Directing a Non-Heme Iron(III)-Hydroperoxide Species on a Trifurcated Reactivity Pathway

Wegeberg, Christina; Lauritsen, Frants R.; Frandsen, Cathrine; Mørup, Steen; Browne, Wesley R.; Mckenzie, Christine J.

Published in:
Chemistry: A European Journal

Link to article, DOI:
10.1002/chem.201704615

Publication date:
2018

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):
Abstract: The reactivity of [Fe\textsuperscript{III}(tpena)]\textsuperscript{2+} (tpena = N,N,N\textsuperscript{-}tris(2-pyridylmethyl)ethylenediamine-N\textsuperscript{-}-acetate) as a catalyst for oxidation reactions depends on its ratio to the terminal oxidant H\textsubscript{2}O\textsubscript{2} and presence or absence of sacrificial substrates. The outcome can be switched between: 1) catalysed H\textsubscript{2}O\textsubscript{2} disproportionation, 2) selective catalytic oxidation of methanol or benzyl alcohol to the corresponding aldehyde, or 3) oxidative decomposition of the tpena ligand. A common mechanism is proposed involving homolytic O–O cleavage in the detected transient purple low-spin (S = 1/2) [(tpenaH)Fe\textsuperscript{III}O(OH)]\textsuperscript{2+}. The resultant iron(IV) oxo and hydroxyl radical both participate in controllable hydrogen-atom transfer (HAT) reactions. Consistent with the presence of a weaker o-donor carboxylate ligand, the most pronounced difference in the spectroscopic properties of [Fe(OO)(tpenaH)]\textsuperscript{2+} and its conjugate base, [Fe(OO)(tpenaH)]\textsuperscript{+}, compared to non-heme iron(III) peroxide analogues supported by neutral multidentate N-only ligands, are slightly blue-shifted maxima of the visible absorption band assigned to ligand-to-metal charge-transfer (LMCT) transitions and, corroborating this, lower Fe\textsuperscript{III}/Fe\textsuperscript{II} redox potentials for the pro-catalysts.

Introduction

Oxygen-coordinated iron complexes, such as iron(II)-O\textsubscript{2} (dioxygen), iron(III)-O\textsubscript{2} (superoxo and peroxido), iron(III)-OOH (hydroperoxido), and iron(III)-OO\textsuperscript{•} (alkylperoxido), along with high-valent iron(IV) and iron(V) oxides formed upon homolytic or heterolytic cleavage of the O–O bond in these complexes, have been proposed as key catalytically competent intermediates in oxidations catalysed by heme\textsuperscript{1–2} and non-heme\textsuperscript{3–6} enzymes, as well as in synthetic model compounds.\textsuperscript{3,5–8} To date, the field of non-heme peroxido compounds has been largely dominated by systems employing neutral aminopyridyl chelating ligands.\textsuperscript{6,8} However, akin to the modulation of O\textsubscript{2} activation by heme enzymes mediated by a donor ligand trans to the oxygen binding site, we can reasonably expect that the introduction of anionic oxygen donors into the coordination sphere of an iron ion will stabilize higher oxidation states. Concomitantly, the O–O bond of peroxido ligands coordinated to the same iron centre will be weakened. This hypothesis is supported by the fact that many oxidation processes catalysed by non-heme iron O\textsubscript{2}-activating enzymes, such as Rieske dioxygenases, tetrahydropterin-dependent hydroxylases, and 2-oxoglutarate-dependent dioxygenases and hydroxylases, possess an active site consisting of two histidine residues and one carboxylate group from Asp or Glu (Scheme 1). The reaction pathways followed by these enzymes proceed through cleavage of the O–O bond of peroxide/superoxide ligands derived from O\textsubscript{2} to form high-valent iron(oxid) species, followed by direct oxidation of a substrate by the generated non-heme iron(IV).\textsuperscript{4,9} Despite the biological precedence, the weakening of the O–O bond of an iron-coordinated peroxido ligand by the proximity of a carboxylato group has, to our knowledge, not yet been evaluated through systematic studies in model complexes.

Iron(III)-hydroperoxido and -peroxido complexes based on neutral pentadentate (NS) aminopolypyridyl ligands with an ethylenediamine backbone as the supporting scaffold, N-alkyl-N'/N'-tris(2-pyridylmethyl)ethylenediamine (Rtpen; Scheme 2a) were the first systems for which peroxide derivatives were spectroscopically characterized, and these have been extensively studied.\textsuperscript{10–18} Typically, these are generated by the reaction of air-stable iron(II) precursor complexes with H\textsubscript{2}O\textsubscript{2}, a prerequisite for which is oxidation of the iron centre from the Fe\textsuperscript{II} to the Fe\textsuperscript{III} oxidation state prior to formation of the Fe\textsuperscript{III}-OOH

1. C. Wegeberg, Prof. F. R. Lauritsen, Prof. C. J. McKenzie Department of Physics, Chemistry and Pharmacy University of Southern Denmark, Campusvej 55 5230 Odense M (Denmark) E-mail: mckenzie@sdu.dk
2. Prof. C. Frandsen, Prof. S. Mørup Department of Physics, Technical University of Denmark 2800 Kongens Lyngby (Denmark)
3. Prof. W. R. Browne Molecular Inorganic Chemistry, Stratingh Institute for Chemistry University of Groningen, Nijenborgh 4 9747 AG, Groningen (The Netherlands)
4. Supporting information, including crystallographic tables as well as MIMS data and EPR and 'H NMR spectroscopy data, and the ORCID numbers for the authors of this article can be found under https://doi.org/10.1002/chem.201704615.
species. Analogously to one of the functions of the protein in non-heme enzymes, the presence of more than four donors in these supporting ligands serves to inhibit hydrolytic polymerization reactions. This must be particularly important in the presence of terminal oxidants such as peroxides. Purple transient Fe$^{III}$ adducts, [Fe$^{III}$OOH(Rtpen)]$^{2+}$, have been observed at room temperature with half-lives of up to 2 h following their initial formation over several seconds (i.e., after the Fe$^{II}$ to Fe$^{III}$ oxidation step and coordination of a deprotonated H$_2$O$_2$ ligand). Kinetic studies with [Fe$^{III}$Rtpen]$^{2+}$ precursors have indicated that the reaction is essentially instantaneous when the metal pre-oxidation step is circumvented.\(^{[11]}\) The Rtpen ligands also support iron(IV) species. However, although their formation by homolytic cleavage of the O–O bond of peroxide precursors has been proposed, it is important to note that such species have not actually been prepared using H$_2$O$_2$ as the terminal oxidant, but instead by reaction of the Fe$^+$ precursor with PhIO, m-CPBA, or ClO$^-$.$^{[19]}$

Since monodentate carboxylate ligands are strong $\alpha$ donors, we reasoned that iron(III) precursor compounds suitable for the rapid preparation of peroxido adducts would be accessed if one of the pyridyl arms were to be substituted by a biomimetic glycinate group. Our initial foray using this strategy produced the N4O ligands N-R-N'/N'-bis(2-pyridylmethyl)ethylenediamine-N'-acetate (Rtpena), N= methyl, benzyl (Scheme 2b), which indeed favoured the formation of iron(III) complexes.$^{[18]}$

Reactions of these iron(III) complexes with H$_2$O$_2$ (and alkyl peroxides or O$_2$ plus ascorbic acid) did not, however, produce detectable peroxide adducts, but instead oxygenation of the Rtpena ligands was observed. Aryl C–H oxidation of bzbpena gave the iron(III) complex, in which an O atom was installed in the ligand, N-(2-oxidobenzyl)-N,N'-bis(2-pyridylmethyl)ethylenediamine-N'-acetate, and O atom insertion into an Fe–N$_{amine}$ bond provided an N-oxide ligand, 2-((2-(methyl(pyridin-2-ylmethyl)amino)ethyl)-oxido(pyridin-2-ylmethyl)azanyl)acetate (Scheme 2c), for the iron(III) complex of the mepena ligand. These O atom C–H and Fe–N insertion reactions provide circumstantial evidence for the in situ formation of Fe$^{$III}$-peroxide adducts and subsequent heterolytic Fe$^{IV}$–O–O(H) bond cleavage to give putative high-valent Fe$^{IV}$ oxo species capable of engaging in selective two-electron oxygen-atom transfer (OAT) reactions.

By adding a sixth heteroatom donor to replace the alkyl/aryl group in the N40 Rbpena ligand systems, namely a third pyridine group to give the NSO ligand N,N,N'-tris(2-pyridylmethyl)ethylenediamine-N'-acetate (tpena, Scheme 2d), we demonstrate here that the ability to generate detectable transient iron(III)-peroxide adducts is reinstated. In other words, behaviour similar to that observed for the iron(III) complexes of N5 Rtpen can be observed, and this contrasts with that for the iron(III) complexes of N40 Rbpena. However, the Fe$^{III}$-OOH species formed from the tpena-iron complex has a significantly shorter lifetime than those derived from the corresponding Rtpen-based systems. At first sight, it might seem surprising that the ostensibly coordinatively saturated iron(III) precursor [Fe(tpena)]$^{2+}$ can form heterolytic complexes with co-ligand peroxide donors. However, we have previously demonstrated that external substrates can be selectively oxidized using the terminal oxygen-atom-transfer reagents iodosylbenzene and N-morpholine-N-oxide catalysed by [Fe(tpena)]$^{2+}$, and a seven-coordinated intermediate heteroleptic Fe$^{IV}$-oxo adduct was isolated.$^{[20,21]}$

Herein, we demonstrate the formation and characterization of the species [tpenaH][Fe$^{III}$-OOH]$^{2+}$ and [tpenaH][Fe$^{IV}$-OO]$^{+}$ and show that the reactivity of these complexes is highly de-
Results and Discussion

Fe\textsuperscript{III}/Fe\textsuperscript{II} redox potentials for analogous iron complexes of NSO and N\textsubscript{6} ligands

Solutions of [Fe\textsuperscript{III}(tpena)]\textsuperscript{2+} in acetonitrile are obtained by the dehydration of [(tpenaH)Fe(\mu-O)Fe(tpenaH)]\textsuperscript{4+} upon dissolution\textsuperscript{[21]} [(tpenaH)Fe(\mu-O)Fe(tpenaH)]\textsuperscript{4+} → 2 [Fe(tpena)]\textsuperscript{2+} + H\textsubscript{2}O.

The cyclic voltammogram of [Fe\textsuperscript{II}(tpena)]\textsuperscript{2+} in acetonitrile shows a broad wave due to overlapping reversible Fe\textsuperscript{III}/Fe\textsuperscript{II} redox couples at 0.02 V and 0.06 V vs Fc/Fc\textsuperscript{+} (Figure 1a). The redox waves are associated with the high-spin (S = 5/2) mer-py\textsubscript{3}-[Fe(tpena)]\textsuperscript{2+/+} and low-spin (S = 1/2) fac-py\textsubscript{2}-[Fe(tpena)]\textsuperscript{2+/+} diastereoisomers (Figure 1b). Both the mer-py\textsubscript{3} and fac-py\textsubscript{2} isomers have been previously identified in both the solid and solution states by Mössbauer spectroscopy and in the frozen-solution state by EPR spectroscopy\textsuperscript{[21]}. The potentials are 0.38 and 0.40 V vs Fc/Fc\textsuperscript{+}, tpen = N,N',N'-tetraakis(2-pyridylmethyl)ethylenediamine; Figure 1b). This result is consistent with our expectation that the binding of a negatively charged carboxylate group in place of a pyridyl moiety will stabilize higher iron oxidation states. It is also consistent with the tendency, in the presence of air, for the tpen and neutral N\textsubscript{5} Rtpen ligands to form iron(II) complexes, whereas iron(III) complexes are formed with tpen, irrespective of the oxidation state of the precursor iron starting salt (+2 or +3). The minor redox wave at 0.46 V is due to the oxo-bridged precursor, [(tpenaH)Fe(\mu-O)Fe(tpenaH)][ClO\textsubscript{4}]\textsubscript{4-}[23].

Reaction of HCl and H\textsubscript{2}O with [Fe(tpena)]\textsuperscript{2+} to form [FeX(tpena)]\textsuperscript{2+} (X = Cl\textsuperscript{-}, OOH\textsuperscript{-})

Addition of concentrated HCl to solutions of either the brown complex [(tpenaH)Fe(\mu-O)Fe(tpenaH)]\textsuperscript{4+} (in water/EtOH) or of the red-orange complex [Fe\textsuperscript{III}(tpena)]\textsuperscript{2+} (in acetonitrile) resulted in immediate formation of [Fe(Cl)(tpenaH)]\textsuperscript{2+}, as manifested by a colour change to yellow, λ\textsubscript{max} = 312 and 361 nm [Eqs. (1 a) and (1 b), respectively].

\begin{equation}
[(tpenaH)Fe(\mu-O)Fe(tpenaH)]^{4+} + 2HCl \rightarrow 2[Fe(Cl)(tpenaH)]^{2+} + H_2O \quad (1a)
\end{equation}

\begin{equation}
fac/mer-[Fe(tpena)]^{2+} + HX \rightarrow FeX(tpenaH)^{2+} \quad X = Cl\textsuperscript{-}, OOH\textsuperscript{-} \quad (1b)
\end{equation}

The single-crystal X-ray structure of [Fe(Cl)(tpenaH)]\textsuperscript{2+} (ClO\textsubscript{4})\textsubscript{2-EtOH-2H\textsubscript{2}O (Figure 2a) shows that the iron(III) ion is pentacoordinated by tpenaH, with a chlorido ligand occupying the sixth site. The pyridine arm attached to the same amine group, as the glycyl arm does not coordinate to the iron(III)
Addition of H₂O₂ to [Fe(tpena)]²⁺ in acetonitrile resulted in an immediate colour change from red to purple, indicative of the formation of an Fe³⁺-hydroperoxido adduct structurally analogous to the HCl adduct, namely [Fe³⁺(OOH)(tpena)]²⁺ [Eq. (1b)]. The concentration of the transient peroxido complex in acetonitrile is maximized under conditions that minimize the concentration of the hemihydrate, ([tpena]Fe(μ-O)O-tpenaH)]⁺, supporting the view that the anhydrate [Fe(tpena)]²⁺ is the immediate precursor for reaction with H₂O₂. Purple solutions of [Fe³⁺(OOH)(tpena)]²⁺ in acetonitrile, decay over 30 s at room temperature and over several hours at −40 °C. The rate of decay for [Fe³⁺(OOH)(tpena)]²⁺ is significantly faster than that for [Fe³⁺(OOH)(metpen)]²⁺ generated in methanol from [Fe(metpen)Cl](PF₆) with 50 equiv of H₂O₂ at room temperature. Of relevance to the oxidizing ability of [Fe³⁺(OOH)(tpena)]²⁺ (see below) is that it cannot be observed in methanol; this is in stark contrast to the [Fe³⁺(OOH)(Rtpen)]²⁺ complexes, for which methanol is the favoured solvent for generation.

Spectroscopic properties of [Fe(OOH)(tpena)]²⁺

The transient purple species, assigned as [Fe³⁺(OOH)(tpena)]²⁺, shows an absorption band at 520 nm (ε = 465 M⁻¹ cm⁻¹), consistent with an Fe³⁺ → ROO⁻ charge-transfer transition (Figure 3a, red curve). The Raman spectrum elicited at λₑᵥ₃ = 532 nm shows resonantly enhanced bands at 613 and 788 cm⁻¹ (Figure 3b), which can be assigned to Fe–O and O–O stretching modes, respectively, by comparison with previous literature; see Table 1. The EPR spectrum of a frozen solution shows a rhombic signal (g = 2.21, 2.15, 1.96; Figure 3c). The frozen-solution-state Mössbauer spectrum displays a doublet with δ = 0.21 mm s⁻¹ and ΔE₀ = 2.08 mm s⁻¹ (14%, Figure 3d), which is consistent with a low-spin Fe³⁺ species. The spectrum also shows the presence of the EPR-silent starting complex ([tpena]Fe-O-Fe(tpenaH)]⁺ (δ = 0.43 mm s⁻¹, ΔE₀ = 1.63 mm s⁻¹, 14%)[21] The structure of [Fe³⁺(OOH)(tpena)]²⁺ can be any of six diastereoisomers (Scheme 4). However, the simplicity of the Raman, Mössbauer, and EPR spectra implies that one of these isomers dominates, notwithstanding the possibility that the differences between the stereoisomers are insufficient to cause significant changes in the vibrational, nuclear, and spin characteristics. In the present study, the precise stereochemistry of the intermediate is not of specific concern and for simplicity of the data analyses, it is assumed that a single diastereoisomer of [Fe³⁺(OOH)(tpena)]²⁺ is formed, cor-

**Figure 2.** a) Crystal structure of [Fe(Cl)(tpenaH)]²⁺. b) The hydrogen-bonded 1D helical chain of cations parallel to the b-axis. Thermal ellipsoids are drawn at 50% probability and the protons are omitted for clarity. The intermolecular hydrogen bond is shown with dashed lines (C=O–H···Npy 1.845 Å).

**Scheme 4.** Possible diastereoisomers of [Fe(X)(tpenaH)]²⁺; X = Cl⁻, OH⁻, OOH⁻.
responding to that observed in the crystal structure of the HCl adduct, Figure 2 (i.e., A in Scheme 4).

**Deprotonation of [Fe(OOH)(tpenaH)]^{2+}**

The addition of NEt₃ (30 equiv) to solutions of [Fe(III)(OOH)(tpenaH)]^{2+} and excess H₂O₂ in acetonitrile results in an instant colour change from purple to blue and the appearance of a new absorption band at 675 nm (Figure 3 a, blue line). The lifetime of the new species is about 10 min at 0 °C when generated from 50 equiv of H₂O₂ and 30 equiv of Et₃N. Immediate loss of the Fe/C₀O and O/C₀O bands of the end-on Fe(III)-OOH in the Raman spectrum is accompanied by the appearance of the corresponding bands of a side-on peroxido complex at 473 and 815 cm⁻¹ (Figure 3 b), consistent with assignment of the species as [Fe(III)(OO)(tpenaH)]^{+}. The band positions are close to those reported for [Fe(III)(OO)(tpen)]^{+} and [Fe(III)(OO)(metpen)]^{+} (Table 1). A high-spin signal (g_{eff} = 8.8, 5.0, 4.3, 4.2, 3.5) appears in the EPR spectrum (Figure 4 a). The Mössbauer spectrum (Figure 4 b) of a sample composed of ⁵⁷Fe-labelled [Fe(II)(tpena)]^{2+} (microwave frequency 9.31542 GHz, 110 K, [Fe] = 2 mm, fit in grey). d) Mössbauer spectrum of a mixture containing [Fe(OOH)(tpenaH)]^{2+} (14%), [Fe₂O(tpenaH)₂]^{4+} (14%), and unidentified species (72%) ([Fe] = 2 mm).

---

**Figure 3.** Solution-state spectroscopic characterization of [Fe(OOH)(tpenaH)]^{2+} and [Fe(OO)(tpenaH)]^{+}. Colour coding: [Fe(tpena)]^{2+} in black, [Fe(OOH)(tpenaH)]^{2+} in red, [Fe(OO)(tpenaH)]^{+} in blue, [Fe(III)(Ot(tpenaH))₃]^{+} in green. Unidentified species depicted in orange (see text). The sum of the fitted data is coloured in grey. [Fe(OOH)(tpenaH)]^{2+} was generated by addition of 50 equiv of H₂O₂ to [Fe(tpena)]^{2+} in MeCN, and subsequent addition of 30 equiv of Et₃N gave [Fe(OO)(tpenaH)]^{+}. a) UV/Vis absorption spectra (RT, [Fe] = 1.5 mm). b) Resonance Raman spectra (-30 °C, [Fe] = 3 mm, λ_ex = 532 nm for [Fe(OOH)(tpenaH)]^{2+} and λ_em = 691 nm for [Fe(OO)(tpenaH)]^{+}). All spectra were normalized to the solvent band at 750 cm⁻¹. * = solvent bands. c) X-band EPR spectrum of [Fe(OO)(tpenaH)]^{2+} (microwave frequency 9.31542 GHz, 110 K, [Fe] = 2 mm, fit in grey). d) Mössbauer spectrum of a mixture containing [Fe(OOH)(tpenaH)]^{2+} (14%), [Fe₂O(tpenaH)₂]^{4+} (14%), and unidentified species (72%) ([Fe] = 2 mm).

---

**Figure 4.** Frozen-solution-state spectroscopic characterization of [Fe(OOH)(tpenaH)]^{2+} (blue). a) EPR spectrum (microwave frequency 9.315392 GHz, 110 K, 2 mm [Fe(tpena)]^{2+} and 50 equiv of H₂O₂ followed by 30 equiv of Et₃N). b) Mössbauer spectrum of a solution containing [Fe(OOH)(tpenaH)]^{+} (blue, 47%) and [Fe(III)(Ot(tpenaH))₃]^{+} (green, 53%). Fitting in grey ([⁵⁷Fe] 2 mm, 30 equiv of Et₃N followed by 50 equiv of H₂O₂).

---


These are not the final page numbers!
followed by rapid freezing in liquid N₂. This protocol meant that the presumably more labile [Fe(OOH)(tpenaH)]²⁺ did not get the chance to form in any significant concentration.

Spectroscopic data for [Fe(tpena)]⁺⁻ peroxide adducts are consistent with a side-on bound peroxide Fe⁶ complex in [Fe⁶(OO)(tpenaH)]²⁺ by comparison with iron complexes of Rtpen (Table 1, R = Me, BzCH₂, PyCH₂). This species is potentially intramolecularly (Scheme 5) or intermolecularly H-bonded, with the solid-state structure of [Cr(r⁵-OO)(tpenaH)]⁺ furnishing a structural analogue for the latter.[25] The pendant pyridinium moiety of the tpenaH ligand is a second site available for deprotonation by a base, and [Fe⁶(OO)(tpena)] is a plausible product from the reaction of [Fe⁶(OOH)(tpenaH)]²⁺ with two equivalents of base (Scheme 5). However, in this situation, the pyridine is expected to re-coordinate to the iron atom to form a seven-/eight-coordinated product for η⁵- and η⁶-OO²⁻, respectively. This is not expected to be sterically too demanding, because the N-Fe-N angles for multidentate ligands with ethyl-enediamine backbones are generally less than 90°, thereby providing a relatively open face on the opposite side of the metal ion. Indeed, heptacoordination has been structurally characterized in the high-spin d⁵ metal ion complexes [Fe⁶(OIPh)(tpena)][ClO₄]²⁺ and [Mn(OH₂)(tpena)][ClO₄]²⁺. The relatively open face presented by tpena in these structures suggests that formation of a heteroleptic complex with an η⁵-diatomic ligand is also a reasonable structure for the peroxido complex, especially since η⁵-OO²⁻ ligands are no more sterically demanding than monodentate oxide (O²⁻) ligands.[27] Addition of further base leads to the formation of yellow solutions, with vigorous decomposition of H₂O₂ and ultimately decomposition of the complex (see below), such that the precise details of the protonation state cannot be readily determined experimentally.

Consideration of Table 1 shows that the most significant spectroscopic difference is that the Fe⁺³ — OOH⁻ and Fe⁺³ — OO²⁻ LMCT bands for the end-on hydroperoxo and side-on peroxido Fe⁶-tpena complexes are at shorter wavelengths than those for the analogous Rtpen-based complexes. The

Table 1. Spectroscopic properties of [(tpenaH)Fe-O-Fe(tpenaH)]²⁺, fac-[Fe(tpena)]⁺⁻, mer-[Fe(tpena)]⁺⁻, [Fe(OOH)(tpenaH)]²⁺, [Fe(OO)(tpenaH)]²⁺, and related Fe⁶-hydroperoxo and peroxo complexes of neutral N₅ and N₆ donor ligands.

<table>
<thead>
<tr>
<th>Complex</th>
<th>λUV/Vis (nm)</th>
<th>νO-O (cm⁻¹)</th>
<th>νOO (cm⁻¹)</th>
<th>rRaman (cm⁻¹)</th>
<th>Exp. conditions</th>
<th>δMössbauer (mm s⁻¹)</th>
<th>EPR (mm s⁻¹)</th>
<th>g-values</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe⁶(OO)(tpenaH)]²⁺</td>
<td>258</td>
<td>830</td>
<td>n/a</td>
<td>solid state</td>
<td>0.43</td>
<td>1.63</td>
<td>silent</td>
<td>½</td>
<td>[24]</td>
</tr>
<tr>
<td>fac-[Fe(tpena)]⁺⁻</td>
<td>360</td>
<td>1330</td>
<td>H</td>
<td>0.18</td>
<td>2.26</td>
<td>2.74, 2.29, 1.68</td>
<td>[21]</td>
<td>½</td>
<td>[21]</td>
</tr>
<tr>
<td>mer-[Fe(tpena)]⁺⁻</td>
<td>361</td>
<td>4150</td>
<td></td>
<td>0.25</td>
<td>4.20</td>
<td>4.00</td>
<td>[21]</td>
<td>½</td>
<td>[21]</td>
</tr>
<tr>
<td>[Fe⁶Cl(tpenaH)]²⁺</td>
<td>312</td>
<td>3940</td>
<td></td>
<td>0.46</td>
<td></td>
<td></td>
<td>[21]</td>
<td>½</td>
<td>[21]</td>
</tr>
<tr>
<td>[Fe⁶(OO)(tpenaH)]²⁺</td>
<td>520</td>
<td>4630</td>
<td></td>
<td>solid state</td>
<td>0.21</td>
<td>2.08</td>
<td>2.21, 2.15, 1.96</td>
<td>½</td>
<td>this work</td>
</tr>
<tr>
<td>[Fe⁶(OOH)(tpen)]²⁺</td>
<td>541</td>
<td>900, 200</td>
<td>617</td>
<td>0.19</td>
<td>2.01</td>
<td>2.19, 2.12, 1.95</td>
<td>½ [10,14,15], this work</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Fe⁶(OOH)(metpen)]²⁺</td>
<td>537</td>
<td>1000</td>
<td>617</td>
<td>0.19</td>
<td>2.07</td>
<td>2.20, 2.16, 1.96</td>
<td>½ [11,16], this work</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Fe⁶(OOH)(btztpen)]²⁺</td>
<td>542</td>
<td>140</td>
<td>473</td>
<td>0.19</td>
<td>2.07</td>
<td>2.20, 2.16, 1.96</td>
<td>½ [11,16]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Fe⁶(OO)(tpen)]²⁻</td>
<td>755</td>
<td>450</td>
<td>470</td>
<td>0.64</td>
<td>1.37</td>
<td>7.5, 5.9, 4.4</td>
<td>[12,14,15]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Fe⁶(OO)(metpen)]²⁻</td>
<td>740</td>
<td>500</td>
<td>470</td>
<td>0.64</td>
<td>1.37</td>
<td>7.5, 5.9, 4.4</td>
<td>[12,14,15]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Fe⁶(OO)(btztpen)]²⁻</td>
<td>770</td>
<td></td>
<td></td>
<td>0.63</td>
<td>1.12</td>
<td>7.60, 5.74</td>
<td>[11,16]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[a] Data on tpena-based complexes were recorded in MeCN; all other complexes were examined in MeOH. In the case of UV/Vis absorption data, caution should be exercised in direct comparison of the molar absorptivities of Fe⁶ peroxide complexes with those in the literature due to their reactivity under the experimental conditions (temperature, water concentration, purity, etc.), which will affect lifetimes. [b] Molar absorptivities were calculated using solutions showing the maximum absorbance at 530 nm and differences in handling explain the difference between the molar absorptivities of the complexes with 50 equiv of H₂O₂ or 50 equiv of H₂O₂ plus 30 equiv of Et₃N, respectively. This is not expected to be sterically too demanding, because the N-Fe-N angles for multidentate ligands with ethylenediamine backbones are generally less than 90°, thereby providing a relatively open face on the opposite side of the metal ion. Indeed, heptacoordination has been structurally characterized in the high-spin d⁵ metal ion complexes [Fe⁶(OIPh)(tpena)][ClO₄]²⁺ and [Mn(OH₂)(tpena)][ClO₄]²⁺. The relatively open face presented by tpena in these structures suggests that formation of a heteroleptic complex with an η⁵-diatomic ligand is also a reasonable structure for the peroxido complex, especially since η⁵-OO²⁻ ligands are no more sterically demanding than monodentate oxide (O²⁻) ligands.[27] Addition of further base leads to the formation of yellow solutions, with vigorous decomposition of H₂O₂ and ultimately decomposition of the complex (see below), such that the precise details of the protonation state cannot be readily determined experimentally.

Consideration of Table 1 shows that the most significant spectroscopic difference is that the Fe⁺³ — OOH⁻ and Fe⁺³ — OO²⁻ LMCT bands for the end-on hydroperoxo and side-on peroxido Fe⁶-tpena complexes are at shorter wavelengths than those for the analogous Rtpen-based complexes. The
\( \lambda_{\text{max}} \) for [Fe(OOH)(tpenaH)]\(^{2+} \) is hypsochromically shifted by about 20 nm, and \( \lambda_{\text{max}} \) for [Fe\(^{III}\)(OO)(tpenaH)]\(^{+} \) is shifted by 60, 75, and 95 nm compared to those reported for [Fe\(^{III}\)(OO)(tpen)]\(^{+} \), [Fe\(^{III}\)(OO)(metpen)]\(^{+} \), and [Fe\(^{III}\)(OO)(btpen)]\(^{+} \), respectively. The larger difference for the peroxido complexes may be related to the intramolecular H-bonding.

**Competition between H\(_2\)O\(_2\) disproportionation and ligand decomposition**

A large excess (20–50 equiv with respect to iron) of H\(_2\)O\(_2\) is required to generate maximum steady-state concentrations of [Fe(\(^{18}\)O)(OO)(tpenaH)]\(^{2+} \) and [Fe(\(^{18}\)O)(OO)(tpena)]\(^{+} \), under which conditions evolution of gas is observed. Analysis of the dissolved and evolved volatiles by means of membrane inlet mass spectrometry (MIMS) and head-space Raman spectroscopy (HS-RS; \( \lambda_{\text{max}} = 532 \text{ nm} \)) confirmed that the gas evolved was predominantly O\(_2\). Addition of \(^{18}\)O-labelled water in a 1:1:1 ratio of H\(_2\)O\(_2\):H\(_2\):\(^{18}\)O/H\(_2\)\(^{18}\)O mixture, confirmed that the O\(_2\) evolved did not contain \(^{18}\)O and hence that the two oxygen atoms in the evolved O\(_2\) were derived from H\(_2\)O\(_2\). Thus, [Fe\(^{II}\)(tpena)]\(^{2+} \) catalyses H\(_2\)O\(_2\) disproportionation rather than a more demanding oxidation of water.[28] To the best of our knowledge, H\(_2\)O\(_2\) disproportionation catalysed by exclusively N-donor-supported iron(III) peroxides (Scheme 2; R = CH\(_3\), PyCH\(_2\)) has not been reported.[10, 11, 17, 29] Since it seemed plausible that this reaction had simply been overlooked (because bubbles were not visible) in previous studies of the generation of non-heme Fe\(^{III}\)-peroxides, we checked for this possible reaction in the present study by applying MIMS to monitor the reactions of [FeCl(tpen)]\(^{+} \) with 50 equiv of H\(_2\)O\(_2\). We can verify that O\(_2\) evolution, and hence catalase activity, does not occur as a side reaction when these exclusively N-donor ligands support the peroxido complexes.

In further contrast to the exclusively N-donor-supported iron peroxido complexes, the hyderoxperoxido species, [Fe(\(^{18}\)O)(OO)(tpenaH)]\(^{2+} \), is not regenerated by the addition of a second portion (50 equiv) of H\(_2\)O\(_2\) after the cessation of O\(_2\) evolution, nor does catalytic H\(_2\)O\(_2\) disproportionation resume. These observations indicate that either the catalyst is decomposed by H\(_2\)O\(_2\), when the concentration of H\(_2\)O\(_2\) is sufficiently low for competing C–H oxidation of the tpena ligand to become kinetically competent, or the increase in water concentration (introduced with and formed from H\(_2\)O\(_2\)) drives the formation of a kinetically inert oxido-bridged species [(tpenaH)Fe(\(^{18}\)O)(tpenaH)]\(^{2+} \). To determine which of these pathways is pertinent, two equivalents of H\(_2\)O\(_2\) were added to solutions of [Fe(tpena)]\(^{2+} \) in acetonitrile. A colour change to purple was not observed. Head-space infrared spectroscopy (HS-IRS), however, showed that CO\(_2\) was produced. The only carbon sources available for CO\(_2\) production were the solvent acetonitrile and/or tpena. Monitoring both the O\(_2\) and CO\(_2\) releases by MIMS (Figure 5a) following the addition of 50 equiv of H\(_2\)O\(_2\) revealed that O\(_2\) was predominantly released in the early stages of the reaction. Quantitative analysis of the CO\(_2\) release by HS-IRS showed that approximately seven CO\(_2\) molecules per iron centre (Figure 5b) were produced. Increasing the amount of H\(_2\)O\(_2\) added did not result in an increase in CO\(_2\) formation, and it can therefore be concluded that the source of CO\(_2\) was degradation of tpena rather than oxidation of acetonitrile. Specifically, the CO\(_2\) must be derived from the aliphatic and carboxylate carbon atoms of tpena, as would be expected for aliphatic C–N oxidative cleavage/hydrolysis reactions.

The changes in iron speciation after the addition of 50 equiv of H\(_2\)O\(_2\) were monitored by UV/Vis absorption, Raman, EPR, and Mössbauer spectroscopies. The band at 520 nm due to the purple [Fe\(^{III}\)(OO)(tpenaH)]\(^{2+} \) chromophore decayed completely, and then a new and more intense band appeared at 469 nm (Figure 6a). The absence of an isosbestic point suggests that the conversion between these iron-based chromophores involves relatively long-lived intermediates that do not absorb in the visible region. Time-resolved head-space FTIR and UV/Vis absorption data indicated that the growth of the band at 469 nm was concomitant with the release of CO\(_2\) and the consequent growth of the absorbance at 2360 cm\(^{-1}\) in the HS-IR spectra. A fit of an EPR spectrum recorded from a reac-

![Figure 5. Detection of O\(_2\) and CO\(_2\) release. a) MIMS spectra of [Fe(tpena)]\(^{2+} \) (0.5 mm in acetonitrile) (black) and 2 min after addition of 50 equiv of H\(_2\)O\(_2\) (red). m/z 33–43 is omitted due to dominating intense MeCN signals (full spectrum: Supporting Information Figure S1). Inset: Time dependence of the ion current for the ions O\(_2\)\(^{+} \) (m/z 32) and CO\(_2\)\(^{+} \) (m/z 44). b) Time-resolved head-space FTIR spectroscopy showing evolution of CO\(_2\) upon reaction of [Fe(tpena)]\(^{2+} \) (2 mm) with 50 equiv of H\(_2\)O\(_2\). Inset: Time dependence of absorbance at 2360 cm\(^{-1}\). The acetonitrile bands at 2253 and 2292 cm\(^{-1}\) settle over time, concomitant with the decrease of effervescence due to both CO\(_2\) and O\(_2\).](image)
2.44, 2.29, 1.86, and a signal at g = 4.3. See Supporting Information Figure S3 for a summarized fit. c) Resonance Raman spectrum (λexc = 532 nm) recorded after the appearance of the absorption band at 469 nm. [Fe] = 1 mM, * = solvent bands.

Figure 6. Time-resolved conversion of [Fe\(^{III}\)(OOH)(tpenaH)]\(^{+}\) (red) to a low-spin Fe\(^{II}\) species (orange) with the addition of 50 equiv of H\(_2\)O\(_2\). a) UV/Vis absorption spectroscopy. [Fe] = 0.5 mM. b) EPR spectrum recorded 2 min after the addition of H\(_2\)O\(_2\) (black). Fitted data of [Fe\(^{III}\)(OOH)(tpenaH)]\(^{+}\) (red), a low-spin iron(III) species (pink, g = 2.44, 2.29, 1.86), and a high-spin iron(III) species (green, g eff = 4.3). c) Resonance Raman spectrum (λexc = 532 nm) recorded after the appearance of the absorption band at 469 nm. [Fe] = 1 mM, * = solvent bands.

Catalytic alcohol oxidation overrides catalase activity and ligand decomposition

In stark contrast to the reactions of [Fe\(^{II}\)(Cl)(Rtpena)]\(^{+}\) with excess H\(_2\)O\(_2\) in methanol,\(^{10,11,17}\) the addition of 50 equiv of H\(_2\)O\(_2\) to solutions of [Fe\(^{III}\)(tpena)]\(^{2+}\) in methanol does not give rise to detectable amounts of purple [Fe\(^{III}\)(OOH)(tpenaH)]\(^{2+}\). This is because methanol is oxidized. Analysis using the Hantzsch reaction\(^{33}\) and UV/Vis absorption spectroscopy showed that formaldehyde was produced in approximately 35% yield based on the initial H\(_2\)O\(_2\) concentration. Thus, the activation of H\(_2\)O\(_2\) by [Fe\(^{III}\)(tpena)]\(^{2+}\) can be directed to perform substrate oxidation. This observation inspired us to examine a more readily oxidizable substrate, benzyl alcohol, in acetonitrile (bond dissociation energies for H–CH\(_2\)OH and H–CH(OH)Ph are 96 and 79 kcal mol\(^{-1}\), respectively).\(^{16}\) The addition of 50 equiv of H\(_2\)O\(_2\) to [Fe(tpena)]\(^{2+}\) in the presence of 500 equiv of benzyl alcohol did not result in either O\(_2\) or CO\(_2\) evolution, and hence formation of tpenaH-derived CO\(_2\). The signals remaining in the aromatic region (7–9 ppm) suggested that the pyridine groups remained intact. Positive- and negative-ion ESI-MS did not provide evidence for the formation of a complex with pyridine ligands that might be associated with the species at 469 nm. Indirectly, however, the ESI-MS data provide further evidence that all of the aliphatic C atoms of the ligands were converted into CO\(_2\) through the absence, for example, of picolinato complexes that have previously been observed to form through the reaction of aminopyridyl-metal complexes with peroxides.\(^{32}\) Overall, the data lead to the conclusion that reaction of [Fe(tpena)]\(^{2+}\) with a large excess of H\(_2\)O\(_2\) results primarily in H\(_2\)O\(_2\) disproportionation, but is accompanied by concurrent oxidative deactivation of the tpena ligand, which occurs primarily when the concentration of H\(_2\)O\(_2\) is low. A mixture of heteroleptic iron(II) complexes of pyridine, ammonia, and/or acetonitrile ligands is ultimately formed through the oxidative decomposition of [Fe\(^{III}\)(tpena)]\(^{2+}\).

*These are not the final page numbers!*
neither H₂O₂ disproportionation nor tpena decomposition occurred. In contrast to the reactions performed in methanol, under these conditions, [Fe³⁺(OOH)(tpenaH)]²⁺ was observed spectroscopically due to the lower concentration of the alcohol substrate. The addition of a second portion of H₂O₂ (50 equiv) resulted in reappearance of the absorption band of [Fe³⁺(OOH)(tpenaH)]²⁺ with the same intensity as after the first addition (Figure 7). Continued batchwise addition of H₂O₂ eventually led to decomposition of the ligand, that is, the band at 469 nm intensified and the purple colour, due to eventually led to decomposition of the ligand, that is, the

Mechanistic considerations
The reaction of [(tpenaH)Fe-O-Fet(tpenaH)]⁺ with Ce⁴⁺ in water produces the iron(IV) oxo complex, [Fe⁴⁺(O)(tpenaH)]²⁺, and recently we have generated this same species electrochemically, also in water. In both of these studies, we demonstrated [Fe⁴⁺(O)(tpenaH)]²⁺ to be a promiscuous oxidant in the absence of hydroxyl radicals. It attacks a broad range of C–H bonds by hydrogen-atom transfer. Thus, [Fe⁴⁺(O)(tpenaH)]²⁺ displays radical character. Calculations by Faponle et al. show that [Fe⁴⁺=O(metpen)]²⁺ can be generated by homolytic cleavage of [Fe(OOH)(metpen)]²⁺, and it is the Fe⁴⁺ oxo species that reacts with substrates. This reaction has been demonstrated in the gas phase. However, the phase of the reaction medium (and second coordination sphere) is likely to tune the O–O bond cleavage reaction. With these facts in mind, we propose that the H₂O₂ activation and reactivity described in the present study can be rationalized in terms of homolytic O–O bond cleavage of the hydroperoxide ligand in [Fe³⁺(OOH)(tpenaH)]²⁺.

Perspective on the tunability by varying the supporting ligand in H₂O₂ activation by non-heme iron complexes
Compared to analogous iron(III)-hydroperoxide complexes based on supporting N5 and N6 ligands containing exclusively pyridine and tertiary amine donors (Scheme 2a) and analogous N,N-bis(2-pyridylmethyl)-N-bis(2-pyridyl)methylamine (N₄py) systems, the influence of a biomimetic carboxylato donor is demonstrated by the significant difference in Fe⁴⁺/Fe³⁺ redox potentials of the parent [Fe(tpen)]⁴⁻³ and [Fe(tpena)]⁴⁻³ complexes. The latter is shifted to lower values by an average of 360 mV for the diastereoisomers in acetonitrile. A practical consequence of the lower redox potential is that tpena-Fe III complexes are isolated, and these are redox-stable in the gas phase. These are thermodynamic sinks,
retarding their reactivity with H₂O₂. This tendency towards greater stability in higher iron oxidation states will have a significant impact on the chemistry of the iron-tpena complexes and hence on the construction of proposed catalytic cycles. The pro-catalyst and resting state is iron(III) and not iron(II). As such, the process of peroxide adduct formation does not require a prior oxidation step from iron(II) to iron(III). The Fe⁴⁺/Fe⁴⁺ couple can be reasonably expected to follow this trend towards lower potentials, and this will favour promotion of the homolytic cleavage of the FeO–OH bond in the hydroperoxo species. This reactive species can then lower potentials, and this will favour promotion of the methanol oxidation to formaldehyde and stoichiometric yields.

Conclusions

Methanol oxidation to formaldehyde and stoichiometric yields of benzaldehyde from the [Fe(tpena)]³⁺-catalysed oxidation of benzyl alcohol by H₂O₂ have been realized in the present study. In the absence of a large excess of a second substrate, H₂O₂ disproportionation is catalysed by [Fe(tpena)]³⁺ through a related mechanism. However, in the absence of other oxidizable substrates (methanol, benzyl alcohol, and H₂O₂), oxidative decay of [Fe(tpena)]³⁺ occurs through the spectroscopically detectable intermediate [Fe(OOH)(tpenaH)]²⁺. Release of all of the aliphatic carbon atoms and amine groups as CO₂ and NH₃, respectively, has been demonstrated. The reactivity patterns observed (catalysis of the oxidation of alcohols, catalase activity, and tpena degradation, Scheme 3) reflect the higher C–H bond strength in MeCN compared to MeOH, the aliphatic C–H bonds in tpena, and the O–H bond in H₂O₂, respectively. Overall, the H₂O₂ activation chemistry described here stands in contrast to that reported previously for the pentadentate NS supporting ligands [Fe⁵⁺(OOH)(Rtpen)]²⁻ and [Fe⁵⁺(OOH)(N4py)]²⁻ and a carboxylate-containing N4O4 pentadentate supporting ligand [Fe⁵⁺(OOH)(Rbpena)]²⁻. We have shown: 1) facile homolytic FeO–OH cleavage in solution to produce two aggressive H-atom abstractors, Fe⁵⁺–O and HO²⁻; 2) catalytic H₂O₂ disproportionation, 3) catalytic alcohol oxidation with stoichiometric yields, and 4) total destruction of the aliphatic part of tpena in the presence of low concentrations of H₂O₂. By tuning the penta- and hexadentate ethylenediamine-backboned ligands (Scheme 2), a tendency towards the limiting reaction types depicted in Equations (2), (3), and (4) for Fe⁵⁺-peroxide adducts has been exposed. It seems that H₂O₂ activation is more effective for the carboxylato ligands and the difference in reactivity seen for the N4O (Rbpena) and N5O (tpena) ligand systems must be due to the availability of a second base in the coordination sphere for the latter. The proximity of this group suggests that it may participate at many stages, from its decoordination to allow adduct formation by charge-separated H₂O₂ addition to H-bonding in the peroxide intermediates. In turn, this electronic modulation may effect a homolytic O–O cleavage rather than the heterolytic cleavage and intramolecular oxygenation that occurs with the otherwise stereochemically and electronically similar N4O Rbpena as a supporting ligand.

Dissociation:

\[
\text{Fe}^{	ext{III}}(\text{OOH})(\text{Rtpen})^{2+} + \text{HX} \rightarrow [\text{Fe}^{	ext{II}}(\text{X})(\text{Rtpen})]^{2+} + \text{HOOH} \quad (2)
\]

O–O heterolysis:

\[
\text{Fe}^{	ext{III}}(\text{OOH})(\text{Rbpena})^{2+} \rightarrow [\text{Fe}^{	ext{II}}(\text{RbpenaO})]^{2+} + \text{OH}^{-} \quad (3)
\]

O–O homolysis:

\[
[\text{Fe}^{	ext{III}}(\text{OOH})(\text{tpenaH})]^{2+} \rightarrow [\text{Fe}^{	ext{IV}}(\text{O})(\text{tpenaH})]^{2+} + \text{OH}^{+} \quad (4)
\]

Our work not only presents a germane mimic for non-heme iron chemistry, especially in terms of the carboxylato group and the second coordination sphere base, but also adds to our knowledge of the ligand design features important for activating H₂O₂, demonstrates controllable bifurcation in catalysed external substrate oxidation reactions, and indicates that destruct...
itive oxidation of the supporting ligand can be avoided through appropriate experimental design [Eqs. (2–4)].

**Experimental Section**

**Materials and preparations**

$\text{N,N,N-Tris-(2-pyridinylmethyl)ethylenediamine-N'}$-$\text{acetic acid}$ (tpenaH), [40] $\text{[tpenaHFe-O-Fe(tpenaH)]ClO}_4\cdot\text{(H}_2\text{O)}$, [20] $\text{[FeCl(tpena)Cl]}$, and $\text{[Fe(tpena)]ClO}_4\cdot\text{EtOH}$·2(H$_2$O) were prepared as described previously. $\text{[tpenaHFe-O-Fe(tpenaH)]}^+ \cdot \text{H}_2\text{O}$ was allowed to stand for 10 min until $\text{[tpenaHFe-O-Fe(tpenaH)]}^+ \cdot \text{H}_2\text{O}$ had dehydrated to $\text{[tpenaHFe-O-Fe(tpenaH)]}^+$. This solution was then treated with 50 equiv of $\text{H}_2\text{O}_2$ (50 % in water, w/w) to give $\text{[FeOO(tpenaH)]}^+ \cdot \text{H}_2\text{O}$ and $\text{[Fe(OOH)(tpenaH)]}^+$ was formed by the subsequent addition of 30 equiv of Et$_3$N.

**Results**

$\text{[Fe(tpenaH)]ClO}_4\cdot\text{(EtOH)}\cdot2\text{(H}_2\text{O)}$ (773 mg, 1.7 mmol) was added to tpenaH (655 mg, 1.7 mmol) in acetonitrile (5 mL), water (5 mL), and ethanol (5 mL), and the mixture was adjusted to pH 3 with HCl(aq.). Upon slow evaporation of the volatile, yellow crystals of $\text{[FeCl(tpenaH)]ClO}_4\cdot\text{EtOH}$·2(H$_2$O) (702 mg, 54%) were deposited after two weeks. ESI-MS (MeCN; m/z: 479.1 ([Fe(tpenaH)]·2H$_2$O), 78%), 481.1 ([Fe(tpenaH)]$^+$, 81%), 482.1 ([Fe(tpenaH)]$^+$, 100%), ESI-MS (H$_2$O; m/z: 446.1 ([Fe(tpenaH)]$^+$, 34%), 454.1 ([tpenaH2Fe-SaFe(tpena)], 100%), 463.1 ([Fe(OH)-tpena$^-$], 85%); IR (KBr): v = 1610 (C=O), 1098 cm$^{-1}$ (ClO$_4^-$), vs; elemental analysis calcd (%) for C$_{36}$H$_{29}$N$_5$O$_{12}$Cl$_3$Fe ([Fe(tpenaH)]$^+$·2(H$_2$O)): C 36.82, H 4.07, N 9.76; found: C 36.21, H 3.65, N 9.27.

**Instrumentation and methods**

UV/Vis spectra were recorded from solutions in 1 cm quartz cuvettes on either an Agilent 8453 spectrophotometer with a UNISOKU CoolSpek UV USP-203 temperature controller or an Analytik Jena Spectrophotometer (mod. amp.: 10 G, attenuation: 10 dB) on a Hitachi 270-30 UV/VIS spectrometer from samples in KBr pellets. The electrolyte was also 0.1 M TBAClO$_4$ in MeCN. The working electrode was cleaned by polishing with 0.05 µm alumina followed by sonication, and the solutions were purged with nitrogen prior to measurements. The oxidation potential ofFc/Fc$^+$ against Ag/Ag$^+$ was measured at 0.08 V, and all oxidation potentials were converted accordingly.

CCDC 1559278 ([FeCl(tpenaH)]ClO$_4$·(EtOH)·2(H$_2$O)) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

**Acknowledgements**

This work was supported by the Danish Council for Independent Research | Natural Sciences (grant 4181-00329 to C.McK.). C.W. thanks COST action CM1305 (ECOSTBio) for the travel grant STSM #30679. Dr. Anne Nielsen, Dr. Anders Lennartsson, and Dr. Mads Vad are acknowledged for some preliminary experimental work. Lars Braendegaard Hansen is thanked for designing the reaction cell for the MIMS setup.

**Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** H$_2$O$_2$ activation · high-valent iron · hydroxyl radical · iron(IV) · N$_2$O ligands · peroxides


Although not directly comparable, we have observed the oxidation of [tpenaHFeIII(tpenaH)4]2+ in water to give [FeIV(O)-(tpenaH)]2+ and [FeV(O)-(tpenaH)]3+ in fact results in a deactivation of H2O2 at least with respect to this particular reaction.


Although not directly comparable, we have observed the oxidation of [tpenaHFeIII(tpenaH)4]2+ in water to give [FeIV(O)-(tpenaH)]2+ and [FeV(O)-(tpenaH)]3+ in fact results in a deactivation of H2O2 at least with respect to this particular reaction.


E. Bill 2016, Max-Planck-Institute for Chemical Energy Conversion, Mülheim; available from the author by mail to: eckhard.bill@cecc.mp.dg.
Peroxide activation at Fe: A transient Fe$^{III}$-hydroperoxide intermediate has been spectroscopically identified during [Fe$^{III}$(tpena)]$^{2+}$-catalysed H$_2$O$_2$ disproportionation in acetonitrile (see graphic). If benzyl alcohol is present, or methanol is used as solvent, H$_2$O$_2$ disproportionation is inhibited in favour of high-yielding alcohol oxidation to the corresponding aldehyde. In the absence of excess substrate (alcohol or H$_2$O$_2$), tpena is oxidatively degraded.