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

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


In memory of Professor John J. McGarvey

Abstract: The reactivity of [FeIII(tpena)]^{2+} (tpena = N,N,N'-tris(2-pyridylmethyl)ethylenediamine-N'-acetate) as a catalyst for oxidation reactions depends on its ratio to the terminal oxidant H_2O_2 and presence or absence of sacrificial substrates. The outcome can be switched between: 1) catalysed H_2O_2 disproportionation, 2) selective catalytic oxidative decomposition 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]FeIII-OO–OH]^{4+}. 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)]^{2+} and its conjugate base, [Fe(OO)(tpenaH)]^{3+}, 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 Fe⁵⁷/Fe⁴⁷ redox potentials for the pro-catalysts.

Introduction

Oxygen-coordinated iron complexes, such as iron(II)-O_2 (dioxo), iron(III)-O_2 (superoxido and peroxido), iron(III)-OOH (hydroperoxido), and iron(III)-OOR (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 and non-heme enzymes, as well as in synthetic model complexes. [3, 5–8] To date, the field of non-heme peroxido compounds has been largely dominated by systems employing neutral aminopyridyl chelating ligands. [6, 8] However, akin to the modulation of O_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 peroxide 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_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_2 to form high-valent iron-oxido species, followed by direct oxidation of a substrate by the generated non-heme iron(IV). [4, 9]

Despite the biological precedence, the weakening of the O–O bond of an iron-coordinated peroxide ligand by the proximity of a carboxylato group has, to our knowledge, not yet been evaluated through systematic studies in model complexes.

Iron(III)-hydroperoxide and -peroxido complexes based on neutral pentadentate (N5) 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. [10–18] Typically, these are generated by the reaction of air-stable iron(II) precursor complexes with H_2O_2, a prerequisite for which is oxidation of the iron centre from the FeII to the FeIV oxidation state prior to formation of the FeV-OOH...
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 study of biologically relevant iron(III) chemistry in the presence of terminal oxidants such as peroxides. Purple transient Fe(III) adducts, [Fe(III)(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_2O_2 ligand). Kinetic studies with [Fe<sup>3+</sup>(Rtpen)]^{2+} precursors have indicated that the reaction is essentially instantaneous when the metal pre-oxidation step is circumvented.\textsuperscript{[11]} The Rtpen ligands also support iron(IV) oxo 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_2O_2 as the terminal oxidant, but instead by reaction of the Fe<sup>3+</sup> precursor with PhIO, m-CPBA, or ClO<sub>2\textsuperscript{-.}\textsuperscript{[19]}.

Since monodentate carboxylate ligands are strong O 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'-bis(2-pyridylmethyl)ethylenediamine-N'-acetate (Rbpena), R = methyl, benzyl (Scheme 2b), which indeed favoured the formation of iron(III) complexes.\textsuperscript{[18]} Reactions of these iron(III) complexes with H_2O_2 (and alkyl peroxides or O_2 plus ascorbic acid) did not, however, produce detectable peroxide adducts, but instead oxygenation of the Rbpena 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<sub>amine</sub> bond provided an N-oxide ligand, 2-((2-(methyl(pyridin-2-yl-methyl)aminomethyl)ethoxy)oxo(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<sup>3+</sup>-peroxide adducts and subsequent heterolytic Fe<sup>3+</sup>-O–O(H) bond cleavage to give putative high-valent Fe<sup>5+</sup> 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 N4O Rbpena. However, the Fe<sup>3+</sup>-O<sub>H</sub> 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 heteroleptic 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<sup>5+</sup>-oxo adduct was isolated.\textsuperscript{[20,21]}

Herein, we demonstrate the formation and characterization of the species [(tpenaH)(Fe<sup>3+</sup>-O<sub>H</sub>)]^2+ and [(tpenaH)(Fe<sup>5+</sup>-O)]^+ and show that the reactivity of these complexes is highly de-
Results and Discussion

FeIII/FeII redox potentials for analogous iron complexes of NSO and N6 ligands

Solutions of [FeIII(tpena)]2+ in acetonitrile are obtained by the dehydration of [(tpenaH)Fe(μ-O)Fe(tpenaH)]3+ upon dissolution:[21] [(tpenaH)Fe(μ-O)Fe(tpenaH)]3+ → 2 [Fe(tpena)]2+ + H2O.

The cyclic voltammogram of [FeII(tpena)]2+ in acetonitrile shows a broad wave due to overlapping reversible FeIII/FeII redox couples at 0.02 V and 0.06 V vs FeC/C+ (Figure 1 a). The redox waves are associated with the high-spin ($S = \frac{5}{2}$) mer-py3-[Fe(tpena)]2+/+ and low-spin ($S = \frac{1}{2}$) fac-py3-[Fe(tpena)]2+/+ diastereoisomers (Figure 1 b). Both the mer-py3 and fac-py3 isomers have been previously identified in both the solid and solutions states by Mössbauer spectroscopy and in the frozen-solution state by EPR spectroscopy.[21] The potentials are 0.38 and 0.34 V lower compared to that for the FeII/Fe3 couple of [Fe(tpen)]3+/2+ (0.40 V vs FeC/C+; tpen = N,N',N',N'-tetrakis(2-pyridylmethyl)ethylenediamine; Figure 1 b). 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 N5 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(μ-O)Fe(tpenaH)](ClO4)4.[23]

Reaction of HCl and H2O2 with [Fe(tpena)]2+ to form [FeX(tpena)]3+ (X = Cl−, OOH−)

Addition of concentrated HCl to solutions of either the brown complex [(tpenaH)Fe(μ-O)Fe(tpenaH)]3+ (in water/EtOH) or of the red-orange complex [Fe(tpena)]2+ (in acetonitrile) resulted in immediate formation of [Fe(Cl)(tpenaH)]2+, as manifested by a colour change to yellow, $\lambda_{\text{max}} = 312$ and 361 nm [Eqs. (1 a) and (1 b), respectively].

\[
\begin{align*}
\text{[(tpenaH)Fe(μ-O)Fe(tpenaH)]3+} + 2\text{HCl} & \rightarrow 2\text{[Fe(Cl)(tpenaH)]2+} + \text{H}_2\text{O} \quad (1\text{a}) \\
\text{fac/mer-[Fe(tpena)]2+} + \text{HX} & \rightarrow \text{FeX(tpenaH)}^{2+} \quad X = \text{Cl}−, \text{OOH}− \quad (1\text{b})
\end{align*}
\]

The single-crystal X-ray structure of [Fe(Cl)(tpenaH)](ClO4)2·EtOH·2H2O (Figure 2 a) shows that the iron(III) ion is pentacoordinated by tpenH, with a chlorido ligand occupying the sixth site. The pyridine arm attached to the same amine group, as the glycol arm does not coordinate to the iron(III)
Addition of H$_2$O$_2$ to [Fe(tpena)]$^{2+}$ in acetonitrile resulted in an immediate colour change from red to purple, indicative of the formation of an Fe$^{III}$-hydroperoxido adduct structurally analogous to the HCl adduct, namely [Fe$^{III}$(OOH)(tpenaH)]$^{2+}$ [Eq. (1 b)]. The concentration of the transient peroxydo complex in acetonitrile is maximized under conditions that minimize the concentration of the hemihydrate, ([tpenaH]Fe(μ-O)Fe-(tpenaH))$^{4+}$, supporting the view that the anhydride [Fe(tpena)]$^{2+}$ is the immediate precursor for reaction with H$_2$O$_2$. Purple solutions of [Fe$^{III}$(OOH)(tpenaH)]$^{2+}$ in acetonitrile, decay over 30 s at room temperature and over several hours at $-40$ °C. The rate of decay for [Fe$^{III}$(OOH)(tpenaH)]$^{2+}$ is significantly faster than that for [Fe$^{III}$(OOH)(metpen)]$^{2+}$ generated in methanol from [Fe(metpen)Cl](PF$_6$) with 50 equiv of H$_2$O$_2$ at room temperature. Of relevance to the oxidizing ability of [Fe$^{III}$(OOH)(tpenaH)]$^{2+}$ (see below) is that it cannot be observed in methanol; this is in stark contrast to the [Fe$^{III}$(OOH)(Rtpen)]$^{2+}$ complexes, for which methanol is the favoured solvent for generation.

Spectroscopic properties of [Fe(OOH)(tpenaH)]$^{2+}$

The transient purple species, assigned as [Fe$^{III}$(OOH)(tpenaH)]$^{2+}$, shows an absorption band at 520 nm ($\varepsilon = 465$ M$^{-1}$ cm$^{-1}$), consistent with an Fe$^{III}$ $\rightarrow$ ROO$^\cdot$ charge-transfer transition (Figure 3 a, red curve). The Raman spectrum elicited at $\lambda_{ex} = 532$ nm shows resonantly enhanced bands at 613 and 788 cm$^{-1}$ (Figure 3 b), 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 3 c). The frozen-solution-state Mössbauer spectrum displays a doublet with $\delta = 0.21$ mm s$^{-1}$ and $\Delta E_Q = 2.08$ mm s$^{-1}$ (14%, Figure 3 d), which is consistent with a low-spin Fe$^{III}$ species. The spectrum also shows the presence of the EPR-silent starting complex ([tpenaH]Fe-O-Fe(tpenaH))$^{4+}$ ([d$_{5}$] = 0.43 mm s$^{-1}$, $\Delta E_Q = 1.63$ mm s$^{-1}$, 14%).[21] The structure of [Fe$^{III}$(OOH)(tpenaH)]$^{2+}$ 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 [Fe$^{III}$(OOH)(tpenaH)]$^{2+}$ 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 inter-molecular hydrogen bond is shown with dashed lines (C=O···H-N$_p$ 1.845 Å).

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

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

The addition of \(\text{NEt}_3\) (30 equiv) to solutions of \([\text{Fe(OOH)(tpenaH)}]^2+\) and excess \(\text{H}_2\text{O}_2\) 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 \(\text{H}_2\text{O}_2\) and 30 equiv of \(\text{Et}_3\text{N}\). Immediate loss of the \(\text{Fe}^\text{II}/\text{CO}\) and \(\text{O}^\text{II}/\text{CO}\) bands of the end-on \(\text{Fe}^\text{III}-\text{OOH}\) 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 \([\text{Fe}^\text{III}(\text{OO})(\text{tpenaH})]^+\). The band positions are close to those reported for \([\text{Fe}^\text{III}(\text{OO})(\text{tpen})]^+\) and \([\text{Fe}^\text{III}(\text{OO})(\text{metpen})]^+\) (Table 1). A high-spin signal (\(g\text{eff} = 8.8, 5.0, 4.3, 4.2, 3.5\)) appears in the EPR spectrum (Figure 4 a). The Mössbauer spectrum (Figure 4 b) of a sample composed of \(\text{Fe}^\text{III}(\text{OO})(\text{tpena})^+\) (microwave frequency 9.31542 GHz, 110 K, \([\text{Fe}] = 2 \text{ mm}\)) shows a doublet with \(\delta = 0.48 \text{ mm} \text{s}^{-1}\) and \(\Delta E_Q = 1.21 \text{ mm} \text{s}^{-1}\) (47%), which is consistent with a high-spin \(\text{Fe}^\text{III}\) species. The doublet due to \([\text{Fe}(\text{OO})(\text{tpenaH})]^+\) is not observed, and the spectrum also shows the presence of a significant amount of the EPR-silent starting material \((\text{tpenaH})\text{Fe-O-Fe(tpenaH)}^4^+\) (\(d = 0.46 \text{ mm} \text{s}^{-1}\) and \(\Delta E_Q = 1.68 \text{ mm} \text{s}^{-1}\), 53%\(^{21}\)). It is interesting to note that this spectrum does not show the presence of unidentified iron complexes derived from the decomposition of tpena (see below) in contrast to the spectrum for \([\text{Fe}(\text{OO})(\text{tpenaH})]^3^+\) (Figure 3 d). This lack of decomposition might suggest that the peroxide species is less reactive than the hydroperoxide species. This idea is supported by the fact that in order to acquire this clean spectrum it was necessary to add the base before the \(\text{H}_2\text{O}_2\),

Figure 3. Solution-state spectroscopic characterization of \([\text{Fe}(\text{OO})(\text{tpenaH})]^3^+\) and \([\text{Fe}(\text{OO})(\text{tpenaH})]^+\). Colour coding: \([\text{Fe}(\text{tpena})]^2^+\) in black, \([\text{Fe}(\text{OO})(\text{tpenaH})]^3^+\) in red, \([\text{Fe}(\text{OO})(\text{tpenaH})]^+\) in blue, \([\text{Fe}(\text{OO})(\text{tpena})]^3^+\) in green. Unidentified species depicted in orange (see text). The sum of the fitted data is coloured in grey. \([\text{Fe}(\text{OO})(\text{tpenaH})]^3^+\) was generated by addition of 50 equiv of \(\text{H}_2\text{O}_2\) to \([\text{Fe}(\text{tpena})]^2^+\) in MeCN, and subsequent addition of 30 equiv of \(\text{Et}_3\text{N}\) gave \([\text{Fe}(\text{OO})(\text{tpenaH})]^+\). a) UV/Vis absorption spectra (RT, \([\text{Fe}] = 1.5 \text{ mm}\)). b) Resonance Raman spectra (30°C, \([\text{Fe}] = 3 \text{ mm}\), \(\lambda_{\text{ex}} = 532 \text{ nm}\) for \([\text{Fe}(\text{OO})(\text{tpenaH})]^+\) and \(\lambda_{\text{ex}} = 681 \text{ nm}\) for \([\text{Fe}(\text{OO})(\text{tpenaH})]^+\)). All spectra were normalized to the solvent band at 750 cm\(^{-1}\). * = solvent bands. c) X-band EPR spectrum of \([\text{Fe}(\text{OO})(\text{tpenaH})]^+\) (microwave frequency 9.31542 GHz, 110 K, \([\text{Fe}] = 2 \text{ mm}\)). d) Mössbauer spectrum of a mixture containing \([\text{Fe}(\text{OO})(\text{tpenaH})]^+\) (14%), \([\text{Fe}(\text{OO})(\text{tpena})]^3^+\) (14%), and unidentified species (72%) (\([\text{Fe}] = 2 \text{ mm}\)).

Figure 4. Frozen-solution-state spectroscopic characterization of \([\text{Fe}(\text{OO})(\text{tpenaH})]^3^+\) (blue). a) EPR spectrum (microwave frequency 9.315392 GHz, 110 K, 2 mm \([\text{Fe}(\text{tpena})]^2^+\) and 50 equiv of \(\text{H}_2\text{O}_2\) followed by 30 equiv of \(\text{Et}_3\text{N}\)). b) Mössbauer spectrum of a solution containing \([\text{Fe}(\text{OO})(\text{tpenaH})]^+\) (blue, 47%) and \([\text{Fe}(\text{OO})(\text{tpenaH})]^3^+\) (green, 53%). Fitting in grey (\([\text{Fe}] = 2 \text{ mm}\), 30 equiv of \(\text{Et}_3\text{N}\) followed by 50 equiv of \(\text{H}_2\text{O}_2\)).


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followed by rapid freezing in liquid N$_2$. 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)]$^{2+}$ peroxide adducts are consistent with a side-on bound peroxide Fe$^{II}$ complex in [Fe$^{II}$(OO)(tpenaH)]$^{2+}$ by comparison with iron complexes of Rtpen (Table 1, R = Me, BzCH$_2$, PyCH$_2$). This species is potentially intramolecularly H-bonded, with the solid-state structure of [Cr(η$^2$-OO)(tpenaH)]$^+$ furnishing a structural analogue for the latter.\cite{25} The pendant pyridinium moiety of the tpenaH ligand is a second site available for deprotonation by a base, and [Fe$^{II}$(OO)(tpena)] is a plausible product from the reaction of [Fe$^{II}$(OO)(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 η$^1$- and η$^3$-OO$^2$-, 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 d$^5$ metal ion complexes [Fe(OIPh)(tpena)]ClO$_4$\cite{220} and [Mn(OH)$_2$(tpena)]ClO$_4$.\cite{226} The relatively open face presented by tpena in these structures suggests that formation of a heteroleptic complex with an η$^1$-diatomic ligand is also a reasonable structure for the peroxido complex, especially since η$^1$-OO$^-$ ligands are no more sterically demanding than monodentate oxide (O$^-$) ligands.\cite{227} Addition of further base leads to the formation of yellow solutions, with vigorous decomposition of H$_2$O$_2$ 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$^{3+}$...OO$^-$ and Fe$^{2+}$...OO$^-$ LMCT bands for the end-on hydroperoxido and side-on peroxido Fe$^{III}$-tpena complexes are at shorter wavelengths than those for the analogous Rtpen-based complexes. The

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**Table 1.** Spectroscopic properties of [[tpenaH]Fe-O-Fe(tpenaH)]$^{4+}$, fac-[Fe(tpena)]$^{2+}$, mer-[Fe(tpena)]$^{2+}$, [Fe(OOH)(tpenaH)]$^{2+}$, [FeOOO(tpenaH)]$^{4+}$, and related Fe$^{III}$-hydroperoxo and peroxo complexes of neutral N5 and N6 donor ligands.

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<th>$\nu_{\text{O-H}}$ [cm$^{-1}$]</th>
<th>$\Delta\nu$ [cm$^{-1}$]</th>
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<th>Mössbauer$^{(a)}$</th>
<th>EPR$^{(a)}$</th>
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</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 Fe$^{III}$ 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) $g$-values are denoted for $S = \frac{3}{2}$. All $g$ values were determined with X-band frequencies. (c) The UV/Vis absorption spectra of the two diastereoisomers fac-[Fe(tpena)]$^{2+}$ and mer-[Fe(tpena)]$^{2+}$ are dominated by the former, based on analysis of Mössbauer spectroscopic data.\cite{21} (d) Molar absorptivities were calculated using solutions showing the maximum chromophore absorbance achieved with 50 equiv of H$_2$O$_2$ at RT in MeCN. [e] The signs of the quadrupole splittings for [Fe(OOH)(metpen)]$^{2+}$ and [Fe(OOH)(btztpen)]$^{2+}$ were determined by applied parallel field Mössbauer spectroscopy; similar data for [Fe(OOH)(tpena)]$^{2+}$ are not available. (f) Measured under the same conditions as those applied to observe [Fe$^{III}$(OO)(tpena)]$^{2+}$ and [Fe$^{III}$(OO)(tpenaH)]$^{+}$ in this work [Fe$^{III}$(tpena)]$^{2+}$ with 50 equiv of H$_2$O$_2$ or 50 equiv of H$_2$O$_2$ plus 30 equiv of Et$_3$N, respectively. Calculated extinction coefficients for labile species should always be taken with caution, and it should be noted that we have observed that decay rates, and hence visible-light absorption, depend on concentration. (This and differences in handling) explain the difference between the molar absorptivities calculated from our measurements and those in the literature, which are otherwise internally consistent.

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**Scheme 5.** Single- and double-deprotonation of [Fe(OOH)(tpenaH)]$^{2+}$, leading to side-on peroxide coordination with speculative intramolecular hydrogen bonding.
\( \lambda_{\text{max}} \) for \([\text{Fe(OOH)(tpena)}H]^{2+}\) is hypsochromically shifted by about 20 nm, and the \( \lambda_{\text{max}} \) for \([\text{Fe}(\text{OO})\text{(tpena)}H]^{+}\) is shifted by 60, 75, and 95 nm compared to those reported for \([\text{Fe}(\text{OO})(\text{tpen})]^{-}\), \([\text{Fe}(\text{OO})(\text{metpen})]^{-}\), and \([\text{Fe}(\text{OO})(\text{bztpen})]^{-}\), respectively. The larger difference for the peroxido complexes may be related to the intramolecular H-bonding.

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

A large excess (20–50 equiv with respect to iron) of \( \text{H}_2\text{O}_2 \) is required to generate maximum steady-state concentrations of \([\text{Fe}(\text{OO})(\text{tpena})H]^{2+}\) and \([\text{Fe}(\text{OO})(\text{tpena})]^{+}\), 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; \( \lambda_{\text{exc}} = 322 \text{ nm} \)) confirmed that the gas evolved was predominantly \( \text{O}_2 \). Addition of \( ^{18}\text{O} \)-labelled water in a 1:1:1 ratio of \( \text{H}_2\text{O}_2:\text{H}_2\text{O}:\text{H}_2\text{O} \) mixture, confirmed that the \( \text{O}_2 \) evolved did not contain \( ^{18}\text{O} \) and hence that the two oxygen atoms in the evolved \( \text{O}_2 \) were derived from \( \text{H}_2\text{O}_2 \). Thus, \([\text{Fe}(\text{tpena})]^{1+}\) catalyses \( \text{H}_2\text{O}_2 \) disproportionation rather than a more demanding oxidation of water.[28] To the best of our knowledge, \( \text{H}_2\text{O}_2 \) disproportionation catalysed by exclusively N-donor Rtpen-supported iron(III) peroxides (Scheme 2 a; \( \text{R} = \text{CH}_2\text{PyCH}_2 \)) has not been reported.[10,11,12,29] 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(II) peroxides, we checked for this possible reaction in the present study by applying MIMS to monitor the reactions of \([\text{Fe}(\text{Cl})(\text{tpena})]^{2-}\) and \([\text{Fe}(\text{tpen})]^{2+}\) with 50 equiv of \( \text{H}_2\text{O}_2 \). We can verify that \( \text{O}_2 \) 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 hydroperoxido species, \([\text{Fe}(\text{OO})\text{(tpena)}H]^{2+}\), is not regenerated by the addition of a second portion (50 equiv) of \( \text{H}_2\text{O}_2 \) after the cessation of \( \text{O}_2 \) evolution, nor does catalytic \( \text{H}_2\text{O}_2 \) disproportionation resume. These observations indicate that either the catalyst is decomposed by \( \text{H}_2\text{O}_2 \) when the concentration of \( \text{H}_2\text{O}_2 \) 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 \( \text{H}_2\text{O}_2 \)) drives the formation of a kinetically inert oxido-bridged species \([\text{tpenaH}]\text{Fe}(\mu-\text{O})\text{Fe}(\text{tpenaH})]^{4+}.[24,30]\) To determine which of these pathways is pertinent, two equivalents of \( \text{H}_2\text{O}_2 \) were added to solutions of \([\text{Fe}(\text{tpena})]^{2+}\) in acetonitrile. A colour change to purple was not observed. Head-space infrared spectroscopy (HS-IRS), however, showed that \( \text{CO}_2 \) was produced. The only carbon sources available for \( \text{CO}_2 \) production were the solvent acetonitrile and/or tpena. Monitoring both the \( \text{O}_2 \) and \( \text{CO}_2 \) releases by MIMS (Figure 5 a) following the addition of 50 equiv of \( \text{H}_2\text{O}_2 \) revealed that \( \text{O}_2 \) was predominantly released in the early stages of the reaction. Quantitative analysis of the \( \text{CO}_2 \) release by HS-IRS showed that approximately seven \( \text{CO}_2 \) molecules per iron centre (Figure 5 b) were produced. Increasing the amount of

\( \text{H}_2\text{O}_2 \) added did not result in an increase in \( \text{CO}_2 \) formation, and it can therefore be concluded that the source of \( \text{CO}_2 \) was degradation of tpena rather than oxidation of acetonitrile. Specifically, the \( \text{CO}_2 \) 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 \( \text{H}_2\text{O}_2 \) were monitored by UV/Vis absorption, Raman, EPR, and Mössbauer spectroscopies. The band at 520 nm due to the purple \([\text{Fe}(\text{OO})(\text{tpena})H]^{2+}\) chromophore decayed completely, and then a new and more intense band appeared at 469 nm (Figure 6 a). 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 \( \text{CO}_2 \) 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](https://www.chemeurj.org/)

**Figure 5.** Detection of \( \text{O}_2 \) and \( \text{CO}_2 \) release. a) MIMS spectra of \([\text{Fe}(\text{tpena})]^{2+}\) (0.5 mm in acetonitrile) (black) and 2 min after addition of 50 equiv of \( \text{H}_2\text{O}_2 \) (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 \( \text{O}_2^{2+} \) (m/z 32) and \( \text{CO}_2^{+} \) (m/z 44). b) Time-resolved head-space FTIR spectroscopy showing evolution of \( \text{CO}_2 \) upon reaction of \([\text{Fe}(\text{tpena})]^{2+}\) (2 mm) with 50 equiv of \( \text{H}_2\text{O}_2 \). 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 \( \text{CO}_2 \) and \( \text{O}_2 \).
2.44, 2.29, 1.86, and a signal at 634, 1192, and 2094 cm$^{-1}$ appeared in the Raman spectrum ($\nu_{\text{acc}} = 532$ nm) of equivalently treated solutions (Figure 6c). The band at $\nu = 2094$ cm$^{-1}$ is consistent with the presence of Fe$^4$-coordinated acetonitrile. A $^1$H NMR spectrum of the reaction mixture in CD$_3$CN recorded after 16 h (and hence coinciding with the presence of the EPR-silent species with an absorption at 469 nm showed the characteristic signal of NH$_3$ (three resonances of equal intensity centred at $\delta = 6.61$ ppm, $J_{\text{NH}-\text{H}} = 52$ Hz; Supporting Information, Figure S52). This demonstrated that the production of NH$_3$ occurred concomitantly with the production 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. Overall, the data lead to the conclusion that reaction of $[\text{Fe}(\text{tpena})]^2^{+}$ with a large excess of H$_2$O$_2$ results primarily in H$_2$O$_2$ disproportionation, but is accompanied by concurrent oxidative decay 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 $[\text{Fe}^4(\text{tpena})]^2^{+}$.

**Catalytic alcohol oxidation overrides catalase activity and ligand decomposition**

In stark contrast to the reactions of $[\text{Fe}^4(\text{Cl})(\text{Rtpena})]^+$ with excess H$_2$O$_2$ in methanol,$[10, 11, 17]$ the addition of 50 equiv of H$_2$O$_2$ to solutions of $[\text{Fe}^4(\text{tpena})]^2^{+}$ in methanol does not give rise to detectable amounts of purple $[\text{Fe}^6(\text{OOH})(\text{tpena})]^2^{+}$. 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 $[\text{Fe}^4(\text{tpena})]^2^{+}$ 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$^{[36]}$). The addition of 50 equiv of H$_2$O$_2$ to $[\text{Fe}(\text{tpena})]^2^{+}$ in the presence of 500 equiv of benzyl alcohol did not result in either O$_2$ or CO$_2$ evolution, and hence...
Neither H₂O₂ disproportionation nor tpena decomposition occurred. In contrast to the reactions performed in methanol, under these conditions, [Fe⁴⁺(O)(tpenaH)]²⁺ was observed spectroscopically due to the lower concentration of the oxidant substrate. The addition of a second portion of H₂O₂ (50 equiv) resulted in reappearance of the absorption band of [Fe⁴⁺(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 eventual loss of tpenaH oxidation competes with alcohol oxidation and the presence of a large excess of alcohol, or its use as the solvent delays the onset of ligand oxidation. ¹H NMR spectroscopic analysis showed, after five additions of 50 equiv of H₂O₂ over 10 min, 50% conversion of benzyl alcohol to benzaldehyde and hence near-stoichiometric conversion with respect to the oxidant. A control reaction in the absence of [Fe(tpena)]²⁺ showed that, under otherwise identical conditions, benzyl alcohol was oxidized by H₂O₂ with only 32% conversion after 20 h.¹³¹

**Mechanistic considerations**

The reaction of [(tpenaH)Fe-O-Fet(tpenaH)]⁺ with Ce⁶⁺ in water produces the iron(IV) oxo complex, [Fe⁴⁺(O)(tpenaH)]²⁺ and recently we have generated this same species electrochemically, also in water.¹³¹ In both of these studies, we demonstrated [Fe⁴⁺(O)(tpenaH)]²⁺ to be a promising 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)(tpenem)]²⁺ can be generated by homolytic cleavage of [Fe(OOH)(tpenem)]²⁺, and it is the Fe⁴⁺ oxo species that reacts with substrates.¹³⁶ This reaction has been demonstrated in the gas phase.¹³¹ 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 [Fe⁴⁺(OOH)(tpenaH)]²⁺.

This reactivity is in contrast to the behaviour of Fe⁴⁺-OOH based on neutral N₅ donor systems. In fact, peroxide dissociation¹³⁷,¹³⁸ is a highly competitive pathway for the decomposition of (NS)Fe⁴⁺-OOH species. It can thus be concluded that for the iron-tpena system, homolytic O–O bond cleavage occurs in [Fe⁴⁺(OOH)(tpenaH)]²⁺, resulting in the formation of [Fe⁴⁺(O)(tpenaH)]²⁻ and a hydroxyl radical. Both are aggressive hydrogen-atom abstractors and will react with methanol, benzyl alcohol, and hydrogen peroxide to form the methanol, benzoyl, and hydroperoxide (CH₃OH, C₆H₅CHOH, ‘OOH) radicals, respectively. In turn, these radicals will propagate chain reactions and radical terminations to give the detected products, C₆H₅O, C₆H₅CHO, and O₂. Interconnected catalytic cycles for H₂O₂ disproportionation and alcohol oxidation are proposed in Scheme 6.

**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)ethyleneamine²³ (N₄py) systems, the influence of a biomimetic carboxylato donor is demonstrated by the significant difference in Fe⁴⁺/Fe⁶⁺ redox potentials of the parent [Fe(tpen)]²⁻ and [Fe(tpena)]²⁻ 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-Fe⁴⁺ complexes are isolated, and these are redox-stable in the +3 oxidation state in all solvents examined.²⁰⁻¹ This result stands in contrast to observations for the complexes of tpen and related N₅ neutral pentadentate ligands (Scheme 2a), for which the iron(II) complexes are those most readily isolated, especially in solvents such as acetonitrile. These are thermodynamic sinks,
retarding their reactivity with H$_2$O$_2$. 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 Fe$^{IV}/V$ couple can be reasonably expected to follow this trend towards lower potentials,[38] and this will favour promotion of the homolytic cleavage of the Fe$^{IV}$O–OH bond in the hydroperoxide adduct to readily attain an iron(IV) oxo species. This is manifested in significantly shorter lifetimes for [Fe(OOH)(tpenaH)]$^{2+}$ and [Fe(OO)(tpenaH)]$^+$ compared to the corresponding systems based on N5/N6 Rtpen ligands. A further contrast to the N5/N6 donor-supported systems for the reaction of H$_2$O$_2$ with the resting state iron(III) in [Fe(tpena)]$^{2+}$ is that no deprotonation of the H$_2$O$_2$ is needed. It is an addition reaction accompanied by charge separation due to concomitant pyridine decoordination and pyridinium formation. The ligand is converted from monooanionic hexadentate (tpena) to zwitterionic pentadentate (tpenAH). With one carbonylato donor and a second base in the coordination sphere, [Fe(OOH)(tpenaH)]$^{2+}$ and its conjugate base [Fe(OO)(tpenaH)]$^+$ are particularly germane biometrics for non-heme iron(III) peroxides. The peroxide activation chemistry that we have observed is pertinent to elucidating mechanisms for O$_2$-activating enzymes in which Gly/Asp groups are coordinated to the O$_2$-binding site on iron.[39] In particular, we note that the non-heme 1 Asp/3 His-coordinated iron superoxide dismutase[39] evolves O$_2$ in a similar manner to the Fe-tpena system studied here (although the disproportionation, 3) catalytic H$_2$O$_2$ disproportionation, 3) catalytic alkoxy oxidation with stoichiometric yields, and 4) total destruction of the aliphatic part of tpena in the presence of low concentrations of H$_2$O$_2$. By tuning the pentadentate ethylenediamine-backboned ligands (Scheme 2), a tendency towards the limiting reaction types depicted in Equations (2), (3), and (4) for Fe$^{IV}$-peroxide adducts has been exposed. It seems that H$_2$O$_2$ activation is more effective for the carbonylato 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 H$_2$O$_2$ 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:

\[
[Fe^{IV}(OOH)(Rbpena)]^{2+} + HX = [Fe^{IV}(X)(Rbpena)]^{2+} + HOOH \tag{2}
\]

O–O heterolysis:

\[
[Fe^{IV}(OOH)(Rbpena)]^{2+} \rightarrow [Fe^{IV}(RbpenaO)]^{2+} + OH^- \tag{3}
\]

O–O homolysis:

\[
[Fe^{IV}(OOH)(tpenaH)]^{2+} \rightarrow [Fe^{IV}(O)(tpenaH)]^{2+} + OH^- \tag{4}
\]

Our work not only presents a germane mimic for non-heme iron chemistry, especially in terms of the carbonylato group and the second coordination sphere base, but also adds to our knowledge of the ligand design features important for activating H$_2$O$_2$, demonstrates controllable bifurcation in catalysed external substrate oxidation reactions, and indicates that destruct-

Conclusions

Methanol oxidation to formaldehyde and stoichiometric yields of benzaldehyde from the [Fe(tpena)]$^{2+}$-catalysed oxidation of benzyl alcohol by H$_2$O$_2$ have been realized in the present study. In the absence of a large excess of a second substrate, H$_2$O$_2$ disproportionation is catalysed by [Fe(tpena)]$^{2+}$ through a related mechanism. However, in the absence of other oxidizable substrates (methanol, benzyl alcohol, and H$_2$O$_2$), oxidative decay of [Fe(tpena)]$^{2+}$ occurs through the spectroscopically detectable intermediate [Fe(OOH)(tpenaH)]$^{2+}$. Release of all of the aliphatic carbon atoms and amine groups as CO$_2$ and NH$_3$, 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 H$_2$O$_2$, respectively. Overall, the H$_2$O$_2$ activation chemistry described here stands in contrast to that reported previously for the pentadentate NS supporting ligands [Fe$^{IV}$(OOH)(Rbpena)]$^{2+}$ and [Fe$^{IV}$(OOH)(N4py)]$^{2+}$ and a carboxylato-containing N4O pentadentate supporting ligand [Fe$^{IV}$/(OOH)(Rbpena)]$^{2+}$. We have shown: 1) facile homolytic Fe$^{IV}$O–OH cleavage in solution to produce two aggressive H-atom abstractors, Fe$^{IV}$O and HO; 2) catalytic H$_2$O$_2$ disproportionation, 3) catalytic alkoxy oxidation with stoichiometric yields, and 4) total destruction of the aliphatic part of tpena in the presence of low concentrations of H$_2$O$_2$. By tuning the pentadentate ethylenediamine-backboned ligands (Scheme 2), a tendency towards the limiting reaction types depicted in Equations (2), (3), and (4) for Fe$^{IV}$-peroxide adducts has been exposed. It seems that H$_2$O$_2$ activation is more effective for the carbonylato 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 H$_2$O$_2$ 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.

\[
[Fe^{IV}(OOH)(Rbpena)]^{2+} + HX = [Fe^{IV}(X)(Rbpena)]^{2+} + HOOH \tag{2}
\]

O–O heterolysis:

\[
[Fe^{IV}(OOH)(Rbpena)]^{2+} \rightarrow [Fe^{IV}(RbpenaO)]^{2+} + OH^- \tag{3}
\]

O–O homolysis:

\[
[Fe^{IV}(OOH)(tpenaH)]^{2+} \rightarrow [Fe^{IV}(O)(tpenaH)]^{2+} + OH^- \tag{4}
\]

Our work not only presents a germane mimic for non-heme iron chemistry, especially in terms of the carbonylato group and the second coordination sphere base, but also adds to our knowledge of the ligand design features important for activating H$_2$O$_2$, demonstrates controllable bifurcation in catalysed external substrate oxidation reactions, and indicates that destruct-

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tive oxidation of the supporting ligand can be avoided through appropriate experimental design [Eqs. (2–4)].

**Experimental Section**

**Materials and preparations**

$N,N,N$-Tris-(2-pyridylmethyl)ethylenediamine-$N'$-acetic acid (tpenaH)$_{2.0}$, [(tpenaH)Fe-O-Fe(tpenaH)]$^2$[ClO$_4$]$_2$($H_2$O)$_2$, [(tpena)tpen(PF$_6$)$_2$], [(tpena)Cl(tpena)EtOH]$_2$, and [(Fe(tpena)][ClO$_4$]$_2$ were prepared as described previously. [(tpenaH)[Fe-O-Fe(tpenaH)]$^4$]$_2$ClO$_4$·H$_2$O$^2$ was dissolved in acetonitrile and the solution was allowed to stand for 10 min until [(tpenaH)Fe-O-Fe(tpenaH)]$^4$ had dehydrated to [Fe(tpena)]$^2$. This solution was then treated with 50 equiv of $H_2$O$_2$ (50% in water, w/w) to give [Fe(OOH)(tpena)]$^3$ and [Fe(OO)(tpena)]$^4$ was formed by the subsequent addition of 30 equiv of Et$_3$N.

**[Fe(ClO$_4$)(tpena)]$^2$[EtOH]$_2$H$_2$O:** Fe(ClO$_4$)$_2$·$H_2$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 volatiles, yellow crystals of [FeCl(tpenaH)]$^2$[EtOH]$_2$H$_2$O (702 mg, 54%) were deposited after two weeks. ESI-MS (MeCN): m/z: 479.1 ([Fe(Cl)(tpena)-2H$_2$O]$^+$, 78%), 481.1 ([Fe(tpena)]$^2$+, 81%), 482.1 ([Fe(tpena)]$^2$+, 100%). ESI-MS ($H_2$O): m/z: 446.1 ([Fe(tpena)]$^4$+, 34%), 454.1 ([tpena]Fe-O-Fe(tpena)]$^4$+, 100%), 463.1 ([Fe(OH)$(tpena)]^2+$, 85%); IR (KBr): v = 1610 (C=O, s), 1098 cm$^{-1}$ (ClO$_4$ $\cdot$ vs); elemental analysis calcd (%) for $C_{22}H_{29}N_5O_{12}Cl_3Fe$: 446.1 ([Fe(tpena)]$^2$+, 100%).

**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 Spectro Scan600 with a Quantum Northwest TC 125 temperature controller. Raman spectra were recorded from samples in 1 cm quartz cuvettes at either 532 nm (300 mW at source, Cobalt Lasers) or 691 nm (75 mW at sample, Ondax Lasers). The solutions were cooled with a Quantum Northwest TC 125 temperature controller and the spectra were obtained at $-30\, ^\circ\mathrm{C}$. Data were recorded and processed using Solis (Andor Technology) with spectral calibration with respect to the Raman spectrum of MeCN/toluene (50/50, w/w). Baseline correction was performed for all spectra, and normalised to the solvent band at 750 cm$^{-1}$. EPR spectra (X-band) were recorded on a Bruker EMX Plus CW spectrometer (mod. amp.: 10 G, attenuation: 10 dB) on frozen solutions at 110 K. In order to follow the decay of the iron species, the samples for measurements (200 µL) were transferred to EPR tubes and frozen in liquid nitrogen at different times. The software packages eview4vr and esimX were used for simulation. $^1$H NMR (400.12 MHz) spectra were recorded on a Bruker Avance III 400 spectrometer at ambient temperature. Chemical shifts are denoted relative to the residual solvent peak (CD$_3$CN, 1.94 ppm). Mössbauer spectra were obtained with conventional constant acceleration spectrometers with sources of $^{57}$Co in rhodium foil. The spectra were collected at 14 K. Isomer shifts are given relative to that of α-Fe at 295 K. Infrared spectra (IR) were obtained on a Hitachi 270-30 IR spectrometer from samples in KBr pellets. Head-space FTIR spectra were recorded from samples in sealed 1 cm quartz cuvettes on a JASCO FT-NIR/MIR-4600 spectrometer with a resolution of 8 cm$^{-1}$. The concentration of CO$_2$ released was quantified on the basis of standard solutions of Na$_2$CO$_3$ in water with addition of 3 equiv acid (HCl) to force the release of CO$_2$. Aliquots (1 mL) of the solution were placed in a sealed cuvette, and the head-space was measured before and after the addition of acid. A standard curve based on the absorbance at 2360 cm$^{-1}$ was fitted to [CO$_2$] < 5 mm: $A$ (2360 cm$^{-1}$) = 0.0300 mm$^{-1}$·[CO$_2$] + 0.0084 and [CO$_2$] > 5 mm: $A$ (2360 cm$^{-1}$) = 0.0281 mm$^{-1}$·[CO$_2$] + 0.0213. MIMS spectra were recorded using a Prisma quadrupole mass spectrometer (Pfeiffer Vacuum, Asllar, Germany). A flat sheet membrane (250 µm) of polydimethylsiloxane (Sil-Tec sheeting, Technical Products, Decatur, GA, USA) separated the vacuum chamber (1× 10$^{-3}$ mbar) from the solution in the sample chamber (total volume 2.5 mL), which was stirred mechanically. The data were recorded and processed using Quadstar 422 (Pfeiffer Vacuum, Asllar, Germany). The reaction chamber was filled with a solution of [Fe(tpena)]$^2$, and H$_2$O$_2$ was injected directly into the solution in the sample chamber as the resulting gas evolution was simultaneously measured. Electrospray ionisation (ESI) mass spectra were recorded in high-resolution positive-ion mode on a Bruker microTOF-QII mass spectrometer. Single-crystal X-ray diffraction data were collected on a Rigaku R-Axis IIC image-plate system (Mo$_{\alpha\alpha}$ radiation) at 100 K. Cyclic voltammetry was performed on an Eco Chemie Autolab PGSTAT10 potentiostat/galvanostat using a standard three-electrode setup with a Pt disc as the working electrode, an Ag/AgCl as the reference electrode (0.11 m AgNO$_3$ in 0.1 m TBAClO$_4$ in MeCN; TBA: tert-butylammonium). 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 of Fe(III) ·Fe$^{\text{IV}}$ against Ag/Ag$^+$ was measured as 0.08 V, and all oxidation potentials were converted accordingly.

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**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

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Peroxide activation at Fe: A transient Fe<sup>III</sup>-hydroperoxide intermediate has been spectroscopically identified during [Fe<sup>III</sup>(tpena)]<sup>2+</sup>-catalysed H<sub>2</sub>O<sub>2</sub> disproportionation in acetonitrile (see graphic). If benzyl alcohol is present, or methanol is used as solvent, H<sub>2</sub>O<sub>2</sub> disproportionation is inhibited in favour of high-yielding alcohol oxidation to the corresponding aldehyde. In the absence of excess substrate (alcohol or H<sub>2</sub>O<sub>2</sub>), tpena is oxidatively degraded.