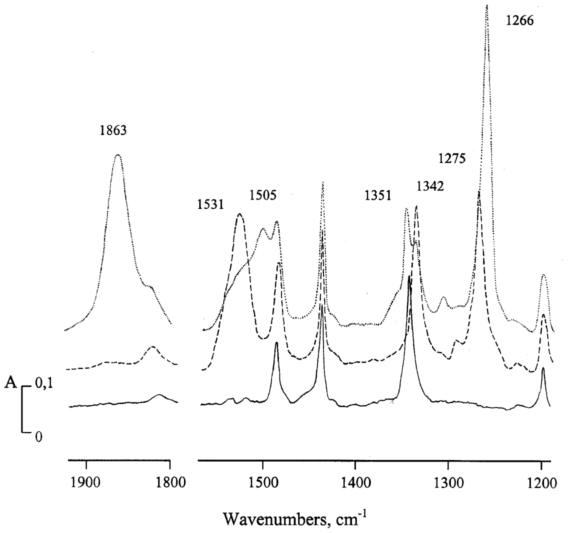

Fig. 1 IR spectra of Fe(TPP) derivatives in sublimed layers at 80 K: (a) Fe(TPP) (solid line), (b) $Fe(TPP)(O_2NO)$ formed by exposure of Fe(TPP) to NO_2 (P = 1 Torr) for 10 min at 293 K followed by exhaustive high vacuum pumping (dashed line), (c) $Fe(TPP)(O_2NO)(^{15}NO)$ formed by supplying ^{15}NO (10 Torr) to (b) at 80 K, warming to 160 K and re-cooling (dotted line).

The IR spectrum of the related nitro-nitrosyl complex $Fe(TPP)(NO_2)(NO)$ (in chloroform) was reported to display a comparable band at 549 cm^{-1} with an isotopic shift of 6 cm^{-1}.[10]

In $Fe(TPP)(O_2NO)$ the nitrate ligand is bound in a slightly asymmetric bidentate mode.[11] The Fe(III) is d^5 high-spin and

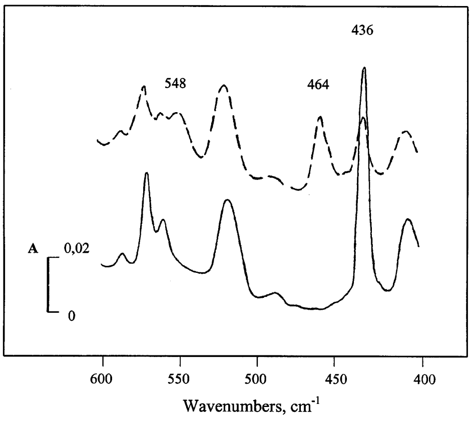

Fig. 2 Low frequency IR spectra at T = 80 K of thin layers containing $Fe(TPP)(O_2NO)$ (solid line) and $(NO)Fe(TPP)(ONO_2)$ (dashed line).

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† Electronic supplementary information (ESI) available: IR and UV-Visible spectra of **A**. See http://www.rsc.org/suppdata/cc/b3/b302061d/

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Table 1 IR spectral data (in cm^{-1}) of nitrosyl and nitrate groups for: **I** – Fe(TPP)(O^{14}NO$_2$)(^{14}NO); **II** – Fe(TPP)(O^{14}NO$_2$)(^{15}NO); **III** – Fe(TPP)(O^{15}NO$_2$)(^{14}NO); **IV** – Fe(TPP)(O^{15}NO$_2$) (^{15}NO)

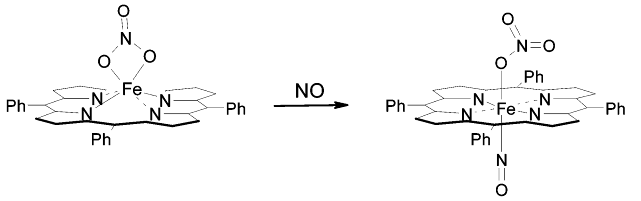
I	II	III	IV	Assignment
1901 s	1862 s	1901 s	1863 s	ν(N=O)
1505 m	1505 m	1470 m	1470 m	ν_a(NO$_2$)
1266 s	1266 s	1247 s	1248 s	ν_s(NO$_2$)
978 w	978 w	963 w	963 w	ν(N–O)
548 vw	542 vw	548 vw	542 vw	ν{Fe–N(NO)}

reveals a large out-of-plane displacement (0.6 Å) toward the lone axial ligand. The η^2-nitrate ligand would be expected to show three IR active stretching modes for such a structure, a high frequency ν(N=O) stretch for the uncoordinated oxygen plus symmetric and asymmetric modes for the coordinated NO$_2$ fragment. However, only two bands at 1531 and 1275 cm^{-1} of compatible intensities are seen (Fig. 1, dashed line)[7,11] so one of the expected bands, perhaps the symmetric ν_s(NO$_2$) mode, is too weak to be observed or is masked by porphyrin absorptions. Upon adding NO to Fe(TPP)(O$_2$NO), these bands shift to lower frequencies by 26 and 9 cm^{-1}, respectively (Fig. 1, dotted line). More importantly, the relative intensities change, with the high frequency band diminishing and the lower frequency one becoming much stronger. In addition a new isotopically sensitive band appears at ~980 cm^{-1}.

These IR spectra changes can be interpreted in terms of the bidentate–monodentate transition of nitrate coordination illustrated by Scheme 1. The highest frequency nitrato band now represents ν_a(NO$_2$), while that in the vicinity of 1250 cm^{-1} is assigned to ν_s(NO$_2$). The previously described η^1-nitrato complex Fe(OEP)(ONO$_2$) (OEP = octaethylporphyrinato^{2-}) displays an IR band for the coordinated nitrate at 1515 cm^{-1} (KBr pellet)[12] similar to the high frequency nitrato band seen here. Closer disposition of the high frequency bands is considered as a criterion of monodentate coordination in nitrate complexes.[13] The weak band at 980 cm^{-1} can be assigned to the N–O vibration for the O atom coordinated to the Fe(III) ion.[13] Thus, as indicated by Scheme 1, we conclude that the product of the reaction of NO with Fe(TPP)(O$_2$NO) is the η^1-nitrato nitrosyl complex Fe(TPP)(ONO$_2$)(NO) (**A**).

Additional information regarding the nature of **A** can be drawn from porphyrin vibrational modes that reveal regular changes depending on the spin and oxidation state of axial complexes of Fe(TPP).[14] It has been found that the band in vicinity of 1350 cm^{-1} representing a porphyrin core mode corresponding to ν(C$_a$–C$_m$) mixed with some ν(C$_m$–phenyl) lies at higher frequencies in low-spin complexes. The same character demonstrates a low energy porphyrin core deformation mode in the range 450 cm^{-1}. For the high spin η^2-nitrato complex Fe(TPP)(O$_2$NO), these bands lie at 1342 and 436 cm^{-1}. Upon additional coordination of NO these bands shift to 1351 and 464 cm^{-1} (see Figs. 1 and 2) indicating a low-spin state for the new complex. This result is consistent with other 6-coordinate ferri-heme nitrosyl complexes in which the iron is located close to the center of the porphyrin plane and the electronic state is low-spin.[3]

Electronic absorption spectra (ESI, Fig. S2†) confirm formation of the new complex upon reaction of NO with low-temperature films of Fe(TPP)(O$_2$NO). The bands of the nitrato complex at 423, 511 and 572 nm are significantly shifted to longer wavelengths and disposed at 436, 547 and 582 nm in **A**. This is analogous to other mixed nitrogen oxide complexes of Fe(III)(P) (P = porphyrin); for example, the spectrum of the nitro nitrosyl complex Fe(TPP)(NO$_2$)(NO) displays maxima at 433, 545 and 577 nm in chloroform solution.[10]



Scheme 1

To our knowledge, the only six-coordinate nitrato Fe(P) complex described previously is a *trans* η^1-nitrato aquo complex (Fe(P)(ONO$_2$)(H$_2$O)) (P not identified) in an unpublished study reported in a review by Wyllie and Scheidt.[3] It seems likely that formation of six-coordinate complexes containing the nitrato ligand will be accompanied by bidentate–monodentate transition to alleviate nonbonded repulsions between nitrate oxygens and porphyrin nitrogens. This process should not require the large expenditure of energy as evidenced from the existence of monodentate and bidentate binding in the iron porphyrins Fe(OEP)(ONO$_2$) and Fe(TPP)(O$_2$NO) differing only in the nature of peripheral substituents.[3]

The nitrato nitrosyl complex spectrally characterized here decomposes under ambient conditions, and the nature of the products formed depends on whether this occurs under an NO atmosphere. In the absence of NO it returns to the nitrato complex Fe(TPP)(O$_2$NO), while under NO a series of chemical transformations occur that is now under investigation.

In summary, the low temperature interaction of NO gas with thin films of Fe(TPP)(O$_2$NO) leads to formation of a new six-coordinate complex that is formulated as Fe(TPP)(ONO$_2$)(NO) based on the IR and UV-Vis data. This reaction is accompanied by bidentate–monodentate isomerization of coordinated nitrate and transition of Fe(III) ion from high-spin to low-spin. The complex formed is stable at low temperatures but upon warming undergoes further transformations to products apparently dependent on the presence of an NO atmosphere.

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6 The NO$_2$ (^{15}NO$_2$) used in these studies was obtained by O$_2$ oxidation of NO (^{15}NO) and was purified by fractional distillation until a pure white solid was obtained. The NO (^{15}NO) used was purified by passage through KOH pellets and a dry ice/acetone cooled trap to remove higher NO$_x$ and trace H$_2$O. The purity was checked by IR measurements of the layer obtained by low rate deposition of NO on the cooled substrate of an optical cryostat (77 K). The IR spectra did not show the presence of N$_2$O, N$_2$O$_3$ or H$_2$O.

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