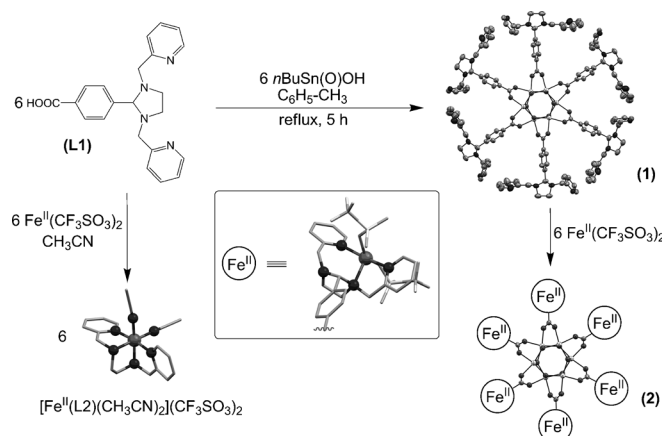


O–O Bond Formation Mediated by a Hexanuclear Iron Complex Supported on a Stannoxane Core

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In recent years, much attention has been focused on the incorporation of redox-active transition-metal complexes into the dendrimer structure owing to their potential applications in various fields.^[1] Also, the antenna-like structure of the dendrimers, in many cases, was found to provide an ideal organization for these chromophores and redox centers to work in synergistic ways in carrying out a number of important transformations.^[2] For example, an extensive co-operative effect between the Cu centers was observed during the cleavage of supercoiled DNA catalyzed by a hexanuclear Cu-porphyrin complex, supported on a stannoxane core.^[2b]

The above-mentioned hexaporphyrin assembly was synthesized in high yields and in a single step utilizing the organostannoxane approach, whereby *n*-butyl stannic acid was made to react with the corresponding porphyrin carboxylic acid in 1:1 stoichiometry in benzene;^[2b] the molecular structure of the ligand was established on the basis of ¹¹⁹Sn NMR and DFT calculations. In the present paper we report the synthesis of a non-heme hexanucleating ligand (**1**) supported on a drum-like stannoxane central core utilizing the same organostannoxane approach (Scheme 1). **1** is characterized by X-ray diffraction, ¹¹⁹Sn NMR, and infrared meth-



Scheme 1. Scheme showing the synthesis of the complexes. Hydrogen atoms and the *n*-butyl groups on tin have been omitted for clarity. Molecular structures of the hexanuclear ligand **1** and the complex $[\text{Fe}^{\text{II}}(\text{L}2)(\text{CH}_3\text{CN})_2]^{2+}$ are determined by X-ray crystallography. Structure of **2** is proposed based on ICP-MS, ¹¹⁹Sn-NMR, ¹⁹F NMR, IR, Mössbauer and DFT methods (see the Supporting Information for a color version of Scheme 1).

ods. Most importantly, we show that the Fe^{II}-metalated hexa non-heme assembly, **2**, in the presence of 2-(*tert*-butylsulfonyl)-iodosylbenzene (^sPhIO), performs a rare O–O bond formation reaction,^[3] thereby generating a Fe^{III}-(O₂^{•−}) Fe^{II} superoxo unit. Such a metal mediated O–O bond formation step is considered to be the most critical part of dioxygen evolution in photosystem II^[4] and hence plays a vital role in the context of attaining a clean renewable energy source.^[5]

The condensation reaction (Scheme 1) of equimolar amounts of *n*-butyl stannic acid and 4-(1,3-bis(2-pyridylmethyl)-2-imidazolidinyl)benzoic acid (**L1**) in toluene afforded a pale yellow solid **1**, whose molecular structure (Scheme 1)^[6] shows a giant-wheel arrangement of the six non-heme ligand units with a drum-like stannoxane central core serving as the structural support for the hexanucleating assembly. The general features of the stannoxane framework are found to be similar to the other structurally characterized drum-shaped molecules and have a crystallographic S₆ symmetry, so that six tin atoms are crystallographically and chemically equivalent.^[7] ¹¹⁹Sn NMR spectrum of **1** exhibits a sharp singlet at −482.4 ppm (Figure S1 top), which is the characteristic signature for a hexameric organostannoxane

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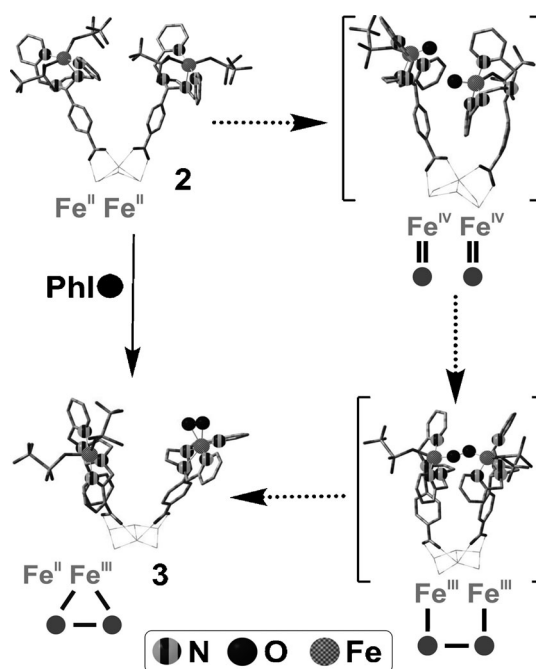
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drum containing a Sn_6O_6 core.^[7] The infrared spectrum shows a symmetric doublet at 1590 cm^{-1} and 1605 cm^{-1} for the carboxyl absorption (ν_{COO}),^[7] and a strong band at 624 cm^{-1} assigned to $\nu_{\text{Sn-O}}$ ^[7] for the drum core (Figure S2 top).

Before describing the hexameric ligand, the chemistry of the monomeric ligand **L1** was first explored. Reaction of **L1** with 1 equiv $\text{Fe}(\text{OTf})_2$ in CH_2Cl_2 resulted in the formation of a yellow oil. ESI-MS analysis (Figure S3 top) showed a signal at $m/z=447.1$, with an isotope distribution pattern consistent with its formulation as $[\text{Fe}^{\text{II}}(\text{L2})(\text{OTf})]^+$, where **L2** is the ligand formed upon opening of the central aminal ring of **L1** (Scheme 1). Similar results were reported previously for related systems.^[8] Slow evaporation of the solvent from a CH_3CN solution of the yellow oil resulted in deep red crystals, which when analyzed by X-ray crystallography established the molecular structure as $[\text{Fe}^{\text{II}}(\text{L2})(\text{CH}_3\text{CN})_2](\text{OTf})_2$ (Scheme 1, Figure S4, Table S7).^[6]

The hexanucleating ligand **1** when reacted with 6 eqv of $\text{Fe}(\text{OTf})_2$ in CH_2Cl_2 yielded the metalated species **2** as a yellowish-green powder (60% yield). Interestingly, the ESI-MS spectrum of **2** did not show any signal at $m/z=447.1$ corresponding to the decomposition product $[\text{Fe}^{\text{II}}(\text{L2})(\text{OTf})]^+$ after aminal ring opening.^[9] The iron content of **2**, determined by the inductively coupled plasma mass spectrometry (ICP-MS) method together with the elemental analysis, established the presence of six iron atoms per hexameric ligand **2**, with two triflates associated with each iron. A major doublet with an isomer shift $\delta=1.10\text{ mm s}^{-1}$ and quadrupole splitting $\Delta E_Q=2.80\text{ mm s}^{-1}$ in the zero-field Mössbauer spectrum of **2** demonstrates equivalent high-spin Fe^{II} centers in a five coordinate geometry.^[10,11] Based on the DFT calculation^[12] the most stable coordination environment of the Fe^{II} centers in **2** corresponds to a distorted trigonal bipyramidal geometry (Scheme 2, Figure S5 and Table S1) with two equatorial triflate ligands. The ligand **L1** acts as a tridentate ligand, with one of the nitrogens of the 5-membered imidazolidinyl ring remaining out of the coordination sphere. The calculated Mössbauer parameters ($\delta=1.17\text{ mm s}^{-1}$; $\Delta E_Q=3.17\text{ mm s}^{-1}$)^[12] for the DFT calculated coordination environment of the Fe^{II} centers in **2** is found to be in good agreement with the experiment. The small deviation of 13% in the calculated quadrupole splitting is typical of DFT functionals.^[13] Consistent with the DFT calculated structure, ^{19}F NMR spectra of **2** at -20°C exhibits a single peak at +15 ppm corresponding to the triflate anions, which are bound to the Fe^{II} high spin centers.^[14a] ^{119}Sn NMR of **2** in CD_2Cl_2 does not exhibit any peak in the range -475 to -490 ppm, which can be attributed to paramagnetic line broadening in the presence of high-spin Fe^{II} ions. In CD_3CN , however, the Fe^{II} centers of **2** become low-spin owing to CD_3CN -binding, as evident from the appearance of the characteristic sharp singlet feature of the drum-like stannoxane core at -485.5 ppm in the ^{119}Sn NMR (Figure S1 bottom), which is also supported by Mössbauer.^[11] Thus, the tin core supporting the hexa non-heme assembly is retained during the metalation of **1** to form **2**.^[15] The mononuclear nonheme



Scheme 2. Plausible mechanism for the O–O bond formation reaction carried out by **2**. The $\text{Fe}^{\text{IV}}(\text{O})$ intermediates are proposed on the basis of reactivity, kinetics, and infrared studies. The peroxo complex is an obvious precursor to the superoxo unit in **3**. Structures of **3**, iron(IV) oxo and peroxo complexes were optimized by DFT calculations,^[12] using a simplified model where the effect of the stannoxane core, which was not included in the model, was simulated by freezing the position of the carboxylate oxygens and by considering only two of the six iron centers. Structure of **2** is based on the DFT calculated geometry of the $S=2$ monomeric unit (see the Supporting Information for details about the calculations and for a color version of Scheme 2).

Fe^{IV} -oxo complexes, which act as models for the high-valent Fe^{IV} -oxo intermediates found in many nonheme iron enzymes that activate oxygen,^[16] can in general be prepared by the reaction of the Fe^{II} precursors with an oxygen donor like iodosobenzene.^[14] They exhibit a signature near-IR band in the absorption spectra, which arises from the low-lying ligand field transitions of an $S=1$ Fe^{IV} center.^[14] The reaction of **2** in CH_2Cl_2 with $^s\text{PhIO}$ at 25°C , however, led to a deep purple complex **3**, whose electronic absorption spectrum with absorption maxima λ_{max} (ϵ_{max} , $\text{M}^{-1}\text{cm}^{-1}$) centered at 500 nm (5150) and 587 nm (8580) (Figure 1 top) lacked the characteristic near-IR feature of the Fe^{IV} -oxo complexes. When the same reaction was done at -80°C instead, a transient intermediate (Figure 1 top inset) was detected during the conversion of **2** to **3**; the time-trace of the reaction monitored at 750 nm shows a sharp increase followed by a slow decrease (Figure 1 bottom inset). This together with our infrared results (see below) may indicate the involvement of a Fe^{IV} -oxo intermediate during the generation of **3**. Reaction of **2** with dioxygen at 25°C in CH_2Cl_2 could also generate **3** in near quantitative yields. No intermediate was, however, observed in this case.

In the infrared (IR) vibrational spectrum of **3** (Figure 2), an oxygen sensitive band at 1173 cm^{-1} ($^{3-16}\text{O}-^{16}\text{O}$; dash-

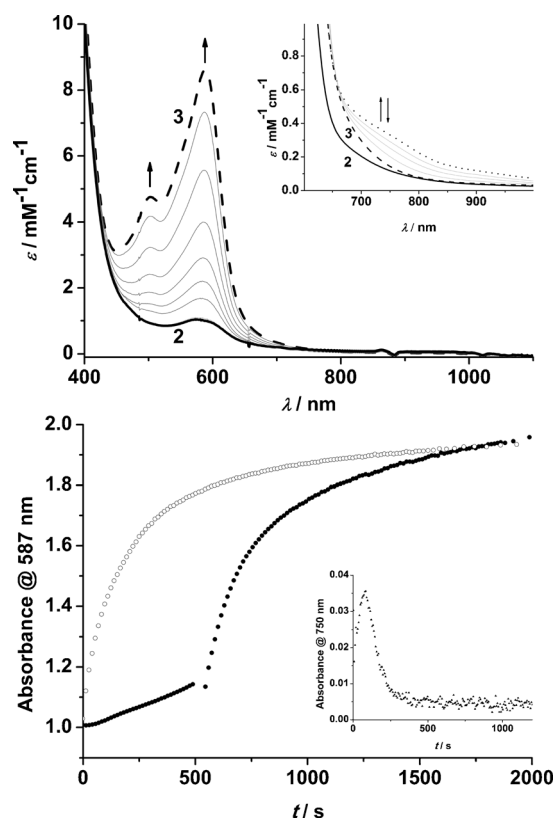


Figure 1. Top: UV/Vis spectra of **2** (solid line) and **3** (dashed line) in CH_2Cl_2 at 25°C . The intermediate spectra show the conversion of **2** to **3** upon addition of $^5\text{PhIO}$ (1 equiv). The inset shows the conversion of **2** (solid trace) to **3** (dashed trace) at -80°C via the intermediate formation of a species with $\lambda_{\text{max}} = 750 \text{ nm}$ (dotted line). Bottom: Plot of absorbance change at 587 nm against time during the reaction of **2** (0.23 mM) with $m\text{CPBA}$ (open circle, $k_1 = 5.3 \times 10^{-3} \text{ s}^{-1}$) and $^5\text{PhIO}$ (closed circle; $k_1 = 0.4 \times 10^{-3} \text{ s}^{-1}$ without $n\text{Bu}_4\text{NOAc}$ addition for the initial 500 s ; $k_1 = 5.0 \times 10^{-3} \text{ s}^{-1}$ in presence of $n\text{Bu}_4\text{NOAc}$) in CH_2Cl_2 at 25°C . Inset: Plot of absorbance change at 750 nm against time during the reaction of **2** with $^5\text{PhIO}$ at -80°C in CH_2Cl_2 .

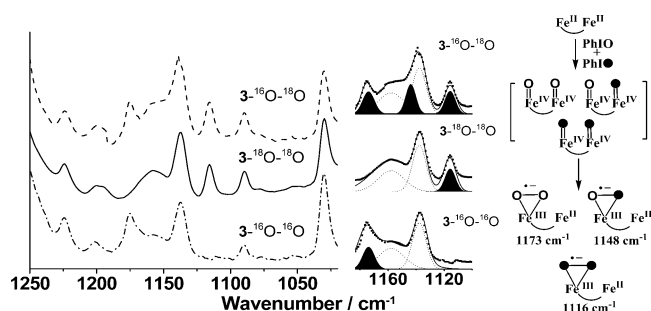


Figure 2. Left: The $\nu(\text{O}–\text{O})$ region in the infrared spectra of **3** generated from the reaction of **2** with $^5\text{PhI}^{16}\text{O}$ (dash-dotted line), $^5\text{PhI}^{18}\text{O}$ (solid line), and a 1:1 mixture of $^5\text{PhI}^{16}\text{O}$ and $^5\text{PhI}^{18}\text{O}$ (dashed line). Middle: Gaussian deconvolution of the bands in the $1100\text{--}1185 \text{ cm}^{-1}$ region (experimental spectra are shown as scattered points and simulation as solid lines). The oxygen sensitive bands at 1173 , 1144 , and 1116 cm^{-1} are shaded in black; bands at 1158 cm^{-1} and 1138 cm^{-1} are not sensitive to ^{18}O labeling and are represented by dotted lines. Right: Scheme showing the formation of the mixed label superoxide in presence of 1:1 $^5\text{PhI}^{16}\text{O}$ and $^5\text{PhI}^{18}\text{O}$.

dotted trace) was observed, which shifted to 1116 cm^{-1} ($3\text{-}^{18}\text{O}\text{-}^{18}\text{O}$; solid trace) in the corresponding ^{18}O labeled **3**. The isotope shift of 57 cm^{-1} agrees well with the calculated (67 cm^{-1})^[12] and experimentally observed (Table S2) shifts for the O–O bond stretching vibrational mode of a selected number of different transition metal-superoxides that are known in the literature. When **3** was generated by the reaction of **2** with a 1:1 $^5\text{PhI}^{16}\text{O}$: $^5\text{PhI}^{18}\text{O}$ mixture, the IR spectrum showed the presence of three oxygen sensitive bands at 1173 , 1144 , and 1116 cm^{-1} with the respective intensity ratios of 1:1.3:1 (dashed trace). The additional band at 1144 cm^{-1} is assigned to the O–O stretch of the mixed label ($3\text{-}^{16}\text{O}\text{-}^{18}\text{O}$) species. Thus, the values of the stretching frequencies found in the infrared studies suggest the presence of a superoxo unit in **3**. Moreover, the presence of the $3\text{-}^{16}\text{O}\text{-}^{18}\text{O}$ stretch at 1144 cm^{-1} may imply the intermediacy of Fe^{IV} -oxo complexes (Figure 2 right),^[17] which is also corroborated by UV/Vis studies. A single $3\text{-}^{16}\text{O}\text{-}^{18}\text{O}$ stretch^[18] also implies that the O–O bond in **3** is symmetric, which may point towards a side-on binding mode of the superoxo unit. DFT calculations on **3** also favor the side-on binding mode (Figure S6 and Table S3) over the alternative end-on mode (Figure S7 and Table S4) by 10 kcal mol^{-1} .^[9,15,19] Moreover, **3** is found to be EPR silent similar to **2**.

The time-trace for the formation of the deep purple complex **3** monitored at 587 nm by reaction of **2** with $^5\text{PhIO}$ is shown in Figure 1 bottom. It can be approximately fitted to a first-order plot with a rate constant k_1 of $0.44 \times 10^{-3} \text{ s}^{-1}$ at 25°C . The value of k_1 was found to be independent on the starting concentration of **2** ($0.2\text{--}1.2 \text{ mM}$), which points towards an intramolecular mechanism (intermolecular processes show concentration-depending kinetics). Interestingly, when the above reaction was performed in the presence of $n\text{Bu}_4\text{N}(\text{OAc})$, a ten-fold increase ($k_1 = 5 \times 10^{-3} \text{ s}^{-1}$) in the first-order rate was observed.^[20] However, when dioxygen was used as the oxidant, no rate enhancement occurred with $n\text{Bu}_4\text{N}(\text{OAc})$. We therefore attribute the increase in the rate of conversion of **2** to **3** to the bridging ability of the acetate anion, which helps to bring the two iron units close to each other, thereby ensuring efficient O–O bond formation. Consistent with our proposition, *meta*-chloroperbenzoic acid ($m\text{CPBA}$) also generated **3** from **2** at a rate similar to what was observed for the $^5\text{PhIO}$ /acetate mixture. In this case the chlorobenzoate anion, formed by the heterolytic O–O cleavage of the initially formed chlorobenzoylperoxo species (Scheme S2), plays the same role as acetate anions by bridging the iron oxo units for efficient O–O bond formation reaction.^[14c]

The reactivity of **3** with different substrates was also explored at 25°C . Reaction with 1 equiv $\text{CF}_3\text{CO}_2\text{H}$ led to the decay of the 587 and 500 nm bands and the appearance of a new band at 415 nm (Figure S8). H_2O_2 was released in $>65\%$ yield (see the Supporting Information for details), thereby confirming the presence of O–O bonds in **3**. Complex **3** reacted with cyclohexane carboxaldehyde (CCA), and benzoyl chloride with a second order rate constant (k_2) of $0.001 \text{ M}^{-1} \text{ s}^{-1}$ and $0.002 \text{ M}^{-1} \text{ s}^{-1}$, respectively (Figure S9). Cy-

clohexene and benzoic acid were obtained in the respective yields of 30 % and 33 %. **3** also exhibited typical superoxide reactivity^[21] by abstracting hydrogen atoms from 2,2,6,6-tetramethylpiperidine-1-hydroxy (TEMPOH) and 2,6-di-*tert*-butyl phenol, thereby forming the TEMPO[•] radical (33 % yield) and 2,2',6,6'-tetra-*tert*-butyl-4,4'-biphenol, respectively.

Efforts were also made to trap the transient oxoiron(IV) intermediate during the conversion of **2** to **3**. Thus, the reaction of **2** with ⁵PhIO at –80 °C in the presence of excess of benzyl alcohol led to the generation of **3** at only 40 % of its original level (Figure S10). Benzaldehyde was generated in 50 % yield. Such reactions are typical of oxoiron(IV) complexes.^[14] Interestingly, dihydroanthracene or 1,4-cyclohexadiene (BDE = 77 kcal mol^{–1}),^[22] which have C–H bond dissociation energies similar to that of benzyl alcohol (BDE (C–H) = 80 kcal mol^{–1}; BDE (O–H) = 101 kcal mol^{–1})^[22] were completely inefficient in trapping the oxoiron(IV) intermediate generated during the conversion of **2** to **3**. Thus the reaction of the benzyl alcohol probably proceeds by the preferential activation of the O–H bond rather than the C–H bond or by a hydride transfer mechanism.^[23] 2,4,6-tri-*tert*-butyl phenol (20 equiv) was also found to be capable of intercepting about 40 % of the oxidant responsible for the O–O bond formation reaction, thereby yielding 2,4,6-tri-*tert*-butyl phenoxy radical in 45 % yield.^[24]

In summary, we have demonstrated the intramolecular O–O bond formation reaction mediated by a hexanuclear Fe^{II} complex **2** using iodosobenzene as the oxygen source. Based on our studies, the O–O bond-forming reaction can be best construed by a mechanism whereby the oxygen progresses through oxo, peroxo, and superoxo states.^[25] Fe^{IV}-oxo complexes are proposed as the plausible intermediates on the basis of a) observation of the mixed labeled **3**-¹⁶O-¹⁸O stretch at 1144 cm^{–1} when **3** was generated with a ⁵PhI¹⁶O: ⁵PhI¹⁸O (1:1) mixture (Figure 2); b) kinetics of the formation of **3**, which shows the involvement of an intermediate with a characteristic band at 750 nm; and c) interception by benzylalcohol and 2,4,6-tri-*tert*-butyl phenol of the ⁵PhIO derived oxidant responsible for the O–O bond formation reaction. Moreover, the rate of formation of **3** was found to be enhanced in the presence of bridging carboxylates (Figure 1 bottom), which implies that more than one iron center is involved in the O–O bond formation step. Accordingly, we suggest a radical coupled mechanism for the formation of **3**, similar to what was proposed earlier for the ruthenium catalyzed O–O bond coupling reaction.^[26] Such a mechanism, however, warrants the initial formation of a peroxo bridged diiron(III) complex, which would then undergo homolysis of the Fe^{III}–(O₂^{2–})–Fe^{III} bond to generate the Fe^{II} (O₂^{•–})–Fe^{III} unit in **3** (Scheme 2). DFT calculations were performed to assess the viability of the peroxo complex with our ligand system. We designed a simplified system containing two monomeric units, where the positions of the carboxylate oxygens were frozen in order to mimic the constraints provided by the stannoxane core of **1**. The optimized structure (Scheme 2, Figure S11 and Table S5) re-

veals two antiferromagnetically coupled *S* = 1/2 Fe^{III} centers in a Fe^{III}–O–O–Fe^{III} unit with the O–O distance of 1.48 Å and Fe–O distances of 1.81 and 1.85 Å, which are characteristic of peroxo complexes.^[27] This result establishes the peroxo species as a viable intermediate in Scheme 2.

In conclusion, the present results together with the recent reports^[28] of iron-based efficient water oxidation catalysts show that iron like ruthenium can also perform O–O bond formation reaction, a finding of extreme importance in the design and discovery of faster water oxidation catalysts involving biologically innocuous, inexpensive elements.

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Keywords: iron • iron-oxo intermediates • O–O bond formation • polynuclear ligands • porphyrinoids

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- [18] No satisfactory simulation of the $3\text{-}^{16}\text{O-}^{18}\text{O}$ spectrum with a split peak by keeping the positions and width (35 cm^{-1}) of the oxygen insensitive bands at 1158 cm^{-1} and 1138 cm^{-1} unchanged could be obtained; an unreasonable fit by changing the position (1161 cm^{-1}) and width (25 cm^{-1}) of the 1158 cm^{-1} is shown in Figure S14.
- [19] The superoxo unit can be terminal or bridging ($\mu\text{-}\eta^1\eta^2$, $\mu\text{-}1,2$ or $\mu\text{-}\eta^2\eta^2$) (Scheme S3, Table S2) but presently we do not have any spectroscopic evidence to discern between the four possibilities. However, based on the thermal stability of **3**, which allowed its generation at 25°C , we favor a terminal binding mode with the superoxide unit attached to Fe^{III} only and not interacting with Fe^{II}. The very few examples of Fe^{II}O₂[•]-Fe^{III} bridging complexes are highly unstable against the intramolecular electron transfer from Fe^{II} to O₂[•], to form a more symmetric Fe^{III}O₂²⁻-Fe^{III} unit. For instance, this is the case for the transient Fe^{II}O₂[•]-Fe^{III} superoxo units in soluble methane monooxygenase (which is not yet isolated) and a synthetic model complex (which is only stable at low-temperature and decays to diiron(III) species at elevated temperatures), where a $\mu\text{-}\eta^1\eta^2$ bridging mode has been proposed based on DFT (D. Rinaldo, D. M. Philipp, S. J. Lippard, R. A. Friesner, *J. Am. Chem. Soc.* **2007**, *129*, 3135) and experiments (M. Zhao, B. Helms, E. Slonkina, S. Friedle, D. Lee, J. DuBois, B. Hedman, K. O. Hodgson, J. M. J. Fréchet, S. J. Lippard, *J. Am. Chem. Soc.* **2008**, *130*, 4352), respectively. Interestingly, a terminal end-on Fe^{II} (O₂[•])-Fe^{III} superoxo complex is also reported to be of transient nature (X. Shan, L. Que Jr., *Proc. Natl. Acad. Sci.* **2005**, *102*, 5340).
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