μ-1,2-Peroxo-diferric intermediates (P) of non-heme diiron enzymes are proposed to convert upon protonation either to high-valent active species or to activated P′ intermediates via hydroperoxo-diferric intermediates. Protonation of synthetic μ-1,2-peroxo model complexes occurred at the μ-oxo and not at the μ-1,2-peroxo bridge. Here we report a stable μ-1,2-peroxo complex {FeIII(μ-O)(μ-1,2-O2)FeIII} using a dinucleating ligand and study its reactivity. The reversible oxidation and protonation of the μ-1,2-peroxo-diferric complex provide μ-1,2-peroxo FeIVFeIII and μ-1,2-hydroperoxo-diferric species, respectively. Neither the oxidation nor the protonation induces a strong electrophilic reactivity. Hence, the observed intramolecular C-H hydroxylation of preorganized methyl groups of the parent μ-1,2-peroxo-diferric complex should occur via conversion to a more electrophilic high-valent species. The thorough characterization of these species provides structure-spectroscopy correlations allowing insights into the formation and reactivities of hydroperoxo intermediates in diiron enzymes and their conversion to activated P′ or high-valent intermediates.
Non-heme diiron enzymes are employed by nature to activate dioxygen for various catalytic oxidation and/or oxygenation reactions\(^1,2\). Their catalytic cycles generally employ a diferrous form that reacts with dioxygen to a peroxo-diferric intermediate (P, Fig. 1a). The active species is supposed to be either this peroxo-diferric species or a species derived from it. In soluble methane monooxygenase (sMMO)\(^3,4\), the pero xo intermediate P converts to a high-valent Fe\(^{III}\)Fe\(^{IV}\) active species (Q, Fig. 1a)\(^5,6\). Kinetic studies revealed a pH-dependence indicating that this step is proton-promoted\(^7,8\). The site of protonation is still unknown. Proposals include protonation of the pero xo ligands resulting in bridging \(\mu-1,1\)- or \(\mu-1,2\)-hydroperoxo ligands\(^9,10\). In other non-heme diiron enzymes\(^11-14\), a pero xo activation step has been proposed by the conversion of P-type to P'-type intermediates that lack the pero xo \(\rightarrow\) Fe\(^{III}\) LMCT around 14,000–15,000 cm\(^{-1}\) and the higher Mössbauer isomer shift characteristic for P-type intermediates. For this pero xo activation step, also a protonation has been suggested\(^15,16,20\). For the two diiron arylamine oxygenases AorF and CniI, \(\mu-1,2\)-hyd pero xo\(^15\) and \(\mu-1,1\)-peroxo intermediates\(^21\) have been proposed, respectively, or a, \(\mu-1,1\)-hydroperoxo intermediate for both (Fig. 1a)\(^14\).

Syntheses and detailed spectroscopy and reactivity studies of \(\mu-1,2\)-peroxo-diferric model complexes\(^22-35\) provided not only important structure-spectroscopy correlations to establish pero xo intermediates in the enzymes but also variations in their stabilities and reactivities by slight variations of the ligands. In most cases, the \(\mu-1,2\)-peroxo-diferric species could only be identified spectroscopically as transient intermediates. Interestingly, protonation of different complexes with a [Fe\(^{III}\)(\(\mu-O\)(\(\mu-1,2\)-O\(_2\))Fe\(^{III}\))]\(^{2+}\) core afforded \(\mu\)-hydroxo-bridged [Fe\(^{III}\)(\(\mu-O\)(\(\mu-1,2\)-O\(_2\))Fe\(^{III}\))]\(^{2+}\) species\(^22,27,36\) questioning the principle accessibility of hydroperoxy-diferric species.

Here, we present the synthesis, characterization, and reactivity of the rationally stabilized \(\mu-1,2\)-peroxo complex ([susan\(^6\)\(^{Me}\)]\(\mu-\)(\(\mu-1,2\)-O\(_2\))Fe\(^{III}\))]\(^{3+}\) using the dinucleating ligand susan\(^6\)\(^{Me}\) (Fig. 1b)\(^37-39\). This \(\mu-1,2\)-peroxo complex is stable even in solution at \(-40\) °C and shows nucleophilic character of the \(\mu-1,2\)-peroxo ligand attenuated for exogenous organic substrates by encapsulation of the ligand scaffold. ([susan\(^6\)\(^{Me}\)]\(\mu-\)(\(\mu-O\_2\))Fe\(^{III}\))]\(^{2+}\) is reversibly oxidized to the high-valen t \(\mu-1,2\)-peroxo complex ([susan\(^6\)\(^{Me}\)]Fe\(^{IV}\)(\(\mu-O\)(\(\mu-1,2\)-O\(_2\)))Fe\(^{III}\))]\(^{3+}\) and reversibly protonated to the \(\mu-1,2\)-hydroperoxo complex ([susan\(^6\)\(^{Me}\)]Fe\(^{III}\)(\(\mu-O\)(\(\mu-1,2\)-O\(_2\))Fe\(^{III}\))]\(^{3+}\). The study of the electrophilic reactivity for oxygen-atom transfer (OAT) using PPh\(_3\) and hydrogen-atom transfer (HAT) using DHA and TEMPOH provides not only a low electrophilic character of the parent \(\mu-1,2\)-peroxo-Fe\(^{III}\)Fe\(^{III}\) complex but also for the oxidized \(\mu-1,2\)-peroxo-Fe\(^{IV}\)Fe\(^{III}\) and protonated \(\mu-1,2\)-hydroperoxo-Fe\(^{III}\)Fe\(^{III}\) species. Only the oxidized \(\mu-1,2\)-peroxo-Fe\(^{IV}\)Fe\(^{III}\) species reacts with the relatively weak substrate TEMPOH. The determination of the \(pK_a\) = 9.5 ± 0.1 and the bond dissociation free energy BDE(FeOH)\(_{CH\_CN}\) = 7.8 ± 2 kcal mol\(^{-1}\) of the protonated \(\mu-1,2\)-hydroperoxo-Fe\(^{III}\)Fe\(^{III}\) species quantifies the low electrophilic character even of the oxidized \(\mu-1,2\)-peroxo-Fe\(^{III}\)Fe\(^{III}\) species. Therefore, the intramolecular C–H activation of preorganized 6-methyl pyridine groups to benzylalcoholato and carboxylato donors in the parent \(\mu-1,2\)-peroxo-Fe\(^{III}\)Fe\(^{III}\) complex should not occur via the \(1,2\)-peroxo-ligand but via conversion to a more reactive but fluent high-valent species. The low electrophilic character and the spectroscopic signatures of this \(\mu-1,2\)-hydroperoxo-diferric model are discussed in relation to assignments of reactive intermediates postulated for diiron enzymes.

**Results**

The complex ([susan\(^6\)\(^{Me}\)]Fe\(^{III}\)(\(\mu-O\)(\(\mu-1,2\)-O\(_2\))Fe\(^{III}\))]\(^{2+}\). The reaction of susan\(^6\)\(^{Me}\) and Fe(ClO\(_4\))\(_2\) in H\(_2\)O provided ([susan\(^6\)\(^{Me}\)]Fe\(^{III}\)(\(\mu-OH\)Fe\(^{II}\))(ClO\(_4\))\(_2\)) (Fig. S1a) and subsequent reaction with O\(_2\) at \(-15\) °C the \(\mu-1,2\)-peroxo complex ([susan\(^6\)\(^{Me}\)]Fe\(^{III}\)(\(\mu-O\)(\(\mu-1,2\)-O\(_2\))Fe\(^{III}\))]\(^{2+}\) (Fig. 2a). Single-crystal X-ray diffraction provides an asymmetric core structure: the \(\mu-1,2\)-peroxo ligand is coordinated with O\(_1\) trans to a tert-amine (N\(_2\)) and O\(_2\) trans to O\(_1\). The Fe\(^{III}\)-hyd pero xo-Fe\(^{III}\) and Fe\(^{III}\)-hydroperoxo-Fe\(^{III}\) species quantitatively to the exchange coupling.

**Fig. 1** Structural formula. a Supposed intermediates in non-heme diiron enzymes. b The dinucleating ligands susan and susan\(^6\)\(^{Me}\). c The mononucleating ligand 6Me\(_2\)BPP\(_2\).
Temperature-dependence of the effective magnetic moment, of [(susan6-Me){Fe\(III\)(μ-O)(μ-\(O_2\))Fe\(III\)}(ClO\(_4\))]\(_2\). The solid line is a simulation to the spin-Hamiltonian (1) in the Supplementary Information with \(J = -155 \text{ cm}^{-1}\), \(g = 2.05\), 0.2% p.i. (\(S = 5/2\)) of same molecular mass and \(\Theta_{m,p} = -8 \text{ K}\). a UV-Vis-NIR spectrum of [(susan6-Me){Fe\(III\)(μ-O)(μ-\(O_2\))Fe\(III\)}(ClO\(_4\))]\(_2\) dissolved in CH\(_3\)CN at -10 °C and the ligand susan6-Me for comparison.

We synthesized all four possible \(^{18}\text{O}^{18}\text{O}_2\)-isotopomers as microcrystalline solids. The resonance Raman (rR) and FTIR spectra (Fig. 3) both reveal several \(^{18}\text{O}\)-sensitive vibrations, which allow their assignments to the \([\text{Fe}^{III}(\mu-O)(\mu-1,2-\text{O}_2)\text{Fe}^{III}]\) core (Table 2)\(^{22,29}\). Only slight changes are observed upon dissolution in CH\(_3\)CN (Fig. S9). The 831 cm\(^{-1}\) band for the two \(^{16}\text{O}_2\)-isotopomers is assigned to the \(\nu(\text{O}-\text{O})\) stretch by isotopic labeling \((\Delta(16\text{O}_2-18\text{O}_2) = 46 \text{ cm}^{-1}\) consistent with a Hooke’s law calculation for a harmonic O–O vibration of 48 cm\(^{-1}\).

The \(\nu(\text{O–O})\) stretch of the crystallographically characterized \([\text{Fe}^{III}(\mu-O)(\mu-1,2-\text{O}_2)\text{Fe}^{III}] (6\text{Me}_2\text{BPP})\) \((\text{6Me}_2\text{BPP})\) (A) appears at higher energy at 847 cm\(^{-1}\) (Table 2)\(^{22}\). Higher \(\nu(\text{O–O})\) stretches were attributed\(^{22}\) to increasing \(\angle(\text{Fe–O–O})\) angles\(^{11}\). However, \(\angle(\text{Fe–O–O})\) is slightly smaller in A than in our complex (115° vs 117°). Interestingly, the lower \(\nu(\text{O–O})\) stretch correlates with a longer O–O distance (1.432(2) Å vs 1.411 Å) indicating a stronger dependence of \(\nu(\text{O–O})\) on \(d(\text{O–O})\) than on \(\angle(\text{Fe–O–O})\).

[(susan6-Me)Fe\(III\)(\(\mu\)-(1,2-\(O_2\))Fe\(III\))]\(_{2}^{2+}\) shows no indication of decay for hours in CH\(_3\)CN at -40 °C (Fig. S10). This stability provides the opportunity for the electro- and spectroelectrochemical investigation of a peroxy-diferric complex. [(susan6-Me)Fe\(III\)(\(\mu\)-O)(\(\mu\)-O\(\_2\))Fe\(III\))]\(_{2}^{2+}\) can be reversibly oxidized at \(E_{1/2}^{ox} = 0.55\) V and irreversibly reduced at \(E_{p}^{red} = -1.28\) V vs Fc+/Fc (Fig. 4a).

Oxidation to [(susan6-Me)Fe(\(\mu\)-O)(\(\mu\)-1,2-\(O_2\))Fe\(^{3+}\)]. Coulometric oxidation of [(susan6-Me)Fe\(III\)(\(\mu\)-(1,2-\(O_2\))Fe\(III\))]\(_{2}^{2+}\) at 0.68 V vs Fc+/Fc (1.18 C, 98% of one-electron) in CH\(_3\)CN at -40 °C resulted in slight changes of the absorption features.
(Fig. 4b). Re-reduction at 0.16 V vsFc+/Fc (0.92 C, 76% of one-electron) restored the initial UV-Vis spectrum to ~95% (Fig. 4c and Fig. S11). The lower charge necessary for re-reduction implies some chemical reduction during the coulometric experiments (1 h, Fig. S12).

Chemical oxidation with thianthrenium perchlorate ((thia)ClO4) generated the UV-Vis spectrum of [(susan6-Me)Fe(μ-O)(μ-1,2-O2)FeIII]3+ (Fig. 4d) within 10 s. Addition of excess NEt3 as aSplit by Fermi-resonance.

Table 1 Compilation of experimental (on solids or on frozen CH3CN solutions) and DFT-calculated (shown in italics) 57Fe Mössbauer parameters of the complexes reported here and some complexes with the ligands susan and susan6-Me for comparison.

| Complex                          | δ/mm s⁻¹ | |ΔE₂O|/mm s⁻¹ | T/K | ref. |
|----------------------------------|----------|----------|----------|----------|----------|----------|
| [(susan6-Me)Fe(μ-OH)FeII]2⁻     | Solid    | 1.13     | 2.23     | 80       | a        |
| [(susan6-Me)FeIII(μ-O)(μ-1,2-O2)FeIII]2⁺ | Solid    | 0.53     | 1.69     | 80       | a        |
| CH3CN                            | 0.53     | 1.68     | 80       | a        |
| Solid                            | 0.49     | 1.68     | 200      | a        |
| DFT: FeI                         | 0.58     | -1.28    |          |          |          |
| Fe2                              | 0.53     | -1.45    |          |          |          |
| DFT: FeIV1 FeIII2 configuration  | FeIV1    | 0.17     | +1.00    |          | a        |
| FeIV2                            | 0.43     | -1.21    |          |          | a        |
| FeIII                            | 0.14     | +0.67    |          |          | a        |
| [(susan6-Me)FeIII(μ-O)(μ-1,2-O2)FeIII]3⁺ | CH3CN    | 0.27     | +0.57    | 180      | a        |
|                                  |         | 0.39     | -1.29    |          |          |
| DFT: FeIV1 FeIV2 configuration   | FeIV1    | 0.17     | +1.00    |          | a        |
| FeIV2                            | 0.43     | -1.21    |          |          | a        |
| FeIII                            | 0.14     | +0.67    |          |          | a        |
| [(susan6-Me)FeIII(μ-O)(μ-1,2-OOH)FeIII]3⁺ | CH3CN    | 0.49     | 2.48     | 80       | a        |
|                                  |         | 0.45     | 1.37     |          |          |
| DFT: μ-peroxy-O1 protonated      | FeI      | 0.54     | -1.69    |          | a        |
|                                  | Fe2      | 0.47     | -1.38    |          |          |
| DFT: μ-peroxy-O2 protonated      | FeI      | 0.49     | +1.05    |          | a        |
|                                  | Fe2      | 0.48     | -2.51    |          |          |
| DFT: μ-peroxy-O3 protonated      | FeI      | 0.61     | -1.74    |          | a        |
|                                  | Fe2      | 0.56     | -0.97    |          |          |
| [(susan6-Me)FeIII(μ-O)(FeIII)2⁺   | Solid    | 0.47     | 1.38     | 80       | 40       |
|                                  |         | 0.45     | 1.68     | 80       | 61       |
| [(susan6-Me)FeIII(μ-O)(FeIII)(OH)2⁺ | CH3CN    | 0.45     | 1.71     | 80       | 62       |

*This work
Quadrapole splittings provided without a sign represent absolute values |ΔE₂O| obtained from zero-field Mössbauer spectra. The signs provided for [(susan6-Me)FeIII(μ-O)(μ-1,2-O2)FeIII]3⁺ were extracted from fits to the magnetic Mössbauer spectra, while signs provided for DFT-calculated values arise from the DFT calculations. Atom labeling scheme related to Fig. 2a.

Characterization of [(susan6-Me)Fe(μ-O)(μ-1,2-O2)FeIII]3⁺. The EPR spectrum of [(susan6-Me)Fe(μ-O)(μ-1,2-O2)FeIII]3⁺ (Fig. 5a, S13) shows a broad anisotropic S = 1/2 signal with g = (2.272, 2.152, 2.021). Mössbauer spectroscopy (vide infra) demonstrates that the iron ions remain high-spin ruling out an interpretation as FeIII l.s. species. The severe deviation of gav > 2.15 from 2.0023 and the large g-anisotropy demonstrate a strong contribution of orbital angular momentum and rule out a ligand-centered oxidation to a μ-oxo,μ-1,2-peroxo-FeIIIFeIII complex, disclosing a metal-centered oxidation to a μ-oxo,μ-1,2-peroxo-FeIIIFeIII complex with antiferromagnetically coupled FeIV(S1 = 2) and FeIII(S2 = 5/2) ions. The FeIV h.s. S1 = 2 configuration results in g1 < 2.0 by spin-orbit coupling, while the FeIII h.s. is close to isotropic g2 = 2.0046. Projection of the local spins onto the antiferromagnetic S1 = 1/2 ground state47 results in gav > 2.00 for the S2 = 1/2 as observed experimentally39. Despite significant efforts, we were not able to obtain resonance-enhanced Raman features of [(susan6-Me)Fe(μ-O)(μ-1,2-O2)FeIII]3⁺ by excitation at 647 (15,500), 568 (17,600), and 514 nm (19,500 cm⁻¹) corresponding to the three absorption features of this oxidized complex.

Table 2 Vibrational (resonance Raman and FTIR) frequencies (cm⁻¹) and isotopic shifts together with some metrical parameters for [(susan6-Me)FeIII(μ-O)(μ-1,2-O2)FeIII]3⁺ and comparisons to those for A.

| Parameter              | exp. rR | exp. FTIR | Δ22   |
|------------------------|---------|-----------|-------|
| v(O-O) [Δ18O, Δ18O, Δ18O, Δ18O] | 831 [0, -46, -46] | 831 [0, -46, -46] | 847 [-, -33, -] |
| νFe(Fe-Fe) [Δ18O, Δ18O, Δ18O, Δ18O]  | 687 [-35, 0, -37] | 686 [-32, 0, -34] | 695 [-, -2, -] |
| νFe(Fe-O) [Δ18O, Δ18O, Δ18O, Δ18O]  | 510 [0, 25, -] | n.o. | n.o. |
| νFe(Fe-O2-Fe) [Δ18O, Δ18O, Δ18O, Δ18O]  | 511 (517/506) [-1, -23, -23] | n.o. | n.o. |
| νFe(Fe-O2-Fe) [Δ18O, Δ18O, Δ18O, Δ18O]  | 448 [-1, -23, -23] | n.o. | n.o. |
| νFe(Fe-O2-Fe) [Δ18O, Δ18O, Δ18O, Δ18O]  | 447 [0, -19, -19] | 465 [-, -19, -] |
| d(O-O)/Å                | 1.43(2) | 1.43(2) | 1.43(2) |
| d(Fe(μ-O)/Å)            | 1.875(1)/1.928(1) | 1.72(1)/1.74(1) | 2.07(1)/2.10(1) |
| d(Fe-1,2-O2)/Å          | 1.83(1)/1.86(1) | 1.16(1)/1.75(1) | 114.7(1)/115.7(1) |

*Split by Fermi-resonance.
The μ-oxo and μ-1,2-peroxo groups are disordered22 prohibiting a rigid comparison.
The 180 K Mössbauer spectrum of $^{57}$Fe-labeled [(susan6-Me){Fe(μ-O)(μ-1,2-O2)Fe}]$^{3+}$ (Fig. 5b) exhibits a 4-line spectrum suggesting the presence of two quadrupole doublets. Two different models are possible, but considerations explained in the Supplementary Information (Fig. S14 and S15) strongly favor the model with δ$_1$ = 0.39 mm s$^{-1}$/ΔE$_Q1$ = -1.29 mm s$^{-1}$ and δ$_2$ = 0.27 mm s$^{-1}$/ ΔE$_Q2$ = +0.57 mm s$^{-1}$ (Table 1). Interestingly, adding excess NEt$_3$ as reductant to the oxidized [(susan6-Me){Fe(μ-O)(μ-1,2-O2)Fe}]$^{3+}$ complex almost superimposes with the electrochemically oxidized species (red).
restores the Mössbauer spectrum of the starting complex \([\text{susan}6-\text{Me})\{\text{Fe}^{III}(\mu-O)(\mu-1,2\text{-O}_2)\text{Fe}^{III}\}]^{2+}\) (Fig. S16) confirming the chemical reversibility.

The decrease of the isomer shift from 0.53 mm s\(^{-1}\) of the starting complex to 0.27 and 0.39 mm s\(^{-1}\) confirms a mainly metal-centered oxidation to a high-valent \(\mu\)-1,2-peroxo complex with both Fe\(^{III}\) ions involved resulting in a mixed-valence Fe\(^{IV}\)Fe\(^{III}\) species. In the Robin-and-Day classification for mixed-valence systems\(^{48}\), class I implies no interaction (ruled out by the coupled \(S_z = 1/2\) spin ground state) while class III stands for quantum-mechanically delocalized states. In class II systems, two different states exist that correspond roughly to the excess electron from the reduced to the oxidized metal ion. Between these two states is an energy barrier and there can be one of these states populated exclusively up to 15,400 cm\(^{-1}\) of the protonation.

Protonation to \([\text{susan}6-\text{Me})\{\text{Fe}^{III}(\mu-O)(\mu-1,2\text{-OOH})\text{Fe}^{III}\}]^{3+}\). Treatment of a solution of \([\text{susan}6-\text{Me})\{\text{Fe}^{III}(\mu-O)(\mu-1,2\text{-O}_2)\text{Fe}^{III}\}]^{2+}\) with HClO\(_4\) at \(-60\) °C resulted in the loss of the 15,400 cm\(^{-1}\) band while the 11,800 and 19,300 cm\(^{-1}\) bands are only slightly affected (Fig. 6a, b). A Job plot analysis\(^{49,50}\) (Fig. 6c) provided a 1:1 stoichiometry for the reaction between the \(\mu\)-1,2-peroxo complex and H\(^+\). Adding NEt\(_3\) as a base restores the initial spectrum (Fig. 6a) showing the reversibility of this protonation.

Characterization of \([\text{susan}6-\text{Me})\{\text{Fe}^{III}(\mu-O)(\mu-1,2\text{-OOH})\text{Fe}^{III}\}]^{3+}\). The disappearance of the \(\mu\)-1,2-peroxo \(\rightarrow\) Fe\(^{III}\) LMCT at 15400 cm\(^{-1}\), while the \(\mu\)-oxo \(\rightarrow\) Fe\(^{III}\) LMCT around 19,000 cm\(^{-1}\) persists, is consistent with protonation of the \(\mu\)-1,2-peroxo ligand. In contrast, protonation of complex A to the \(\mu\)-hydroxo,\(\mu\)-1,2-peroxo complex is accompanied by a shift of the \(\mu\)-1,2-peroxo \(\rightarrow\) Fe\(^{III}\) LMCT from 17300 cm\(^{-1}\) to 15,500 cm\(^{-1}\). A similar shift was observed using a linear \(\text{N}_4\) ligand.\(^{36}\) Moreover, the persistence of the weaker feature at 11800 cm\(^{-1}\) assigns this to a \(\mu\)-oxo \(\rightarrow\) Fe\(^{III}\) LMCT. However, the absence of a \(\mu\)-1,2-hydroperoxo \(\rightarrow\) Fe\(^{III}\) LMCT prohibits excitation for RR spectra at 647 nm (15,500 cm\(^{-1}\)). Neither were resonance-enhanced vibrations observed by excitation at 568...
(1,760) and 514 nm (19,500 cm⁻¹) close to the μ-oxo→FeIII LMCT (Fig. 6a).

The Mössbauer spectrum provided two quadrupole doublets with δ₁ = 0.49 / ΔE/Q₁ = 2.48 mm s⁻¹ and δ₂ = 0.45 / ΔE/Q₂ = 1.37 mm s⁻¹ (Fig. 6d). Since the parent [(susan6-Me){FeIII(μ-1,2-O₂,FeIII)]}²⁺ exhibits only one quadrupole doublet despite the significant differences in its two coordination sites (vide supra) requires a different source of asymmetry for the protonated species to explain its two strongly differing quadrupole doublets. This rules out a μ-1,1-hydroperoxo-bridge, while a μ-1,2-hydroperoxo-bridge provides the different source of asymmetry as the protonated site becomes much less charge-donating. Although a terminally bound hydroperoxo-ligand would be in-line with the absence of a μ-1,2-peroxo→FeIII LMCT and two quadrupole doublets, the persistence of the μ-oxo→FeIII LMCTs around 19,000 and 11,800 cm⁻¹ strongly favors a doubly-bridged structure of almost the same <FeIII(μ-1,2-OOH)FeIII> angle hence ruling out an almost linear [FeIII(μ-1,2-OOH)FeIII] core that is also inaccessible with the ligand susan6-Me (vide infra).

The formation of a μ-1,2-hydroperoxo-bridged complex is supported by DFT calculations (Supplementary Information). Geometry optimizations were achieved for three different tautomers with protonation of the μ-oxo-O1 being 1200 cm⁻¹ higher in energy. Although the μ-hydroxo species (protonation of the μ-oxo-O3) seems energetically feasible, its isomer shifts are even higher than for the starting peroxo complex (Table 1). In contrast, protonation at the μ-oxo-O2 decreases the isomer shifts as experimentally observed. Thus, the μ-1,2-hydroperoxo ligand is most likely protonated at O2.

Further reactivity studies. The straightforward fast protonation of [(susan6-Me){FeIII(μ-μ-O)(μ-μ-O)FeIII}]²⁺ with HClO₄ demonstrates the nucleophilic character of the μ-1,2-peroxo ligand. On the other hand, the reaction of [(susan6-Me){FeIII(μ-μ-O)(μ-μ-O)FeIII}]²⁺ with 2-phenylpropanal as a typical substrate to evaluate the nucleophilic character of peroxo ligands is slow in CH₃CN at -5 °C (Fig. S19). However, the formation of roughly one equivalent of acetoephone by performing this reaction on a preparative scale for 5 days supports the slow nucleophilic reactivity of the μ-1,2-peroxo ligand.

The electrophilic character of the three complexes were initially investigated using 9,10-dihydroanthracene (DHA) and PPh₃ as typical substrates for HAT and OAT, respectively. The reactions with [(susan6-Me){FeIV(μ-μ-O)(μ-μ-O)FeIII}]²⁺ were performed in CH₃CN at -40 °C, while that with [(susan6-Me){FeIV(μ-μ-O)(μ-μ-O)FeIII}]²⁺ and [(susan6-Me){FeIII(μ-μ-O)(μ-μ-O)FeIII}]²⁺ at -60 °C in CH₃CN/CH₃Cl₂ mixtures (vide supra). The parent [(susan6-Me){FeIV(μ-μ-O)(μ-μ-O)FeIII}]²⁺ showed no reactivity towards DHA and PPh₃ (Figs. S20, S21). The oxidized [(susan6-Me){FeIV(μ-μ-O)(μ-μ-O)FeIII}]²⁺ also showed no reactivity towards DHA (Fig. S22), while the reaction with PPh₃ resulted in the reoccurrence of the UV-Vis signature of the parent [(susan6-Me){FeIII(μ-O)(μ-μ-O)FeIII}]²⁺ (Fig. S23). The reformation of the μ-1,2-peroxo→FeIII LMCT excludes an OAT reactivity between [(susan6-Me){FeIV(μ-μ-O)(μ-μ-O)FeIII}]²⁺ and PPh₃ but suggests an oxidation of PPh₃ by [(susan6-Me){FeIV(μ-μ-O)(μ-μ-O)FeIII}]²⁺. Analogous observations were made with the protonated [(susan6-Me){FeIII(μ-μ-O)(μ-μ-O)FeIII}]²⁺ that showed no reactivity with DHA (Fig. S24) and with PPh₃, the partial recovery of the UV-Vis signature of the parent [(susan6-Me){FeIV(μ-μ-O)(μ-μ-O)FeIII}]²⁺ (Fig. S25). Again, the reformation of the μ-1,2-peroxo→FeIII LMCT excludes an OAT reactivity between [(susan6-Me){FeIII(μ-μ-O)(μ-μ-O)FeIII}]²⁺ and PPh₃. The partial recovery of [(susan6-Me){FeIV(μ-μ-O)(μ-μ-O)FeIII}]²⁺ indicates a protonation equilibrium between PPh₃ and [(susan6-Me){FeIII(μ-μ-O)(μ-μ-O)FeIII}]²⁺.

As it is not surprising that [(susan6-Me){FeIII(μ-μ-O)(μ-μ-O)FeIII}]²⁺ exhibits no electrophilic reactivity against DHA, the non-reactivity of both oxidized [(susan6-Me){FeIV(μ-μ-O)(μ-μ-O)FeIII}]²⁺ and protonated [(susan6-Me){FeIII(μ-μ-O)(μ-μ-O)FeIII}]²⁺ is quite surprising. To further understand this non-reactivity, we determined the BDFE(OH)CH₃CN of [(susan6-Me){FeIII(μ-μ-O)(μ-μ-O)FeIII}]²⁺. In this respect, we determined the pKₐ of [(susan6-Me){FeIII(μ-μ-O)(μ-μ-O)FeIII}]²⁺ in CH₃CN that provided 9.5 ± 0.1 (Fig. S26). Using the typical square scheme (Fig. 7a) and the Bordwell relation Eq. (1) provided BDFE(OH)CH₃CN = 78 ± 2 kcal mol⁻¹. This means that [(susan6-Me){FeIV(μ-μ-O)(μ-μ-O)FeIII}]²⁺ should be capable as oxidant for HAT for substrates with a lower BDFE(X-CH₃CN. The BDE(C-H) of DHA is 76.3 kcal mol⁻¹. However, the intrinsic difference between BDFE and BDE37, the temperature-dependence of BDFE especially for transition metal complexes, and the experimental error explain the non-reactivity of [(susan6-Me){FeIV(μ-μ-O)(μ-μ-O)FeIII}]²⁺ with DHA. In this respect, TEMPOH should be a suitable HAT substrate with BDFE(OH)-CH₃CN = 66.5 kcal mol⁻¹ and BDE(O-H) = 70.6 kcal mol⁻¹ especially for [(susan6-Me){FeIV(μ-μ-O)(μ-μ-O)FeIII}]²⁺.

The parent [(susan6-Me){FeIII(μ-μ-O)(μ-μ-O)FeIII}]²⁺ showed no reactivity with TEMPOH (Fig. S27), which is in-line that this one-electron reduced species [(susan6-Me){FeIV(μ-μ-O)(μ-μ-O)FeIII}]²⁺ should have a driving force for HAT significantly lower than 78 kcal mol⁻¹ of [(susan6-Me){FeIV(μ-μ-O)(μ-μ-O)FeIII}]²⁺. The reaction of protonated [(susan6-Me){FeIII(μ-μ-O)(μ-μ-O)FeIII}]²⁺ with TEMPOH resulted in the reoccurrence of the UV-Vis signature of the parent [(susan6-Me){FeIII(μ-μ-O)(μ-μ-O)FeIII}]²⁺ (Fig. S28). The reformation of the parent μ-1,2-peroxo-diferric complex excludes a HAT reactivity between [(susan6-Me){FeIII(μ-μ-O)(μ-μ-O)FeIII}]²⁺ and TEMPOH and suggests a protonation of TEMPOH. The reaction of [(susan6-Me){FeIV(μ-μ-O)(μ-μ-O)FeIII}]²⁺ with TEMPOH resulted in the reoccurrence of the UV-Vis signature of the parent [(susan6-Me){FeIII(μ-μ-O)(μ-μ-O)FeIII}]²⁺ (Fig. S29). This is in-line with HAT from TEMPOH to [(susan6-Me){FeIV(μ-μ-O)(μ-μ-O)FeIII}]²⁺ resulting in [(susan6-Me){FeIV(μ-μ-O)(μ-μ-O)FeIII}]²⁻ that reacts again by protonation of excess TEMPOH to [(susan6-Me){FeIII(μ-μ-O)(μ-μ-O)FeIII}]²⁻.

Thus, only the oxidized [(susan6-Me){FeIV(μ-μ-O)(μ-μ-O)FeIII}]²⁻ is capable for HAT from TEMPOH corroborated by the BDFE while the parent [(susan6-Me){FeIV(μ-μ-O)(μ-μ-O)FeIII}]²⁺ and the protonated [(susan6-Me){FeIII(μ-μ-O)(μ-μ-O)FeIII}]²⁻ does not exhibit enough electrophilic character. However, [(susan6-Me){FeIV(μ-μ-O)(μ-μ-O)FeIII}]²⁻ that shows no decay at -40 °C exhibits a change in the UV-Vis spectra at room temperature with the formation of the typical signature of complexes with a [FeIV(μ-μ-O)FeIII] core without the observation of intermediates.
accompanied by deposition of an inhomogenous solid and a few single-crystals. The crystallographic analysis provided the structure of the decay product (Fig. 7b) based on \([\text{susan}^6\text{Me}][\text{FeIII}(-\text{OH})\text{(μ-O)}\text{FeIIIX}])^{2+}\) including the ligand disorders (please see also Supplementary Fig. 1c): at Fe1 80% carboxylate and 20% hydroxide (shown with dotted lines), at Fe2 35% benzylic alcohoholato and 65% hydroxide (shown with dotted lines). c Space-filling model of \([\text{susan}^6\text{Me}][\text{FeIIIF(μ-O)}\text{FeIIIX}])^{2+}\) to illustrate the encapsulation of the peroxy ligand by a CH₂ group (right Fe) and a 6-methyl group (left Fe).

**Discusion**

To mimic dinuclear active sites of metalloenzymes, we have developed a dinucleating ligand system with varying terminal donors\(^{39,39}\). With the ligand susan, we obtained in straightforward reactions a series of μ-oxo-diferric complexes \([\text{FeIIIX}(\mu-\text{O})\text{FeIIIX}])^{2+}\) bearing anionic exogenous ligands \(X^{37,39,45,61}\). The complex with hydroxides, \([\text{susan}[\text{FeIII}(-\text{OH})(\mu-\text{O})\text{FeIIIX}((\text{OH})])^{2+}\), catalyzes the oxidation of \(\text{CH}_3\text{OH}\) with \(\text{H}_2\text{O}_2\) to \(\text{H}_2\text{O}_2\)\(^{62}\). We could observe the μ-1,2-peroxo intermediate \([\text{susan}][\text{FeIII}(\mu-\text{O})\text{(μ-1,2-O}_2\text{)}\text{FeIIIX}])^{2+}\). However, the temperature-dependencies ruled out this μ-1,2-peroxo intermediate to be the active species indicating the conversion to a high-valent active species. This conversion is faster in the presence of a proton suggesting a transient μ-1,2-hydroperoxo species.

In contrast, formation of μ-oxo-diferric complexes with \(\text{susan}^6\text{Me}\) was not possible under identical aerobic conditions. Only the small ligand F with \(\text{H}_2\text{O}_2\) as oxidant allowed the isolation of \([\text{susan}^6\text{Me}][\text{FeIIIF}(\mu-\text{O})\text{FeIIIX}])^{2+}\). Its comparison to \([\text{susan}][\text{FeIII}(-\text{OH})\text{FeIIIX}])^{2+}\) showed a steric repulsion between the 6-methyl group and the terminal Fe ligand in cis-position, which explains the inaccessibility of \(\text{susan}^6\text{Me}\) complexes with larger terminal ligands as Cl– or OAc– that are easily accessible with susan. Thus, the μ-oxo-bridged core \([\text{FeIIIX}(\mu-\text{O})\text{FeIIIX}])^{2+}\) is not the thermodynamic sink for \(\text{susan}^6\text{Me}\) as it is for susan. Moreover, the steric repulsion of the 6-methyl group enforces longer Fe–N–Me–py than Fe–N–py bonds\(^{63–68}\), and hence a lower electron donation. This results in an anodic shift of +250 mV making FeIV less accessible with \(\text{susan}^6\text{Me}\) than with susan.

In this respect, we thought that \(\text{susan}^6\text{Me}\) should be able to stabilize a μ-1,2-peroxo complex \([\text{FeIIIX}(\mu-\text{O})(\mu-1,2-\text{O}_2\text{)}\text{FeIIIX}])^{2+}\) that is with susan only a reactive intermediate decaying via a high-valent FeIV species to its thermodynamic sink \([\text{FeIIIX}(\mu-\text{O})\text{FeIIIX}])^{2+}\). In contrast, with \(\text{susan}^6\text{Me}\) not only this thermodynamic driving force is absent but FeIV is also less accessible. Indeed, we could present here the synthesis and characterization of the stable μ-1,2-peroxo complex \([\text{susan}^6\text{Me}][\text{FeIII}(\mu-\text{O})(\mu-1,2-\text{O}_2\text{)}\text{FeIIIX}])^{2+}\). Inspection of the space-filling model (Fig. 7c) shows that the μ-1,2-peroxo ligand is even further stabilized by a better encapsulation with the 6-methyl group of \(\text{susan}^6\text{Me}\) (left peroxy-oxygen atom in Fig. 7c) that would be absent with susan. This ligand encapsulation also explains the slower nucleophilic reactivity of the μ-1,2-peroxo ligand for the organic substrate 2-phenylpropanol than for the small H⁺.

Although \(\text{susan}^6\text{Me}\) is less suited for stabilization of FeIV than susan, the principal accessibility of FeIV with \(\text{susan}^6\text{Me}\) is demonstrated by the reversible oxidation to \([\text{susan}^6\text{Me}][\text{FeIV}(\mu-\text{O})(\mu-1,2-\text{O}_2\text{)}\text{FeIIIX}])^{3+}\), which is stabilized by the additional highly coherent μ-1,2-peroxo ligand. It is interesting to note, that this high-valent μ-1,2-peroxo species stores one oxidation-equivalent more than intermediate Q of sMMO. Comparing the FeIVFeII/FeIIIFeII redox potential of \(\text{E}_{1/2} = 0.55 \text{ V to } 0.41 \text{ V vs } \text{Fc/}^-\text{F}^-\) for the analogous redox couple of \([\text{tpa}^6\text{Me}][\text{FeIII}(\mu-\text{O})\text{FeIIIX}])^{2+}\) shows only a slightly lower electron-donating character of the μ-1,2-peroxo bridge than a μ-oxo-bridge.

We could further demonstrate the reversible protonation to the μ-1,2-hydroperoxo-diferric complex \([\text{susan}^6\text{Me}][\text{FeIIIX}(\mu-\text{O})(\mu-1,2-\text{O}_2\text{OH})\text{FeIIIX}])^{3+}\). Generally, protonation of a Fe-coordinated peroxo ligand is regarded to enhance its reactivity, e. g. protonation of the cis-μ-1,2-peroxo intermediate P of sMMO was proposed to promote the conversion to intermediate Q\(^{11}\). The relatively high stability of the μ-1,2-hydroperoxo complex \([\text{susan}^6\text{Me}][\text{FeIII}(\mu-\text{O})(\mu-1,2-\text{O}_2\text{OH})\text{FeIIIX}])^{3+}\) (no decay at −60 °C, \(\tau_{1/2} \approx 11 \text{ min at } −40 °\text{C}\) is thus remarkable and must owe its origin to a low stabilization of the FeIV conversion product by \(\text{susan}^6\text{Me}\).

In contrast to \([\text{susan}^6\text{Me}][\text{FeIIIX}(\mu-\text{O})(\mu-1,2-\text{O}_2\text{)}\text{FeIIIX}])^{2+}\), the μ-1,2-peroxo complex A is protonated at the μ-oxo-bridge forming a \([\text{FeIIIX}(\mu-1,2-\text{O}_2\text{)}(\mu-\text{OH})\text{FeIIIX}])^{2+}\) species\(^{62}\) indicating different nucleophilicities. The nucleophilic character of a ligand should increase with less electron donation to the FeII ions, i.e. less covalent, longer bonds. But for A, the FeII–μ-O bonds are shorter than for \([\text{susan}^6\text{Me}][\text{FeIIIX}(\mu-\text{O})(\mu-1,2-\text{O}_2\text{)}\text{FeIIIX}])^{2+}\).
(1.72/1.74 Å vs 1.82/1.89 Å), whereas the situation is reversed for the FeIII-μ-O-peroxo bonds (2.07/2.10 Å vs 1.88/1.93 Å). This structural argumentation is in contrast to the experimentally determined protonation sites. However, the disorder of the μ-oxo/μ-1,2-peroxo ligands in A questions the significance of this comparison. Moreover, as protonation should occur at a π orbital and a Fe–O bond consists of σ- and π-bonding, a pure structural analysis does not need to provide the answer for the reactivity.

Thus, spectroscopic markers might provide a better correlation to the nucleophilic character of the peroxo group than structural parameters. Solomon and coworkers proposed to extract the donor strength of a given ligand from the integrated absorption intensities of all CT transitions associated with this ligand33. Here, the μ-charge donation from the peroxo π orbitals donor orbital into the Fe 3dπ acceptor orbitals should be extractable from the prominent μ-1,2-peroxo→Fe LMCTs. Complex A exhibits this μ-1,2-peroxo→FeLMCT with ε = 1500 M⁻¹ cm⁻¹ and a much less intense μ-oxo→FeLMCT. In contrast, the μ-oxo→FeLMCT in [(susan6-Me)Fe(μ-1,2-O2)2FeII]²+ is more intense (ε = 1180 M⁻¹ cm⁻¹) than the μ-peroxo→FeII LMCT (ε = 1000 M⁻¹ cm⁻¹). Note also that the integrated absorption intensity is smaller in the susan6-Me complex than in A for the μ-1,2-peroxo→FeII LMCT indicating - without the intention of a quantitative analysis - less charge-donation and hence more nucleophilic character of the μ-1,2-peroxo ligand. This UV-Vis spectroscopic argumentation is supported by the comparison of the vibrational signature in the IR spectra. Interestingly, the strongest difference is observed for the ν(Fe–O2–Fe), which are at 465 and 448 cm⁻¹ for A and [(susan6-Me)Fe(μ-1,2-O2)2FeII]²+, respectively, indicative for less covalent FeIII-μ-O-peroxo bonds and hence a higher nucleophilicity of the μ-1,2-peroxo ligand in [(susan6-Me)Fe(μ-1,2-O2)2FeII]²+.

The study of the electrophilic reactivity demonstrated only a low electrophilic character of the parent μ-1,2-peroxo-FeIIIFeIII complex that is not unexpected for such complexes35,35. Interestingly, also protonation to the μ-1,2-hydroperoxo-FeIIIFeIII species turned out to be not sufficient to increase the electrophilic character for HAT with substrates of weak to modest BDE (TEMPOH and DAH). Only the oxidized μ-1,2-peroxo-FeIVFeIII species react with the relatively weak substrate TEMPPOH. The determination of the pKₐ = 9.5 ± 0.1 and the bond dissociation free energy BDE(O–H)CH₃CN = 78 ± 2 kcal mol⁻¹ of the protonated μ-1,2-hydroperoxo-FeIIIFeIII species quantifies this low electrophilic character even of the oxidized μ-1,2-peroxo-FeIVFeIII species. In this respect, the intramolecular C–H activation of preorganized 6-methyl pyridine groups to benzylalcoholato and carboxylato donors by the parent μ-1,2-peroxo-FeIIIFeIII complex is remarkable. Considering that this complex does not react with TEMPPOH (BDE(O–H) = 70.6 kcal mol⁻¹) and using the BDE(CH₃CN) = 90 kcal mol⁻¹ of the methyl group of toluene as an approximation for the BDE(CH₃) of the 6-methyl groups of the coordinated pyridines, HAT should not occur via the bridging μ-1,2-peroxo-ligand. This indicates that this intramolecular reaction requires the conversion of the μ-1,2-peroxo-diferric core to a more reactive high-valent species as already postulated for the CH₃OH oxidation of the analogous μ-1,2-peroxo-diferric complex of susan (vide supra).

[(susan6-Me)Fe(μ-O)(μ-1,2-OOH)FeIII]²+ is an μ-1,2-hydroperoxo model complex and provides spectroscopic signatures for the assignment of postulated hydroperoxide intermediates in dioxygen enzymes: Upon protonation, the prominent μ-1,2-peroxo→FeII LMCT around 14,000–16,000 cm⁻¹ disappears and the isomer shift decreases. The presence of an μ-oxo-bridge is indicated by the typical μ-oxo→FeII LMCTs around 12,000 and 19,000 cm⁻¹ and large values of |ΔεQ| ≥ 1.3 mm s⁻¹. The best signature to differentiate between a μ-1,1-hydroperoxo and a μ-1,2-hydroperoxo is the appearance of two strongly differing quadrupole doublets for the latter due to the strongly differing donation abilities of the two μ-1,2-hydroperoxo-oxygen atoms.

The protonation of [(susan6-Me)FeIII(μ-O)(μ-1,2-O2)2FeIII]²+ to [(susan6-Me)FeIII(μ-O)(μ-1,2-OOH)FeIII]²⁺ reflect the UV-Vis-NIR and Mössbauer spectroscopic differences between P and the more reactive P* intermediates in non-heme diiron enzymes22,33,34,35. For the latter, a μ-1,2-hydroperoxo structure has been suggested, which is thus strongly supported by the results of this study.

The diferrous form of AurrF exhibits one quadrupole doublet demonstrating structurally rather similar iron places22. Reaction with O₂ provides a diferic species that lacks the typical μ-1,2-peroxo→FeII LMCT around 14,000 cm⁻¹. The Mössbauer spectrum contains two quite different quadrupole doublets with ΔE₂ = 0.54, |ΔεQ| = 0.56 mm s⁻¹ and |ΔεQ| = 0.35 mm s⁻¹13,15. This coupled with the low values of |ΔεQ| and a lack of the μ-1,2-peroxo→FeII LMCT lead us to suggest the formation of the P*-type intermediate in AurrF as a [FeII(μ-1,2-hydroperoxo)FeIII] core without a μ-oxo-bridge, which also supports a recent proposal22.

**Methods**

**Synthesis of [(susan6-Me)Fe(μ-OH)FeIII]ClO₄₂H₂O.** A solution of susan-Me (595 mg, 1.00 mmol) in MeOH (25 mL) was added to a solution of Fe(ClO₄)₂·6H₂O (726 mg, 2.00 mmol, 2.0 equiv) in MeOH (20 mL). This yellow solution was stirred at room temperature for 10 min followed by the addition of a 25% aqueous solution of ammonia (0.16 mL, 2.1 mmol, 2.1 equiv) resulting in a slight intensity increase of the yellow color. Yellow crystals of [(susan6-Me)Fe(μ-OH)Fe]ClO₄·MeOH precipitated at 0 °C, which were filtered off, washed three times with water, a small amount of cold MeOH, three times with Et₂O, and dried under reduced pressure. Yield: 704 mg (7.50 × 10⁻⁴ mol, 73%), IR (KBr): ν/cm⁻¹ = 3642 w, 2976 w, 2856 m, 1603 s, 1476 s, 1429 s, 1303 w, 1273 m, 1164 m, 1100 m, 1056 m, 985 m, 916 m, 834 m, 788 s, 686 m, 624 s, 500 w, 447 w. ESI-MS (±) m/z = [susan6-Me(Fe(OH)₂)FeClO₄]²⁻: 490.0 (100%)

**Synthesis of [(susan6-Me)Fe(μ-(O2)2O2)FeIII]ClO₄·2H₂O.** A solution of [(susan6-Me)Fe(μ-OH)FeClO₄] (63 mg, 6.7 × 10⁻² mol) in CH₂Cl₂ (2 mL) was added to a solution of 25% aqueous ammonia (0.16 mL, 2.1 mmol, 2.1 equiv) resulting in a slight intensity increase of the yellow color. Yellow crystals of [(susan6-Me)FeClO₄·MeOH precipitated at 0 °C, which were filtered off, washed three times with water, a small amount of cold MeOH, three times with Et₂O, and dried under reduced pressure. Yield: 704 mg (7.50 × 10⁻⁴ mol, 73%), IR (KBr): ν/cm⁻¹ = 3642 w, 2976 w, 2856 m, 1603 s, 1476 s, 1303 w, 1273 m, 1164 m, 1100 m, 1056 m, 985 m, 916 m, 834 m, 788 s, 686 m, 624 s, 500 w, 447 w. ESI-MS (±) m/z = [susan6-Me(Fe(O2)₂O2)FeClO₄]²⁻: 490.0 (100%)

**Crystallographic Data.** Crystallographic data generated in this study have been deposited at the Cambridge Crystallographic Data Centre under accession codes 2072304-2072806 (www.ccdc.cam.ac.uk/data_request/cif). Experimental details on synthesis and crystal structure determination, details on DFT calculations, analysis of Mössbauer spectra, ESI-MS, thermal ellipsoid plots, Mössbauer spectra, UV-Vis spectra, R spectra, X-ray crystallographic data ( cif ) generated in this study are provided in the Supplementary Information. Source data are available from the corresponding author upon request.

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