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Incorporation of redox-inactive cations promotes iron catalyzed aerobic C–H oxidation at mild potentials†

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The synthesis and characterization of the Schiff base complexes Fe(II) (**2M**) and Fe(III)Cl (**3M**), where M is a K⁺ or Ba²⁺ ion incorporated into the ligand, are reported. The Fe(III/II) redox potentials are positively shifted by 440 mV (**2K**) and 640 mV (**2Ba**) compared to Fe(salen) (salen = *N,N'*-bis(salicylidene)ethylenediamine), and by 70 mV (**3K**) and 230 mV (**3Ba**) compared to Fe(Cl)(salen), which is likely due to an electrostatic effect (electric field) from the cation. The catalytic activity of **3M** towards the aerobic oxidation of allylic C–H bonds was explored. Prior studies on iron salen complexes modified through conventional electron-donating or withdrawing substituents found that only the most oxidizing derivatives were competent catalysts. In contrast, the **3M** complexes, which are significantly less oxidizing, are both active. Mechanistic studies comparing **3M** to Fe(salen) derivatives indicate that the proximal cation contributes to the overall reactivity in the rate determining step. The cationic charge also inhibits oxidative deactivation through formation of the corresponding Fe₂-μ-oxo complexes, which were isolated and characterized. This study demonstrates how non-redox active Lewis acidic cations in the secondary coordination sphere can be used to modify redox catalysts in order to operate at milder potentials with a minimal impact on the reactivity, an effect that was unattainable by tuning the catalyst through traditional substituent effects on the ligand.

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Introduction

Transition metal complexes are ubiquitous as redox catalysts because they can both activate substrates and mediate electron transfer through multiple accessible redox states. Catalytic function is conventionally optimized through inductive effects by modifying the supporting ligand with electron-withdrawing or -donating substituents (Chart 1, left).¹ Modifying ligands in this fashion impacts both the electronic structure of the metal as well as the redox properties, which can lead to an inverse correlation between the activity and operation at mild redox potentials. Scaling relationships of this type are observed for many classes of homogeneous oxidation catalyst,^{2,3} as well as for polymerization catalysts.⁴ The trade-off between catalytic activity and function at mild potentials has also been found in electrocatalysts for O₂,⁵ CO₂,⁶ and H⁺ (ref. 7) reduction, and is

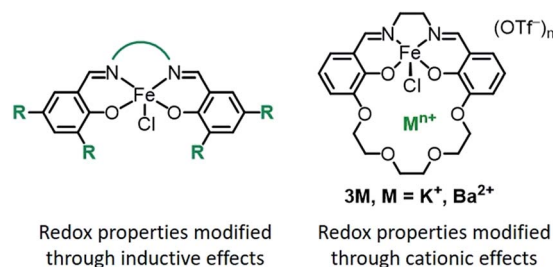
a major challenge in the optimization of catalysts for both high activity and energetic efficiency (low overpotential).

Various strategies have been successfully employed to improve redox reactivity at mild potentials, such as enzyme-inspired cooperative or secondary interactions.^{8–36} An additional approach would utilize the secondary coordination sphere to adjust the redox properties. In nature, only three metal–ligand motifs are commonly used to mediate electron transfer (iron–sulfur clusters, hemes, and cupredoxins), yet the measured redox potentials of each cofactor span a wide range depending on their microenvironment.³⁷ Elegant studies employing site-directed mutagenesis in artificial metalloenzymes demonstrate how secondary coordination sphere interactions, such as hydrogen-bonding or hydrophobicity,

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Redox properties modified
through inductive effects

Redox properties modified
through cationic effects

Chart 1



adjust the redox potential.^{38–40} Local electric field (electrostatic) effects have also been cited as a key component for the high catalytic activity found in enzymes^{41,42} and are emerging as an important tool for achieving selective or increased reactivity in organic synthesis.^{43–59} However, there are fewer examples of applying electrostatic interactions to enable more efficient redox catalysis.^{60–62}

Transition metal complexes that contain crown ether-like functionalities to encapsulate alkali or alkaline earth metal ions have been reported for a variety of applications.^{63–92} We recently reported that the incorporation of non-redox active cations in a Co(II) Schiff base complex leads to significant positive shifts in the Co(II/I) redox potential,⁹³ an effect that has been observed in other synthetic systems.^{94–101} Notably, our spectroscopic studies indicate that the shift in redox potential is likely due to an electric field potential from the cation, since the electronic structure of the metal is not significantly perturbed.⁹³

We were interested in exploring how cation incorporation would impact the redox reactivity compared to complexes tuned through traditional inductive modifications. To this end, we examined the effect of proximal cations on iron catalysts for the aerobic allylic C–H oxidation of cyclohexene. Prior studies on iron Schiff base complexes have demonstrated a strong correlation of the Fe(III/II) redox potential (Table 3) with the overall catalytic activity.¹⁰² When inductive effects were used to modify the iron Schiff base complexes, catalysis was only observed for the tetranitro substituted complexes, which have potentials positive of -0.27 V vs. $[\text{Fe}(\text{Cp})_2]^{+/0}$. For these complexes, the activity increases with the more oxidizing redox potentials.¹⁰²

For this study we synthesized the iron complexes **3M**, shown in Chart 1 and Scheme 1, which have either a proximal $\text{M} = \text{K}^+$ or Ba^{2+} ion in the secondary coordination sphere. **3K** and **3Ba** are both active catalysts despite having Fe(III/II) redox potentials that would be insufficient for catalysis if they had been tuned by installing electron withdrawing groups.

Mechanistic studies with **3M** and **2M** indicate that the K^+ or Ba^{2+} ion facilitates the rate determining step. Aside from their role in adjusting the redox potential, non-redox active Lewis acidic metals are also known to play a role in the activation of dioxygen and the corresponding oxidizing intermediates.^{101,103–114} Thus, the incorporation of non-redox active Lewis metals in the secondary coordination sphere also provides a route toward cooperative reactivity. Increasing the cationic nature of the Fe intermediates also inhibits the major deactivation pathway, which is formation of a diiron μ -oxo complex.

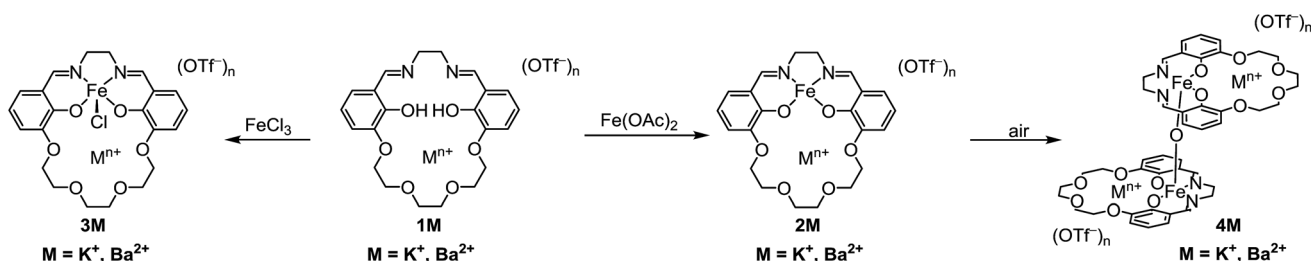
These results demonstrate that the installation of a proximal cation can provide another “knob” to tune the redox reactivity. In contrast to adjusting the ligand field strength through electronic effects in the primary coordination sphere, modifications to the secondary coordination sphere are effectively used to improve the redox activity at a milder potential.

Results and discussion

Synthesis and characterization

The preparation of the ligands **1M** ($\text{M} = \text{K}^+$ or Ba^{2+} , Scheme 1) has previously been reported.^{93,102} The corresponding Fe(II) and Fe(III)Cl complexes, **2M** and **3M**, were synthesized by metalation of the ligand with $\text{Fe}(\text{OAc})_2$ in methanol (MeOH) and anhydrous FeCl_3 in ethanol (EtOH), respectively. The products were recrystallized by the vapor diffusion of diethyl ether (Et_2O) into an acetonitrile (CH_3CN) solution of the complex. **2M** reacts with air in MeOH or CH_3CN to form the diiron μ -oxo species (**4M**), while the Fe(III)Cl complexes (**3M**) are air-stable. The **4M** complexes were isolated by recrystallization (vapor diffusion of Et_2O into concentrated CH_3CN solution). The purity and formulation of the complexes were confirmed using elemental analysis and mass spectrometry. The corresponding complexes Fe(salen) and Fe($\text{Ph}_2\text{salenCl}_4$) (ligands for compound **A** and **C**, respectively, in Table 3), which have a similar primary coordination environment but lack proximal cations, were synthesized according to previously published procedures in order to compare their reactivity with **3M**, as they have similar redox potentials.¹⁰²

X-ray crystallography. Crystals of **2Ba**, **3K**, **3Ba**, **4K**, and **4Ba** suitable for single crystal X-ray analysis were grown under the same conditions used for the recrystallization. The ORTEPs are shown in Fig. 1 and the structural parameters are provided in Table 1. The coordination geometries around the Fe(II) and Fe(III) ions are distorted square pyramidal, with the τ_5 value for all complexes between 0.11 and 0.36, (where $\tau_5 = 0$ for a square pyramidal geometry and $\tau_5 = 1$ for a trigonal bipyramidal geometry). These values are similar to those for the previously reported Fe(Cl)(salen) and Fe(salen) complexes without the crown-appendage.^{115–117} **3M** and **4M** have lower τ_5 values for $\text{M} = \text{Ba}^{2+}$ compared to $\text{M} = \text{K}^+$. Although the ionic radii of K^+ and Ba^{2+} are similar, with values of 138 and 135 pm, respectively, the Fe–Ba distance is longer than the corresponding Fe–K distance in **3M**. We attribute this difference to the stronger charge repulsion between the Fe^{3+} ion and dicationic Ba^{2+} .



Scheme 1



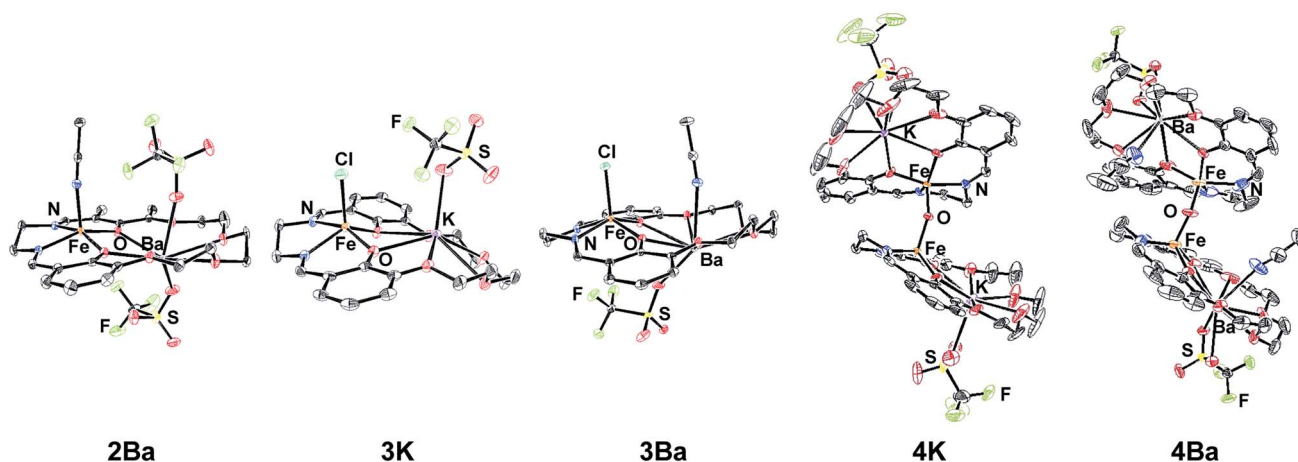


Fig. 1 Solid-state structures of **2Ba**, **3K**, **3Ba**, **4K**, and **4Ba**. Hydrogen atoms and non-coordinating anions are omitted for clarity. **4K** contains two outer sphere triflate ions. Ellipsoids are drawn at 50% probability.

Table 1 Structural parameters of **2Ba**, **3K**, **3Ba**, **4K**, and **4Ba**, and the Fe(III/II) redox potentials vs. $[\text{Fe}(\text{Cp})_2]^{+/0}$ in CH_3CN for **2M**, **3M**, and selected iron salen complexes lacking a proximal cation for comparison

Compound	Fe–M distance (Å)	τ_5	Fe–Cl distance (Å)	Fe–O distance (Å)	$E_{1/2}$ (Fe(III/II)) (V)
2K	—	—	—	—	–0.29
2Ba	3.6592(4)	0.11	—	—	–0.09
Fe(salen)	—	—	—	—	–0.73
3K	3.6596(6)	0.36	2.218	—	–0.69
3Ba	3.8115(3)	0.13	2.228	—	–0.53
$[\text{Fe}(\text{Cl})(\text{salen})]$ (A) ^{102,115}	—	0.20	2.238	—	–0.76 (ref. 102)
4K ^a	3.704(8), 3.751(6)	0.30	—	1.787	—
4Ba	3.780	0.18	—	1.771	—
$[\text{Fe}_2(\mu\text{-O})(\text{salen})_2]$ ¹¹⁶	—	0.27, 0.38	—	1.788, 1.785	—

^a The structure of **4K** contains K^+ that is disordered over 2 positions.

Electrochemistry. Cyclic voltammograms of the Fe(III/II) redox couples for **2M** and **3M** ($\text{M} = \text{K}^+$ and Ba^{2+}) in CH_3CN are shown in Fig. 2. All the Fe(III/II) redox couples are electrochemically reversible, and the standard potentials are reported

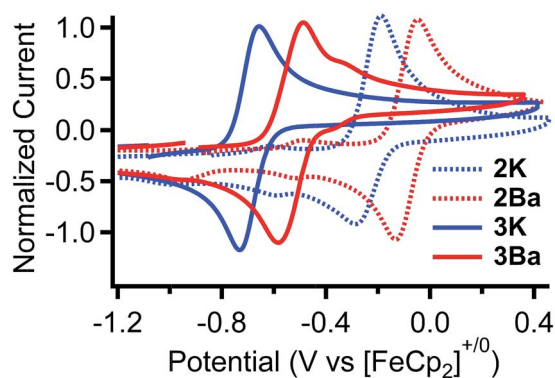


Fig. 2 Cyclic voltammograms of the Fe(III/II) redox couple for **2K**, **2Ba**, **3K**, and **3Ba**, in 0.2 M $n\text{Bu}_4\text{NPF}_6$ in CH_3CN with a glassy carbon disc as the working electrode, glassy carbon rod as the counter electrode, and Ag^+/Ag in 0.2 M $n\text{Bu}_4\text{NPF}_6$ in CH_3CN solution as the pseudo reference electrode, and ferrocene as an internal standard.

in Table 1. The previously measured potentials for Fe(salen), Fe(salen)Cl, and Fe(III)Cl(Ph₂salenCl₄) are provided for comparison to **2M** and **3M**.¹⁰²

The standard potentials for the Fe(III/II) couple for **2K** and **2Ba** are 440 and 640 mV more positive than that for Fe(salen). The standard potentials for **3K** and **3Ba** are 70 and 230 mV more positive compared to that for Fe(salen)Cl. Moreover, the potential for **3Ba** approaches that for FeCl(Ph₂salenCl₄), the derivative with four electron withdrawing chloride functionalities in the ligand backbone.

Catalytic oxidation activity

The aerobic oxidation activity of **3K** and **3Ba** with cyclohexene was tested using a similar protocol to prior studies with iron porphyrin and iron salen complexes.¹⁰² Oxygen-saturated CH_3CN solutions of cyclohexene and **3K** or **3Ba** were mixed (benzene was added as an internal standard). The reaction mixtures were kept under 1 atm of O_2 for 24 hours before being analyzed using ¹H NMR spectroscopy to quantify the concentration of the cyclohexene hydroperoxide, as well as the alcohol and ketone products. Prior studies used gas chromatography



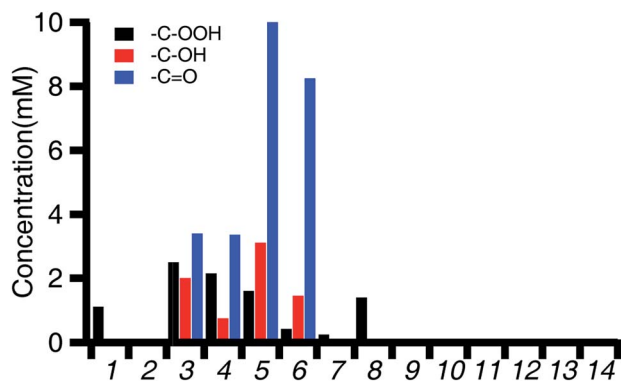


Fig. 3 Concentration of the products detected by ^1H NMR after 24 hours for the 0.5 M solutions of cyclohexene under 1 atm of O_2 and the specified conditions. Conditions for each entry can be found in Table 2.

for the product analysis, so the more reactive hydroperoxide intermediate was unobservable.

The overall activity and product distributions are shown in Fig. 3 and Table 2. **3K** and **3Ba** provide total turnover numbers of 17.4 and 46.6, respectively, for 2-cyclohexen-1-ol and 2-cyclohexenone (Fig. 3 and Tables 2 and 3). The reactivity of $\text{Fe}(\text{Cl})(\text{salen})$ and $\text{Fe}(\text{Cl})(\text{Ph}_2\text{salenCl}_4)$ (compounds **A** and **C** in Table 3), which have similar redox potentials to **3K** and **3Ba**, respectively, was also examined and the compounds showed negligible activity towards aerobic C–H allylic oxidation (entries 1 and 2, Fig. 3 and Table 2). The hydroperoxide intermediate is observed with $\text{Fe}(\text{Cl})(\text{salen})$, indicating that the latter is unreactive towards promoting subsequent oxidation reactions, a supposition supported in our mechanistic studies (*vide infra*).

The addition of external non-redox active metal salts has enhanced the oxidation activity for some transition metal catalysts, in some cases forming adducts *in situ*.^{101,103–114} For this catalyst, the incorporation of cations into the ligand framework is key for the reactivity; the addition of various Ba^{2+} salts to $\text{Fe}(\text{Cl})(\text{salen})$ or FeCl_3 gave no detectable quantity of product, although hydroperoxide was sometimes observed (entries 7, 8,

Table 3 Comparison of the aerobic cyclohexene oxidation activity vs. the $\text{Fe}(\text{III}/\text{II})$ redox potential for the iron Schiff base complexes. Entries are sorted by the redox potential (low to high). Italicized entries: 1, 2, and 5–8 are tuned through electronic induction (left structure), and are reported from ref. 102. Bold entries 3 and 4 are tuned through electrostatic effects (**3M**, right structure)

Entry	Compound	R		$E_{1/2}$ $\text{Fe}(\text{III}/\text{II})$ vs. $[\text{FeCp}_2]^{+/0}$	TON ^c
1	A	H		−0.81	0
2 ^a	B	H		−0.75	0
3 ^b	3K	—	—	−0.71	17
4 ^b	3Ba	—	—	−0.57	46
5 ^a	C	Cl		−0.56	0
6 ^a	D	Cl		−0.44	0
7 ^a	E	NO_2		−0.32	30
8 ^a	F	NO_2		−0.255	165

^a ref. 102. ^b This work. ^c Total turnover numbers for 2-cyclohexen-1-ol and 2-cyclohexenone from a 0.5 M solution of cyclohexene after 24 hours under 1 atm O_2 with the respective iron compound.

and 9, Fig. 2 and Table 2). The absence of product under these conditions indicates that there is no intermolecular role for the non-redox active Lewis acidic metals in promoting catalysis.

Table 2 Concentration of the products, as quantified by ^1H NMR spectroscopy, of a 0.5 M solution of cyclohexene after 24 hours under 1 atm O_2 and the specified conditions

Entry	Conditions	Cyclohexenol (mM)	Cyclohexenone (mM)	Total turnover (alcohol/ketone)
1	$\text{Fe}(\text{Cl})(\text{salen})$ (A)	1.1	0	0
2	$\text{Fe}(\text{Cl})(\text{Ph}_2\text{salenCl}_4)$ (C)	0	0	0
3	3K	2.0	3.4	17.4
4	3K + TBACl	0.8	3.4	14.9
5	3Ba	3.1	10.0	46.4
6	3Ba + TBACl	1.5	8.2	35.9
7	$\text{Fe}(\text{Cl})(\text{salen})$ (A) + $\text{Ba}(\text{18-crown-6})(\text{OTf})_2$	0.2	0	0
8	$\text{Fe}(\text{Cl})(\text{salen})$ (A) + $\text{Ba}(\text{OTf})_2$	0	0	0
9	FeCl_3 + $\text{Ba}(\text{OTf})_2$	0	0	0
10	3K + BHT	0	0	0
11	3Ba + BHT	0	0	0
12	1Ba	0	0	0
13	No Fe control	0	0	0
14	TBACl	0	0	0



The addition of excess tetrabutylammonium chloride (TBACl) to **3M** had a slight inhibitory effect (entries 4 and 6, Fig. 2 and Table 2). When no iron complexes were present, with or without TBACl, or when only the ligand was present, no catalytic activity was observed. Prior studies have indicated that catalysis occurs through a radical mechanism.^{102,118–120} We found that addition of the radical scavenger butylated hydroxytoluene (BHT) inhibited all reactivity, supporting a similar radical-based mechanism for **3K** and **3Ba**.

Water tolerance. A notable difference in the catalytic oxidation activity of **3K** and **3Ba** compared to the prior electron-rich iron salens and porphyrins is a tolerance to water. Maximal activity with the previously reported catalysts was only achieved when the solvent and oxygen source were rigorously dried. In contrast, the activity of **3K** was only slightly diminished in the presence of water, while the activity of **3Ba** was unaffected. Comparisons of the relevant turnover numbers are shown in Table S1 and Fig. S6.†

Mechanistic studies. Gray, Labinger and coworkers previously proposed a Haber–Weiss radical-chain mechanism for catalysis by iron porphyrins (Scheme 2).^{118–120} The organic hydroperoxide is oxidized by the Fe(III) complex to generate a hydroperoxide radical (B in Scheme 2). The hydroperoxide radical can react with the corresponding Fe(II) complex to generate an alkoxy radical and hydroxide, resulting in the regeneration of the Fe(III) active catalyst. The organic radicals propagate and ultimately terminate to yield the ketone and alcohol. Similar to the iron porphyrins, the reactivities of **3K** and **2Ba** are also inhibited upon addition of BHT, indicating that they likely proceed through the same radical-based mechanism. Additionally, the use of cyclohexenol as the substrate instead of cyclohexene, under the same conditions, led to no conversion to cyclohexanone, which is consistent with the proposed mechanisms where cyclohexenol and cyclohexenone result from different termination steps.

In the proposed mechanism, the total catalytic activity of the iron macrocycles, represented by the turnover number, is determined by two factors. The first is the reduction of the Fe(III) Cl complex with the organic hydroperoxide (B in Scheme 2), which is believed to be rate limiting since the hydroperoxide is observable in millimolar concentrations during catalysis. The second is deactivation of the catalyst, which occurs through

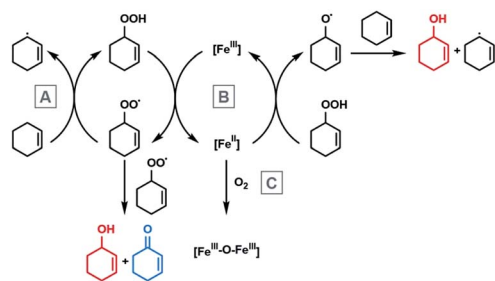
reaction of the Fe(II) intermediate with oxygen (instead of a hydroperoxide) to form the inactive diiron(III) μ -oxo complex (step C in Scheme 2). As this is a redox reaction, it is also expected to exhibit a redox-dependent rate, whereupon the complexes with lower Fe(III/II) redox potentials react more quickly with oxygen. For both the rate-limiting step and the deactivation pathway, the overall reactivity should be more favorable with higher Fe(III/II) standard potentials. These two steps are consistent with the trend observed in previously reported high-spin ($S = 5/2$) iron complexes, in that only complexes with Fe(III/II) couples above -0.27 V are active (Scheme 1). Incorporation of the proximal cation in **3M** results in catalytic activity at significantly less oxidizing potentials.

The reactivity of **3K** and **3Ba** in the rate-determining step and deactivation pathway was also investigated. For the former, the reactivity of **3K**, **3Ba**, and Fe(Cl)(Ph₂salenCl₄) (compound C in Table 3) with *tert*-butyl hydroperoxide (*tert*-BuOOH) was monitored using electronic absorption spectroscopy. *tert*-BuOOH was used as a substitute for cyclohexene hydroperoxide, since the latter cannot be generated in reproducible concentrations. **3K** and **3Ba** showed spectroscopic changes upon the addition of *tert*-BuOOH,¹¹³ while no change was observed for Fe(Cl)(Ph₂salenCl₄) (Fig. S7†). We were unable to measure a rate constant for the reaction of **3M** with *tert*-BuOOH, since the reduced Fe(II) complex (**2M**) can react with another equivalent of *tert*-BuOOH to regenerate **3M**. However, it is evident that the **3M** complexes are both reactive while Fe(Cl)(Ph₂salenCl₄), which has a similar redox potential to **3Ba**, is unreactive. Incorporation of the cation into the ligand framework could also play a role in facilitating intramolecular electron transfer,^{105,121,122} as Lewis acidic metal cations can bind or otherwise interact with the lone pairs on the hydroperoxide.¹⁰³

We also examined whether there was a difference in the rate of deactivation through μ -oxo formation by the Fe(II) intermediates. The rate of reaction of **2K** and **2Ba** with O₂ was also measured using electronic absorption spectroscopy. The diiron μ -oxo complexes were independently synthesized to determine their spectroscopic signatures. While the rate of oxidation was difficult to determine because of the complicated kinetic profile (Fig. S8†), the half-lives for the oxidation of **2K** and **2Ba** are 18 seconds and 37 seconds at 0 °C, respectively. The slower rate of oxidation for **2Ba** (and corresponding higher overall activity) is consistent with the more positive Fe(III/II) redox potential.

Conclusion

For Fe salen complexes modified through traditional inductive effects, only derivatives with four nitro groups and Fe(III/II) potentials greater than -0.27 V were sufficiently oxidizing to catalyze the aerobic oxidation of cyclohexene. However, the incorporation of K⁺ and Ba²⁺ ions in the secondary coordination sphere results in active catalysts despite having Fe(III/II) redox potentials of -0.71 and -0.57 V, respectively. Mechanistic studies indicate that incorporation of the Lewis acidic cation promotes reactivity in the rate-determining step, oxidation of an organic hydroperoxide, and inhibits deactivation through Fe₂- μ -oxo formation.



Scheme 2 The Haber–Weiss radical-chain mechanism of cyclohexene hydroperoxide decomposition and deactivation by diiron μ -oxo formation.



For catalytic reactions in which substrate activation is rate limiting, increasing the catalytic rate through inductive ligand effects often has the undesirable outcome of shifting the redox potential to more extreme values. Overcoming these scaling relationships requires utilizing alternative routes to facilitate reactivity or non-inductive methods to modify redox properties. The incorporation of a non-redox active proximal cation in the secondary coordination sphere was successfully used in this system to achieve catalytic activity at a less oxidizing potential.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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