

## First Observation of Photoinduced Nitrosyl Linkage Isomers of Iron Nitrosyl Porphyrins

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Knowledge of the binding modes of nitric oxide (NO) to synthetic iron porphyrins is essential to an overall understanding of the action of NO-heme-containing biomolecules, which play a crucial role in several biologically important processes.<sup>1</sup> While much is known about the biological effects of NO, the detailed mechanism of NO uptake and release by the heme group remains to be elucidated. Kinetic studies of photochemically induced loss and recombination of NO with hemoproteins<sup>2,3</sup> and metalloporphyrins<sup>4,5</sup> suggest that recombination after photolysis is a fast and multistage process at room temperature.<sup>6–8</sup>

Known geometries of FeNO linkages in iron porphyrins and heme have, to date, been limited to the Fe–N–O arrangement in linear or bent forms.<sup>9</sup> In general, iron nitrosyl porphyrins of the “ferric” {FeNO}<sup>6</sup> formulation have linear Fe–N–O groups, whereas those of the “ferrous” {FeNO}<sup>7</sup> formulation have bent Fe–N–O groups. We have recently reported that photoexcitation of {RuNO}<sup>6</sup> ruthenium nitrosyl porphyrins results in the formation of metastable O-bound ( $\eta^1$ -O; MS1) and side-on ( $\eta^2$ -N,O; MS2) bound linkage isomers.<sup>10</sup> We now report that metastable NO linkage isomers of {FeNO}<sup>7</sup> iron nitrosyl porphyrins are generated upon illumination with light of  $350 < \lambda < 550$  nm wavelength (300 W xenon arc lamp). While NO linkage isomers have been observed for {MNO}<sup>6</sup> (M = Fe, Ru, Os)<sup>11–14</sup> and for {MNO}<sup>10</sup>

complexes (M = Ni),<sup>15</sup> this is also the first observation of photoinduced nitrosyl linkage isomerism for a bent nitrosyl {MNO}<sup>7</sup> complex of any metal.

Irradiation of the Fe(por)(NO) compounds<sup>16</sup> (as KBr pellets) at 25 K for 5–10 min results in the formation of new bands in their IR spectra, downshifted from the parent NO stretching frequencies. The observed frequencies of the photoinduced bands for the <sup>14</sup>N<sup>16</sup>O, <sup>15</sup>N<sup>16</sup>O and <sup>15</sup>N<sup>18</sup>O complexes of Fe(OEP) and Fe(TTP) and their relative shifts are listed in the Supporting Information. Warming the samples to 40 K results in the disappearance of all new bands and the restoration of the intensities of the parent  $\nu_{\text{NO}}$  bands. No free NO was observed in the photolysis experiments.

In the case of Fe(TTP)(NO), photolysis at 25 K for 10 min results in the appearance of a new band at 1532 cm<sup>-1</sup> in the difference IR spectrum (**A** in Figure 1, left), downshifted by ~140 cm<sup>-1</sup>. Measurements on isotope-labeled Fe(TTP)(<sup>15</sup>N<sup>16</sup>O) and Fe(TTP)(<sup>15</sup>N<sup>18</sup>O) show the band to be due to the coordinated NO group (Figure 1; Table S1 of the Supporting Information). A second, much weaker, photoinduced band at 1502 cm<sup>-1</sup> does not change on isotopic substitution (Figure 1, left), and is hence assigned as originating from another part of the complex. Because of the rapid decay of the photoinduced IR features, samples were irradiated continuously during the spectral measurements.

A similar IR band (**A** in Figure 1, right) is generated when Fe(OEP)(NO) is irradiated under the same conditions. The use of the <sup>15</sup>N<sup>16</sup>O and <sup>15</sup>N<sup>18</sup>O isotope labels again reveals the band to be due to the coordinated NO group. However, a second new IR band at 1520 cm<sup>-1</sup> (labeled **B**) is also induced, together with an isotope-substitution insensitive band at 1506 cm<sup>-1</sup> (Figure 1, right). While both the **A** and **B** bands decay at 25 K, the decay of the **B** band is much slower, suggesting the formation of two distinct photoproducts. The isotopic shifts of the IR bands are as expected for Fe(OEP)(<sup>15</sup>N<sup>16</sup>O) and its photoproducts, and for the Fe(OEP)(<sup>15</sup>N<sup>18</sup>O) derivative and its **A** photoproduct. The **B** band of photolyzed Fe(OEP)(<sup>15</sup>N<sup>18</sup>O) appears as a doublet and the shift of ~95 cm<sup>-1</sup> is larger than the expected value of ~68 cm<sup>-1</sup>. Vibrational coupling of this low-frequency band with other modes of the complex may be responsible for the latter observation. Conversion percentages are estimated at 6–10% for Fe(OEP)(NO), and 2–3% for Fe(TTP)(NO).

The observed shifts of  $\nu_{\text{NO}}$  for the Fe(por)(NO) photoproducts are very similar to those recorded for other non-porphyrin Fe and Ru complexes for which the identity of the photoinduced species have been established by photocrystallographic experiments.<sup>11–14</sup> The IR data thus suggests the formation of an MS1 ( $\eta^1$ -ON) isomer upon irradiation. This assignment is supported by the DFT calculations.

A series of theoretical calculations was performed on FeP'(NO) (P' = porphine dianion) with the Amsterdam Density Functional (ADF) package.<sup>17,18</sup>

The ground-state optimization of FeP'(NO) reproduces the structural distortions of the N<sub>4</sub>Fe(NO) core recently observed by

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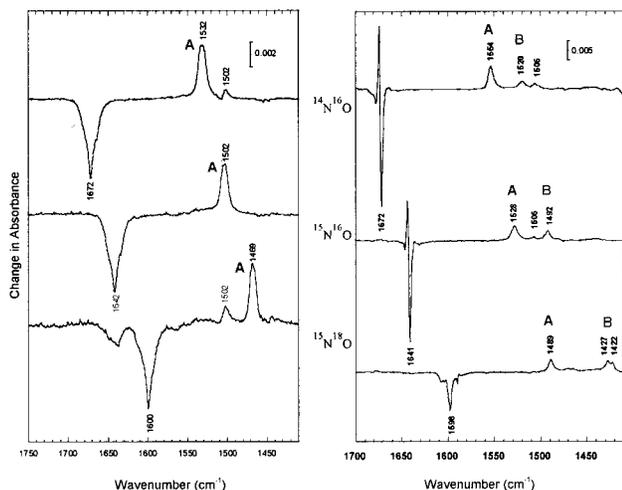
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**Figure 1.** Infrared difference spectra formed by subtracting the spectra of the complex after illumination (at 25 K) from the infrared spectra of the complex in the dark. (Left) Fe(TTP)(NO); (right) Fe(OEP)(NO). Negative and positive features represent IR bands that are depleted, or new or increased in intensity upon illumination, respectively. The differential feature of the highest frequency band of Fe(OEP)(NO) is due to a slight change in peak profile.

Ellison and Scheidt for Fe(OEP)(NO).<sup>19,20</sup> As observed in their X-ray diffraction experiment, the Fe–N(O) vector is tilted toward the oxygen atom from the *z*-axis defined by the normal to the plane through the four equatorial N atoms (by 8° according to the optimization, 6–8° according to experiment), while the NO group is staggered with respect to the equatorial bonds. The four equatorial Fe–N distances divide in two groups with the bonds closest to the direction of the NO tilt being shorter by ~0.025 Å, as observed in the experiment and interpreted by Scheidt and Ellison in terms of the  $d_z^2$ –NO  $\pi^*$  interaction and subsequent tilting of the basal  $\sigma$ -orbitals.<sup>21</sup>

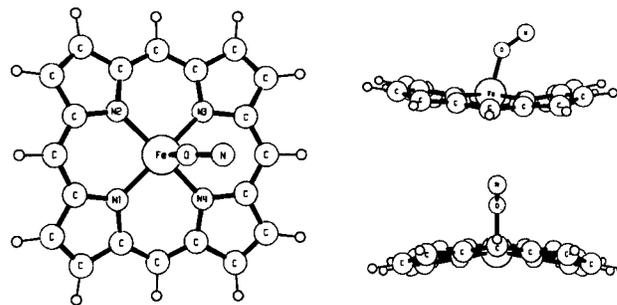
Full optimization of the staggered MS1 isonitrosyl structure for FeP'(ON) confirms that it corresponds to a local energy minimum, with an energy 1.59 eV above that of the ground state. As the B band formation is dependent on the ring substitution (i.e., present for the OEP, but not for the TTP complex), calculations on the ring-unsubstituted complex may not reveal a second energy minimum. In the calculation of metastable linkage isomers by Delley et al. of sodium nitroprusside,<sup>22</sup> energy minima for two related metastable conformations, eclipsed and staggered

(18) The core electrons of C, N, O, and Fe were treated by a frozen core approximation. Basis sets were identical to those used in the Fe(II)P calculations of Kozłowski et al. (Kozłowski, P. M.; Spiro, T. G.; Bérces, A.; Zgierski, M. Z. *J. Phys. Chem. B* **1998**, *102*, 2603–2608). The valence shells of the H, C, N, and O atoms were described by a double- $\zeta$  STO basis set, extended with a polarization function (ADF database III). For the 3s, 3p, and 3d shells on Fe, a triple- $\zeta$  STO basis set was employed (ADF database II). All calculations were spin-unrestricted and based on the local density approximation (LDA) in the parametrization of Vosko, Wilk, and Nusair (VWN). Scalar relativistic effects on Fe were taken into account with the Pauli formalism. In the geometry optimizations a convergence criterion for gradients of  $10^{-5}$  (au/Å) was used, while integrals were evaluated with an accuracy of 8 significant digits.

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**Figure 2.** The theoretical geometry of the metastable state FeP'(ON), viewed from three different directions.

with respect to the equatorial ligands, were found. However, in our work the eclipsed isonitrosyl configuration for the model FeP'(ON) compound invariably reverted to the staggered structure on optimization. Attempts to optimize a side-on  $\eta^2$  MS2 geometry invariably failed, the molecule returning to the ground-state structure after a large number of cycles. This is in complete agreement with the absence of an MS2 spectral feature in all our light-on spectra. The theoretical optimized geometry of the Fe–ON MS1 state is illustrated in Figure 2. The saddle shape of the porphyrin macrocycle for both the optimized ground and metastable states geometries may be a property of the isolated molecule and does not occur in the solid state.

In summary, we have provided the first spectroscopic and theoretical evidence for nitrosyl linkage isomerism in iron porphyrins, and the first observation of linkage isomers for any five coordinate {MNO}<sup>7</sup> complex. The results are relevant to the overall study of NO binding, dissociation, and recombination involving heme proteins. Chance and co-workers, for instance, have characterized two photoproduct states of ferrous MbNO that involve two (dissociated) NO conformations that rebind to the iron center at different rates.<sup>23</sup> Although isonitrosyls were not observed in this latter study, the authors proposed that the fast-binding state has the N-atom of the dissociated NO group closer to the metal center, whereas in the slow-binding state the O-atom is closer to the metal center, which would necessitate the flipping of NO before rebinding.

We are pursuing similar studies on six-coordinate Fe-porphyrin nitrosyl species.

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**Supporting Information Available:** Table of IR frequencies and isotope shifts (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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