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Article

New Example of a Non-Heme Mononuclear Iron(IV) Oxo Complex. Spectroscopic Data and Oxidation Activity

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The green complex $S = 1$ [(TPEN)FeO]$^{2+}$ [TPEN = N,N,N',N'-tetrakis(2-pyridylmethyl)ethane-1,2-diamine] has been obtained by treating the [(TPEN)Fe]$^{2+}$ precursor with *meta*-chloroperoxybenzoic acid (*m*-CPBA). This high-valent complex belongs to the emerging family of synthetic models of Fe^{IV}=O intermediates invoked during the catalytic cycle of biological systems. This complex exhibits spectroscopic characteristics that are similar to those of other models reported recently with a similar amine/pyridine environment. Thanks to its relative stability, vibrational data in solution have been obtained by Fourier transform infrared. A comparison of the Fe=O and Fe=^{18}O wavenumbers reveals that the Fe–oxo vibration is not a pure one. The ability of the green complex to oxidize small organic molecules has been studied. Mixtures of oxygenated products derived from two- or four-electron oxidations are obtained. The reactivity of this [FeO]$^{2+}$ complex is then not straightforward, and different mechanisms may be involved.

Introduction

Non-heme mononuclear Fe^{IV}–oxo species are frequently invoked as key intermediates in the catalytic cycles of biological systems involved in O$_2$ activation. However, only recently has a mononuclear high-spin Fe^{IV}=O complex been detected in the α-ketoglutarate-dependent dioxygenase TauD.[1,2] Thanks to the efforts of chemists, synthetic non-porphyrinic Fe^{IV}–oxo models have also been prepared very recently,[3–8] generally by treating an Fe^{II} precursor bearing an amine/

pyridine ligand with a single oxygen-atom donor, such as ClO$^-$, PhIO, peroxides, or even with dioxygen.[9] All of these complexes are characterized by a green color (associated with a moderately intense absorption band in the low-energy region of the visible region) and a triplet ground state.

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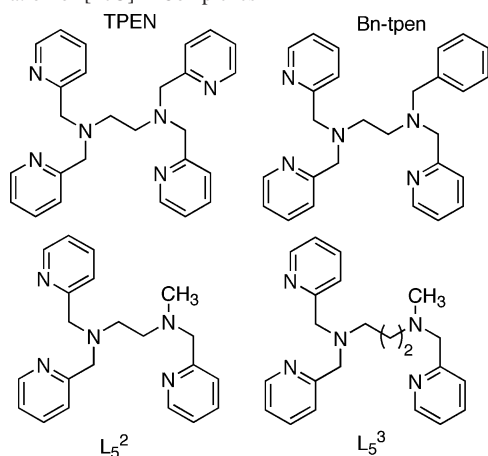§ DSV CEA/Saclay.
|| CEA/Grenoble.
⊥ Ecole Polytechnique.

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Chart 1. Structures of TPEN and Related Ligands That Have Allowed the Formation of [FeO]$^{2+}$ Complexes

Figure 1. Electronic absorption spectra in acetonitrile at 0 °C of (a) [(TPEN)Fe]$^{2+}$ (1 mM) and of (b) [(TPEN)Fe]$^{2+}$ (1 mM) + 1.2 equiv of *m*-CPBA dissolved in a negligible volume of acetonitrile.

However, their stability and their ability to oxidize small organic molecules are dissimilar. For example, the complexes [L$_5^2$FeO]$^{2+}$ and [L$_5^3$FeO]$^{2+}$ are highly unstable[7] compared to [(Bn-tpen)FeO]$^{2+}$,[6,8] despite the similar set of donors provided by the amine/pyridine ligands.

Stable μ-oxodiiron(IV) complexes have also very recently been obtained by Collins and co-workers.[10] These compounds have been isolated from the reaction between Fe^{III} with tetraamido macrocyclic ligands and O$_2$ in noncoordinating solvents. These black complexes contain antiferromagnetically coupled $S = 1$ Fe^{IV} centers.

We report here the synthesis, spectroscopic characterizations, and reactivity study of a new Fe^{IV}−oxo complex obtained with the hexadentate ligand TPEN (Chart 1).[11] Given the sufficient stability of this species, its vibrational characteristics in solution have been studied as well.

Experimental Section

Syntheses. The ligand TPEN was made according to the method reported by Toftlund and Yde-Andersen.[12] The complex [(TPEN)-Fe](PF$_6$)$_2$ was made following the method described by Chang et al.[13] The green complex [(TPEN)FeO]$^{2+}$ was obtained by treating [(TPEN)Fe]$^{2+}$ (1 mM in CH$_3$CN) by 1−2 equiv of *meta*-chloroperoxybenzoic acid (*m*-CPBA) at 0 °C.

Electronic absorption spectra were recorded using a Varian Cary 300 Bio spectrophotometer equipped with a Hellma immersion probe and fiber-optic cable.

Electrospray ionization mass specrometry (ESI-MS) spectra were recorded on a Micromass Quattro II or a Thermo Finnigan MAT 95S (^{16}O/^{18}O exchange). For isotopic labeling, H$_2$^{18}O was preincubated with the Fe^{II} precursor.

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(11) TPEN, *N,N,N′,N′*-tetrakis(2-pyridylmethyl)-1,2-diaminoethane; Bn-tpen, *N*-benzyl-*N,N′,N′*-tris(2-pyridylmethyl)-1,2-diaminoethane; L$_5^3$, *N*-methyl-*N,N′,N′*-tris(2-pyridylmethyl)-1,3-diaminopropane; L$_5^2$, *N*-meth-yl-*N,N′,N′*-tris(2-pyridylmethyl)-1,2-diaminoethane; TMC, 1,4,8,11-tetramethylcyclam; N4Py, *N,N*-bis(2-pyridylmethyl)bis(2-pyridylmethyl)-amine; SBPy$_3$, *N,N*-bis(2-pyridylmethyl)amine-*N*-ethyl-2-pyridine-2-aldimine.

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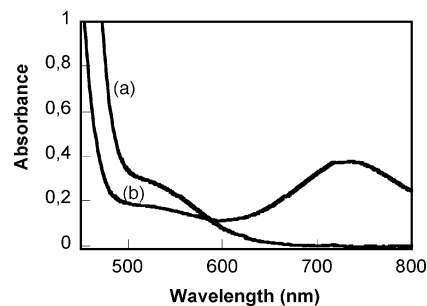
Fourier transform infrared (FT-IR) measurements were performed using a Bruker IFS 66 interferometer equipped with a deuterated triglycine sulfate detector. Acetonitrile samples were held in a NaCl holder mounted on a coldfinger liquid-nitrogen Dewar. Several consecutive spectra of 250 scans were averaged. The resolution was 4 cm^{-1}. Raw averaged spectra are reported. A total of 2 equiv of *m*-CPBA was added to a [(TPEN)Fe](PF$_6$)$_2$ solution (10 mM) to form [(TPEN)FeO]$^{2+}$ at −20 °C. For ^{18}O labeling, 250 equiv of H$_2$^{18}O was previously added to the Fe^{II} solution. Zero-Field Mössbauer data were collected on a solid sample (green powder) at low temperature (4.2 K) with a conventional liquid-helium, horizontal-transmission cryostat. The green powder was collected by adding Et$_2$O to a reaction mixture (prepared as described above) precooled at −40 °C and placed in a 200-μL nylon cell. The green powder was always maintained at low temperature to avoid decomposition. Experimental isomer shifts are reported relative to an iron metal standard at room temperature.

Reactivity. The experimental conditions have been chosen to match as closely as possible single-turnover conditions: a large excess of substrates and only 1 equiv of *m*-CPBA versus Fe have been used in order to avoid overoxidation of products and to determine the reactivity of the green complex itself. The reaction mixtures were typically [(TPEN)Fe^{II}](PF$_6$)$_2$ (4 mM) + 1 equiv of *m*-CPBA in acetonitrile/dichloromethane (1/1) at room temperature + 400 equiv of cyclooctane, 100 equiv of ethylbenzene, 100 equiv of *cis*-stilbene, or 200 equiv of cyclohexene.

Results and Discussion

Characterization of [(TPEN)FeO]$^{2+}$. The reaction of [(TPEN)Fe^{II}]$^{2+}$ (1 mM in acetonitrile) with typically 1−2 equiv of *m*-CPBA at 0 °C yields within 2 min a green species characterized by a 730-nm absorption band ($\epsilon \approx 380$ M^{-1} cm^{-1}; cf. Figure 1). This value is very close to those observed for [FeO]$^{2+}$ complexes obtained with the ligands Bn-tpen,[6] L$_5^2$, or L$_5^3$.[7] The green species is stable for hours at 0 °C but decomposes upon warming ($t_{1/2} \approx 30$ min for such a sample at room temperature; see below).

The ESI-MS spectrum of the green complex exhibits a peak at *m/z* 248.2 (cf. Figure 2). Along with the UV−visible data, this result strongly argues for a [(TPEN)FeO]$^{2+}$ complex.

Upon the addition of H$_2$^{18}O, the peak at *m/z* 248.2 progressively decreases in intensity with the concomitant increase of a peak at *m/z* 249.2, which can be attributed to [(TPEN)Fe^{18}O]$^{2+}$ (see the Supporting Information). The green complex is then readily exchanging its oxygen atom with solvent water. This ^{18}O/^{16}O exchange behavior has been
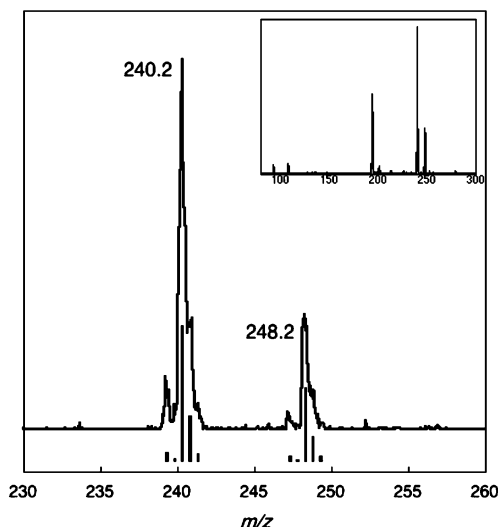
Figure 2. m/z 230−260 range of the ESI-MS spectrum of a solution of [(TPEN)Fe]$^{2+}$ (1 mM) + 2 equiv of m-CPBA prepared in acetonitrile at 0 °C diluted 10 times prior to injection. The structure with the major peak at m/z 248.2 corresponds to [(TPEN)FeO]$^{2+}$, and the structure at m/z 240.2 corresponds to the starting complex [(TPEN)Fe]$^{2+}$. The theoretical isotopic patterns are shown in bars. The full spectrum is shown in the inset.

observed very recently for two other non-heme [FeO]$^{2+}$ complexes obtained with TMC and N4Py.[14] It has been proposed that the exchange followed an oxo−hydroxo tautomerism[15] but with the two oxygenated ligands located in cis around the metal center. An argument for this mechanism is the characterization of the heptacoordinated side-on peroxo complex with N4Py.[16] One can also argue here that the formation of Fe^{III}−OOH complexes with ligands of the TPEN family follows a mechanism that is associative in nature.[8,17] The TPEN ligand can then also accommodate a heptacoordinated metal center in the transition state.

The green complex exhibits at zero applied field a Mössbauer spectrum consisting of a doublet with an isomer shift (δ) of 0.01(1) mm s^{-1} and a quadrupole splitting (ΔE_q) of 0.87(1) mm s^{-1} (see the Supporting Information). These parameters are characteristic of an Fe^{IV} complex.[18] They are indeed close to the parameters reported for all of the mononuclear Fe^{IV}−oxo models recently obtained.[3−7] There-fore, the green complex can be assigned as a low-spin ($S = 1$) [FeO]$^{2+}$ entity. Because these parameters are close to those obtained for [FeO]$^{2+}$ bearing pentadentate ligands,[6,7] it is likely that one pyridyl arm of the TPEN ligand is not bound to the metal center. A possible structure for this complex is represented in Chart 2. Similar structures are observed for the Fe^{II} complexes with pentadentate ligands of the same family and also for [(Bn-tpen)FeO]$^{2+}$.[19]

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Chart 2. Possible Structure for [(TPEN)FeO]$^{2+}$ (R = −Ch$_2$Py)
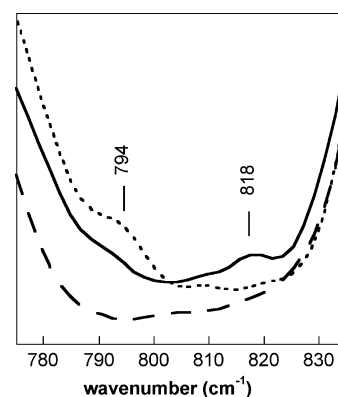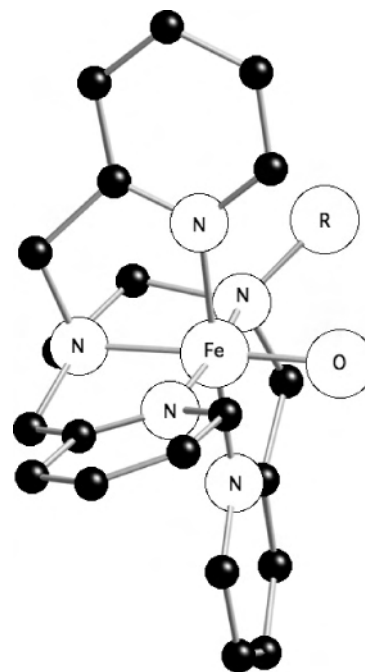
Figure 3. FT-IR spectrum at ca. −25 °C of [(TPEN)Fe](PF$_6$)$_2$ (10 mM) in acetonitrile (− −), [(TPEN)Fe](PF$_6$)$_2$ (10 mM) in acetonitrile + 2 equiv of m-CPBA (—), [(TPEN)Fe](PF$_6$)$_2$ (10 mM) in acetonitrile + 250 equiv of H$_2$^{18}O + 2 equiv of m-CPBA (- - -).

The nature of the near-IR absorption band has been postulated to be mainly due to d−d transitions.[5,7] This has been shown experimentally by magnetic circular dichroism.[20] Most probably, the lowest-energy oxo-to-Fe^{IV} charge transfer lies in the UV, overlapping with the intense $\pi−\pi^*$ transitions of the pyridine rings of the ligand. As a consequence, no reliable resonance Raman evidence for these types of complexes has been obtained to date.[21] We have thus performed FT-IR experiments on cold solutions of the green complex. As shown in Figure 3, the acetonitrile solution of [(TPEN)Fe^{II}](PF$_6$)$_2$ does not exhibit any vibration between 780 and 830 cm^{-1}, where the solvent and counteranion,

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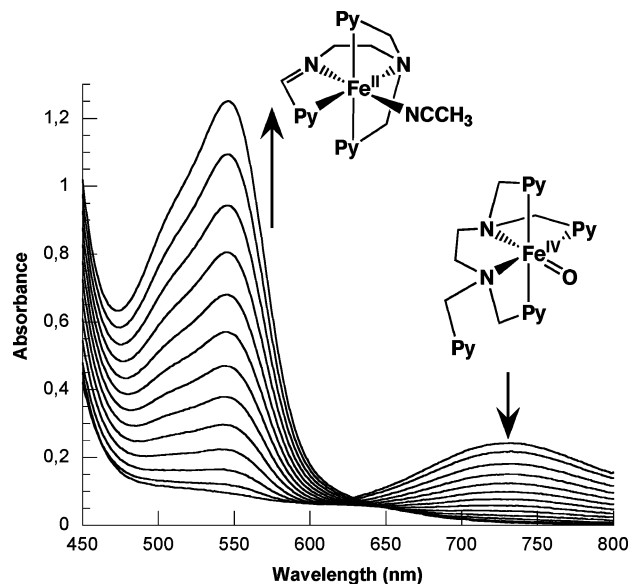
Figure 4. Evolution of the green complex prepared from [(TPEN)Fe^{II}]$^{2+}$ (1 mM in acetonitrile/dichloromethane) with 1 equiv of *m*-CPBA at room temperature over a 2-h period. The structures of the high-valent complex [(TPEN)FeO]$^{2+}$ and of one of the final products [(SBPy$_3$)Fe(CH$_3$CN)]$^{2+}$ are shown.

respectively, absorb. The [(TPEN)FeO]$^{2+}$ complex exhibits a new band at 818 cm^{-1} that vanishes when the temperature increases. This band is a good candidate for the Fe–oxo vibration. It is indeed a value close to those reported for porphyrinic complexes[22,23] or to the value reported for the structurally characterized [FeO(TMC)(NCCH$_3$)](OTf)$_2$.[4] When the [FeO]$^{2+}$ complex is prepared in the presence of 250 equiv of H$_2$^{18}O, the 818-cm^{-1} band is no longer detectable, but a new band appears at 794 cm^{-1}. This new band progressively decreases in intensity when the temperature increases. The observed −24-cm^{-1} isotopic shift upon labeling is lower than what is expected for a pure diatomic Fe=O vibration (−36 cm^{-1}) and thus may be kinematically coupled to other modes.

Reactivity of [(TPEN)FeO]$^{2+}$ in Solution. The green complex decomposes immediately upon addition of PPh$_3$ to give OPPh$_3$, quantitatively.

Interestingly, in the absence of any substrate, a green solution of [(TPEN)FeO]$^{2+}$ progressively turned to pink-red. This evolution, monitored by UV−visible spectroscopy, is shown in Figure 4. It reveals that the green complex disappears to give a species characterized by an intense absorption band peaking at 556 nm with a shoulder at ca. 500 nm. This feature can be assigned to [(SBPy$_3$)Fe^{II}(CH$_3$-CN)]$^{2+}$, a complex with the neutral pentadentate N5 Schiff base ligand SBPy$_3$ previously reported by Patra et al. (557 nm, ϵ = 6780 M^{-1} cm^{-1};[24] cf. Figure 4). This attribution was confirmed by the detection of [(SBPy$_3$)Fe]$^{2+}$ at *m/z* 193.7, together with a peak corresponding to pyridine carboxaldehyde (*m/z* 108.2; M + H$^+$) during the study of [(TPEN)FeO]$^{2+}$ by EI-MS (see the Supporting Information).

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Table 1. Oxidation of Organic Substrates by [(TPEN)Fe](PF$_6$)$_2$ (4 mM) + 1 equiv of *m*-CPBA in CH$_2$Cl$_2$/CH$_3$CN (1/1, v/v) at Room Temperature[a]

		products	
substrate		cyclooctanol	cycloctanone
cyclooctane	Ar	1	
	air	1	4.2
		PhCH$_2$(OH)CH$_3$	PhCH(O)CH$_3$
ethylbenzene	Ar	1.6	4
	air	6	16
		cis-epoxide	*trans*-epoxide
cis-stilbene	Ar	5	11
		cyclohexenol	cyclohexenone
cyclohexene	Ar	33	8

[a] Yields (%) are given with respect to the oxidant.

Because the series of spectra shown in Figure 4 does not exhibit any isosbestic point, it is clear that [(SBPy$_3$)Fe(CH$_3$CN)]$^{2+}$ is not the only final species. Indeed, the intensity of the band at 556 nm allows one to estimate the amount of this later complex to ca. 25% of the total Fe. The degradation of [(TPEN)FeO]$^{2+}$ proceeds then by several reactions, but attempts to fit the absorbance at 730 or 556 nm as a function of time were unsuccessful even when multiple reactions were taken into account. However, self-decay of [(TPEN)FeO]$^{2+}$, monitored by UV−visible spectroscopy, has shown that the half-life of the green complex was dependent on the initial concentration in Fe: the more concentrated the solution, the faster the degradation is. Then, at least one of the degradation pathways is not a first-order process. Moreover, plots of the absorbance at 730 and 556 nm resolved in time show that [(TPEN)FeO]$^{2+}$ is not converted directly to [(SBPy$_3$)Fe(CH$_3$CN)]$^{2+}$ but that one intermediate must be involved (see the Supporting Information). Patra et al.[24] have shown that [(SBPy$_3$)Fe(CH$_3$CN)]$^{2+}$ was formed in acetonitrile by spontaneous reduction of [(SBPy$_3$)Fe(DMF)]$^{3+}$ ($t_{1/2}$ = 100 min). By analogy, one can assume that [(SBPy$_3$)Fe(CH$_3$CN)]$^{2+}$ is obtained by reduction of an Fe^{III} analogue formed after degradation of [(TPEN)FeO]$^{2+}$.

Finally, it has to be noted that single crystals of [(TPEN)-Fe^{II}](PF$_6$)$_2$ and [(TPEN)Fe^{III}](PF$_6$)$_3$ have also been isolated from a solution of [(TPEN)FeO]$^{2+}$ after decay of the green complex.

All of these observations show that [(TPEN)FeO]$^{2+}$ is quite a versatile oxidant. It is capable of transferring its oxygen atom to a substrate (as in the case of PPh$_3$). Also, the detection of [(SBPy$_3$)Fe(CH$_3$CN)]$^{2+}$ shows that the [FeO]$^{2+}$ is able to oxidize the TPEN ligand. That this oxidation does not proceed through an intramolecular process but rather through an intermolecular process is likely (see above). In this hypothesis, it can be postulated that the first step of this reaction is an hydrogen-atom abstraction on a methylene pyridyl arm of a first complex by a second [(TPEN)FeO]$^{2+}$ partner.

Hydrocarbon Oxidation by [(TPEN)FeO]$^{2+}$. The oxidizing potential of the green complex has been studied at room temperature in acetonitrile/dichloromethane (1/1, v/v; Table 1). The experimental conditions have been chosen to match as closely as possible single-turnover conditions in

order to avoid overoxidation of products and to determine the reactivity of the green complex itself.

The green complex is a poor hydroxylating agent because cyclooctanol is obtained in only 1% yield under argon. Under aerobic conditions, a mixture of alcohol and ketone is obtained and the total yield in products is increasing, with the cyclooctanone being the major product. In the case of ethylbenzene, only products deriving from benzylic oxidation are observed, with the ketone as the major product in aerobic or anaerobic conditions. For the oxidation of the alkane, the reactivity observed is quite similar to that of [(Bn-tpen)-FeO]$^{2+}$,[6] but it is distinct from that of [L$_5$^{3}FeO]$^{2+}$, which is capable of oxidizing cyclohexane into cyclohexanol only.[7] The results obtained with ethylbenzene are consistent with those obtained with cyclooctane because 1-phenylethanol and acetophenone are obtained with a alcohol/ketone ratio <1 and increasing yields under aerobic conditions. We had previously observed that an [FeO]$^{2+}$ complex obtained with an amine/pyridine ligand is unable to oxidize an aromatic ring.[25] This is confirmed here.

The epoxidation of *cis*-stilbene is observed at 16% yield with isomerization to the trans isomer preferentially. Interestingly, benzaldehyde is only obtained as trace amounts. This has been previously observed with [L$_5$^{3}FeO]$^{2+}$. Groves et al. have explained the loss of selectivity in heme systems by the involvement of a carbon-radical intermediate formed by radical attack of the olefin by the [FeO]$^{2+}$ entity.[26] On the contrary, cyclohexene is not epoxidized and allylic oxidation products are obtained. Under air, a total yield of ca. 500% versus *m*-CPBA was obtained in 90 min with equimolar amounts of alcohol and ketone. These results most probably indicate the formation of cyclohexenyl radicals during the reaction.

Finally, it has also to be pointed out that all of the samples prepared for this reactivity study turned to pink-red, revealing that a significant amount of [(SBPy$_3$)Fe(CH$_3$CN)]$^{2+}$ was formed in all experiments. As a consequence, the yields of oxidation products given in Table 1 are underestimated.

Conclusion and Comments

By using the potentially hexadentate ligand TPEN and *m*-CPBA as a single-oxygen-atom donor, an [FeO]$^{2+}$ complex has been prepared. It exhibits spectroscopic features that are common to other members of this emerging family of mononuclear non-heme Fe^{IV}=O obtained recently with tetradentate or pentadentate amine/pyridine ligands.[4−7] The Fe−oxo valence vibration has been detected in solution by FT-IR at a frequency consistent with values reported for porphyrinic[22,23] or non-porphyrinic[4] systems. The ^{18}O isotopic effect showed that this vibration does not arise from a pure mode. This is probably the consequence of the nonmacrocyclic nature of the ligand, with the oxo group being necessarily located in trans of a coordinative function of the ligand skeleton. The oxidation ability of this complex has been estimated by using a series of organic substrates. The results obtained suggest that [FeO]$^{2+}$ behaves, at least in part, as an oxidant with some spin density on the terminal oxygen. For the oxidation of C−H bonds for example, the reaction may be initiated by hydrogen-atom abstraction that would generate an alkyl radical prone (i) to diffuse or (ii) to rebound to the metal center to finally lead to oxygen insertion. It has been shown that oxidation of alkanes by oxidants with closed-shell electronic structure such as permanganate follows a rebound mechanism.[27] In the case of a non-heme [FeO]$^{2+}$, the reactivity appears to be less straightforward. Moreover, it is, *apparently*, also dependent on the experimental conditions: [(N4Py)Fe^{IV}O]$^{2+}$ has been reported to be a nonselective oxidant toward oxidation of alkanes in single-turnover conditions,[6] whereas its selectivity for the alcohol formation in catalytic conditions has been demonstrated.[28] The mechanism proposed by Bryant and Mayer[29] for the oxidation of C−H bonds by [(bpy)$_2$(py)Ru^{IV}O]$^{2+}$ may be a starting point to explain this *apparent* contradiction: in the presence of larger concentrations of oxidant (or if [FeO]$^{2+}$ can be easily regenerated, i.e., in catalytic conditions), the alkyl radical initially formed by hydrogen-atom abstraction is frequently trapped by an oxidant (and thus an [Fe(HOR)]$^{2+}$ or [Fe(OR)]$^{2+}$ would be the intermediate before the alcohol release). Other studies are needed to determine more precisely the reactivity of these new types of [FeO]$^{2+}$ complexes.

A question that has also to be addressed concerns the relationship between the nature of the oxidation products and the electronic structure of the [FeO]$^{2+}$ oxidant. Throughout this paper, we used either the notations [FeO]$^{2+}$ or Fe^{IV}=O. In our mind, the attribution of the oxidation state to Fe still deserves to be experimentally and theoretically explored.

Supporting Information Available: Oxygen-atom exchange between [(TPEN)FeO]$^{2+}$ and H$_2$^{18}O monitored by EI-MS (Figure S1), Mössbauer spectrum of [(TPEN)FeO](PF$_6$)$_2$ (Figure S2), ESI-MS spectrum of [(TPEN)FeO]$^{2+}$ during its decay (Figure S3), and absorbance of [(TPEN)FeO]$^{2+}$ and of [(SBPy$_3$)Fe(CH$_3$CN)]$^{2+}$ resolved in time (Figure S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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