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Raman Evidence for a Weakened O–O Bond in Mononuclear Low-Spin Iron(III)–Hydroperoxides

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Iron–peroxo species have been proposed or demonstrated to be catalytic intermediates in the mechanisms of a number of mononuclear iron enzymes1,2 and catalysts involved in alkane and arene hydroxylation and olefin epoxidation.3–5 Among these is a subset that have low-spin iron(III) centers as indicated by rhombic EPR signals at g = 1.9–2.4. Four of these have been formulated to be [LFe−OOH] species based on electrococrystization mass spectral (ESI-MS) data, where L = TPA,6 N4Py,7 Py5,8 and the antitumor drug bleomycin9 and are implicated in hydrocarbon oxidation reactions.10–12 Such low-spin iron(III)–hydroperoxo species are also likely to be involved in the chemistry of heme peroxides, cytchrome P450, and related heme catalysts.13 To date, no vibrational information has been obtained that provides insight into the relative bond strengths of the O−O bond because of the short lifetimes of such complexes and their susceptibility to photodecomposition.14,15 By excitation into the peroxo-to-iron(III) charge-transfer band at much lower energy, we have obtained resonance Raman spectra of [Fe(III)(TPA)(OOH)]2+ (1) and [Fe(III)(N4Py)(OOH)]2+ (2) which shed light into the reactivity of these species.

Previously, we have reported that the addition of excess H2O2 to [Fe(II)(TPA)(CH3CN)2]+ or [Fe(II)(N4Py)(CH3CN)]2+ at low temperatures gives rise to purple low-spin Fe(III)−OOH intermediates, 1 and 2, with 4σa's at 538 nm (ε ≈ 1000 M−1 cm−1) or 532 nm (ε ≈ 1100 M−1 cm−1), respectively. The Raman spectrum of 1 (Figure 1A), obtained by excitation into the long wavelength tail of its peroxo-to-iron(III) charge-transfer band, shows two resonance-enhanced features at 626 and 789 cm−1.

Figure 1. Resonance Raman spectra of 1 and 2. A. 50 mM H2O2 dissolved in CD2CN was added to 10 mM [Fe(II)(TPA)(CH3CN)]2+ in 4/1 CD2CN/THF at −50 °C. The spectrum was obtained with 508.2 nm laser excitation at 20 mW power at the sample. B. 50 mM H2O2 was added to 10 mM [Fe(II)(N4Py)(CH3CN)]2+ in de-acetone at −10 °C. The spectrum was obtained with 615 nm laser excitation at 20 mW power at the sample. C. Same as B, except H218O; and acetone were used. D. Same as B, except H2O2 diluted in D2O was used.

while that of 2 (Figure 1B) shows four features at 632, 651, 672, and 790 cm−1. Excitation profile studies confirm that these vibrations are all associated with the peroxo-to-iron(III) charge-transfer transition. Due to experimental complications,12 isotopic data could only be obtained for 2. With H218O (Figure 1C), only the features at 632 and 790 cm−1 of 2 downshift by 16 and 44 cm−1, respectively, while the 651 and 672 cm−1 features are unaffected.13 The vibrations around 630 and 790 cm−1 are thus associated with the Fe−OOH moiety.

Resonance Raman spectra of iron–peroxide complexes typically exhibit two resonance enhanced features, a ν(O−O) between 800 and 900 cm−1 and a ν(M−O) between 400 and 503 cm−1 (Table 1). The 790 cm−1 feature in 1 and 2 is best assigned as the ν(O−O). This assignment is strongly justified by the −44 cm−1 shift for this feature upon 18O substitution in 2 (Figure 1C), which matches well the shift of −45 cm−1 predicted by Hooke's law for a diatomic O−O stretch. As shown in Table 1, 790 cm−1 is the lowest ν(O−O) of any iron–peroxo species, including the two characterized η5-peroxo–iron species. This comparison suggests that the O−O bond is significantly weakened in 1 and 2.

The assignment of the 632 cm−1 feature is less certain. While it is initially tempting to assign it to ν(Fe−O), Fe−O vibrations for other iron–peroxo species are significantly lower in energy and are typically observed between 400 and 503 cm−1 (Table 1). Furthermore the use of H218O affords a shift of only −16 cm−1, which is about half that predicted by Hooke's law calculations for a pure Fe−O vibration (−28 cm−1). Calculations for an Fe−OO vibration (−23 cm−1) or an Fe−OOH vibration (−22 cm−1) afford shifts that approach the observed value, but it is clear that this vibration must involve the coupling of a number of modes. Similar complications have been noted in the analysis of Raman...
Table 1. Reported Resonance Raman Features of Iron—Peroxo Complexes

<table>
<thead>
<tr>
<th>complex</th>
<th>(\nu_{\text{Fe}-O}) (cm(^{-1}))</th>
<th>(\nu_{\text{O}-O}) (cm(^{-1}))</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(TPA)(OOH)](^{2+})</td>
<td>626(^a)</td>
<td>789</td>
<td>this work</td>
</tr>
<tr>
<td>[Fe(N4Py)(OOH)](^{2+})</td>
<td>632(^b)</td>
<td>790</td>
<td>this work</td>
</tr>
<tr>
<td>[Fe(OEP)((\eta^2)-O(_2))](^-)</td>
<td>n.o.</td>
<td>805</td>
<td>14</td>
</tr>
<tr>
<td>[Fe(II)(EDTAAH)((\eta^2)-O(_2))](^-)</td>
<td>n.o.</td>
<td>815</td>
<td>15</td>
</tr>
<tr>
<td>oxyhemerythrin [Fe((\eta^1)-OOH)]</td>
<td>503</td>
<td>844</td>
<td>16.17</td>
</tr>
<tr>
<td>Fe((\mu)-1,2-O(_2)) species</td>
<td>415–476</td>
<td>848–900</td>
<td>18</td>
</tr>
</tbody>
</table>

\(^a\) L = O or OOH. \(^b\) Observed feature for the coupled Fe—OOH mode.

Fe(III)−OOH species. Given that the fact that the few structurally characterized M−OOH complexes all have \(\eta^1\) (end-on) binding modes,\(^{22,23}\) it is likely that the hydroperoxides in 1 and 2 are similarly bound (Figure 2). The observation that these low-spin Fe(III)−OOH species have a \(\nu(O-O)\) at least 50 cm\(^{-1}\) lower than that of the high-spin peroxo complexes suggests that the low-spin center may weaken the O−O bond. This notion is supported by recent nonlocal DFT calculations on the putative Fe−OOH species in cytochrome P450.\(^{24}\) This weakened bond would then be primed for O−O bond cleavage to convert the low-spin iron(III) (\(t_2^g\)) center with minimal electronic reorganization to low-spin iron(IV) (\(t_2^g\))−oxo or iron(V) (\(t_2^g\))−oxo species, which are generally accepted as the key oxidants in the mechanisms of many heme-catalyzed oxidations.\(^{2,11}\) Indeed 1 and 2 are the only peroxo species in Table 1 associated with the catalytic oxidation of relatively inert hydrocarbons such as cyclohexane.\(^{5,13}\) Similar arguments may be applied to rationalize the involvement of low-spin Fe(III)−OOH species in the catalytic cycles of bleomycin\(^{2,9,10}\) and several heme enzymes.\(^{2,11}\) Our Raman data thus shed light into one mechanism by which dioxygen can be activated at mononuclear iron sites, illustrating a common thread that underlies iron metallobiochemistry in both heme and non-heme systems.

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