

## Single- and Double-Linkage Isomerism in a Six-Coordinate Iron Porphyrin Containing Nitrosyl and Nitro Ligands

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Metals play significant roles in the chemistry of nitrogen oxides in the environment. Nitrite reductase enzymes convert nitrite ( $\text{NO}_2^-$ ) to nitric oxide (NO) in bacterial denitrification.<sup>1</sup> Although many binding modes of the nitrite group in coordination compounds have been established,<sup>2</sup> the relative energies of the observed binding modes in metalloproteins or their bioinorganic model compounds are not always known. NO is a signaling molecule that binds to the iron center of many heme proteins.<sup>3</sup> Information regarding ground states and metastable states of metal– $\text{NO}_x$  groups may help shed light on possible intermediates involved in  $\text{NO}_x$  association and/or dissociation from heme centers. Linkage isomerism of metal– $\text{NO}_x$  compounds has been reviewed recently.<sup>4</sup>

We reported that the five-coordinate nitrosyl porphyrins (por)-Fe(NO) (por = TTP, OEP; TTP = tetratolylporphyrinato dianion, OEP = octaethylporphyrinato dianion) undergo photoinduced NO linkage isomerism at 25 K to generate the isonitrosyls (por)Fe(ON).<sup>5</sup> We were thus interested in investigating related photoisomerizations in six-coordinate iron nitrosyl porphyrins. In this communication, we report that the photolysis of the ground-state nitrosyl–nitro complex (TPP)Fe(NO)( $\text{NO}_2$ ) (TPP = tetraphenylporphyrinato dianion) generates both the nitrito and isonitrosyl linkage isomers.

Irradiation of (TPP)Fe(NO)( $\text{NO}_2$ )<sup>6</sup> (KBr pellet;  $300 < \lambda < 500$  nm; 300 W xenon lamp) at 200 K for 10 min results in the appearance of new N-isotope-sensitive bands in the difference IR spectrum at 1507 and 934  $\text{cm}^{-1}$ , with a concomitant decrease in the bands at 1464, 1302, and 806  $\text{cm}^{-1}$ . These IR spectral changes suggest a change in the binding mode of the  $\text{NO}_2$  group from nitro to nitrito<sup>4</sup> and a conversion of the nitrosyl nitro complex (TPP)-Fe(NO)( $\text{NO}_2$ ) (GS) to the first metastable state (TPP)Fe(NO)(ONO) (MSa). The new IR bands remain after the illumination is ceased, indicating that complex MSa is stable at 200 K. However, continuous irradiation at 250 K is required to maintain spectroscopically detectable amounts of MSa, indicative of its decay at this temperature.

The nitro→nitrito linkage isomerization also occurs at 11 K as determined from the IR difference spectral analysis of the irradiated sample (Figure S1 in the Supporting Information). However, in addition to the bands due to the nitro→nitrito conversion, a new N-isotope-sensitive band at 1699  $\text{cm}^{-1}$  is also observed in the IR spectrum. The  $\Delta\nu_{\text{NO}}$  value of  $-184 \text{ cm}^{-1}$  is consistent with a nitrosyl→isonitrosyl linkage isomerization,<sup>4</sup> suggesting the possibility of an unprecedented double-linkage isomerism. Warming the irradiated sample to 50 K does not change the appearance of

the IR spectral features, implying that the isonitrosyl linkage is stable at 50 K. However, warming the sample to 200 K results in the disappearance of the 1699  $\text{cm}^{-1}$  band but not the nitrito bands. Furthermore, warming the sample to 295 K shows the complete restoration of the bands due to GS, indicative of the reversibility of both the nitro→nitrito and nitrosyl→isonitrosyl linkage isomerism.

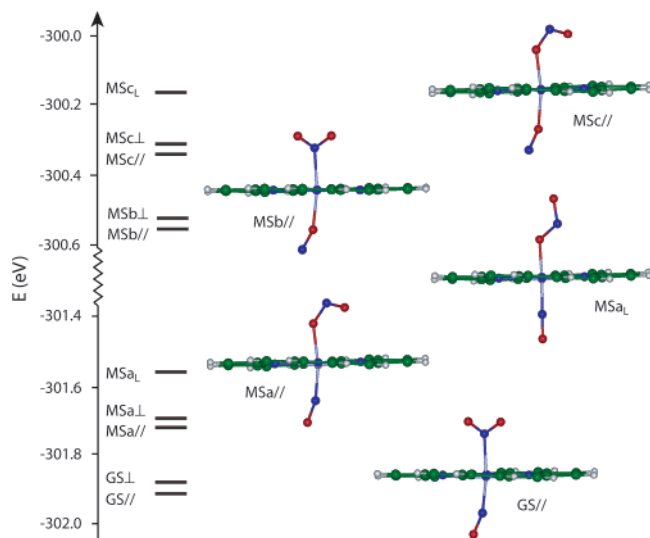
Density Functional Theory calculations on the model compound (porphine)Fe(NO)( $\text{NO}_2$ ) and its isomers were performed to further investigate the experimental observation of both the nitro→nitrito and nitrosyl→isonitrosyl linkage isomerism in the same compound.<sup>7</sup> The compound (porphine)Fe(NO)( $\text{NO}_2$ ) belongs to the {FeNO}<sup>6</sup> class according to the Enemark–Feltham notation.<sup>8</sup> Two locally stable ground-state (GS) conformations are found, which differ with respect to the relative orientation of the axial ligand planes; GS// represents parallel FeNO and Fe– $\text{NO}_2$  planes, and GS⊥ represents perpendicular planes.<sup>9</sup> GS// is the minimum energy structure ( $\Delta E$  |GS// – GS⊥| = 0.03 eV) and exhibits an FeNO bond angle of 157.4° with an off-axis tilt of 8.2° of the axial N(O) atom. The equatorial Fe– $\text{N}_p$  bonds are longer in the direction of the N(O) tilt and shorter in the direction away from the N(O) tilt, consistent with that observed previously for another {FeNO}<sup>6</sup> compound containing a bent NO group, namely, (OEP)Fe(NO)(*p*-C<sub>6</sub>H<sub>4</sub>F).<sup>10</sup> However, this Fe– $\text{N}_p$  bond length asymmetry in (porphine)Fe(NO)-( $\text{NO}_2$ ) is opposite to that observed for the five- and six-coordinate {FeNO}<sup>7</sup> porphyrins.<sup>11–13</sup>

Interestingly, the DFT calculations reveal that not only the nitrosyl–nitrito (MSa) and the isonitrosyl–nitro (TPP)Fe(ON)( $\text{NO}_2$ ) (MSb) but also the isonitrosyl–nitrito (TPP)Fe(ON)(ONO) (MSc) linkage isomers correspond to minima on the ground-state potential energy surface.<sup>14</sup> To the best of our knowledge, the latter result represents the first example of double-linkage isomerism. As is observed with the ground-state and MSa structures, the energy differences between the // and ⊥ forms of both MSb and MSc are small (~0.03 eV) and at room-temperature comparable with kT.<sup>15</sup> Calculated geometrical parameters for the linkage isomers of (porphine)Fe(NO)( $\text{NO}_2$ ) are collected in the Supporting Information, and the relative energies and representative structures are shown in Figure 1. Importantly, the Fe– $\text{N}_p$  bond length asymmetry, off-axis tilts of the nitrosyl N-atoms and isonitrosyl O-atoms, and the bending of the FeNO and FeON groups are general features of all the minimum energy structures of the GS, MSa, MSb, and MSc linkage isomers. The structures of MSa<sub>L</sub> and MSc<sub>L</sub> contain linear FeNO or FeON moieties, respectively, and display nitrito ligand conformations that place the terminal nitrito O-atom closer to the molecular axes; however, these structures correspond to higher energy conformations for MSa and MSc (Figure 1 and Table S2).

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**Figure 1.** Calculated energies and representative structures for the linkage isomers of (porphine)Fe(NO)(NO<sub>2</sub>). The axial nitrogen and oxygen atoms are colored blue and red, respectively. // = ligand planes are coplanar; ⊥ = ligand planes are mutually perpendicular. MSa<sub>L</sub> and MSCL<sub>L</sub> are the isomers displaying linear FeNO and FeON groups, respectively.

The DFT calculations confirm that the double-linkage isomerism is an achievable experimental event; the lowest energy conformation of the double linkage isomer (i.e., MSCL//) is 1.57 eV higher in energy than the ground-state GS//, and this  $\Delta E$  value is very similar to the 1.59 eV value calculated previously for the nitrosyl→isonitrosyl conversion for the five-coordinate (porphine)Fe(NO).<sup>5</sup>

There are several additional interesting points to note. First, photolysis of (TPP)Fe(NO)(NO<sub>2</sub>) as a KBr pellet at low temperature results in linkage isomerism without loss of NO or NO<sub>2</sub>. This contrasts with the observed competitive NO/NO<sub>2</sub> dissociation during photolysis of the compound in toluene solution.<sup>16</sup> Second, it is tempting to speculate that the MSa isomers could be generated as transient intermediates during the reactions of iron porphyrins with NO<sub>x</sub> species to give (por)Fe(NO)(NO<sub>2</sub>). This hypothesis is supported by the fact that both O-bonded and N-bonded NO<sub>2</sub> groups are observed as disordered components in a crystal form of [(TpivPP)Fe(NO)(NO<sub>2</sub>)]<sup>-</sup>.<sup>15</sup>

In summary, we have observed linkage isomerism involving two ligands in the same complex by IR spectroscopy and performed parallel DFT calculations. The possibility that in addition to the two separate linkage isomers a double-linkage isomer is formed,

as indeed suggested by the DFT calculations, cannot be ruled out, though its concentration may be too low to be easily detectable. The fact that this involves Fe–NO<sub>x</sub> species opens up new avenues for further investigations into NO and NO<sub>2</sub> combination and recombination with iron porphyrins.

**Acknowledgment.** Support for this work by the National Institutes of Health (GM 64476 to G.B.R.-A.) and the National Science Foundation (CHE0236317 to P.C.) is gratefully acknowledged.

**Supporting Information Available:** Difference infrared spectra and experimental IR frequencies for (TPP)Fe(NO)(NO<sub>2</sub>) and optimized structures for all linkage isomers of (porphine)Fe(NO)(NO<sub>2</sub>) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA0488986