Iron Complexes

International Edition: DOI: 10.1002/anie.201605099
German Edition: DOI: 10.1002/ange.201605099

A Bispidine Iron(IV)–Oxo Complex in the Entatic State

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Abstract: *For a series of $Fe^{IV}{=}O$ complexes with tetra- and pentadentate bispidine ligands, the correlation of their redox potentials with reactivity, involving a variety of substrates for alkane hydroxylation (HAT), alkene epoxidation, and phosphine and thioether oxidation (OAT) are reported. The redox potentials span approximately 350 mV and the reaction rates over 8 orders of magnitude. From the experimental data and in comparison with published studies it emerges that electron transfer and the driving force are of major importance, and this is also supported by the DFT-based computational analysis. The striking difference of reactivity of two isomeric systems with pentadentate bispidines is found to be due to a destabilization of the $S=1$ ground state of one of the ferryl isomers, and this is supported by the experimentally determined redox potentials and published stability constants with a series of first-row transition metal ions with these two isomeric ligands.*

Since their discovery, the reactivity of high-valent nonheme metal–oxo centers of enzymes and model systems (specifically that of iron–oxo complexes) and their dependence from structure, oxidation, and spin state have intrigued coordination chemists.[1–6] There are a few paradigms, for example the preference for high-spin transition states in $Fe^{IV}{=}O$ catalyzed oxidation and oxygenation reactions,[7,8] the two-state-reactivity principle,[9,10] and the rebound mechanism for alkane hydroxylation and halogenation,[11] but it is not unexpected that even these might not be as general as often is assumed.[12,13] The fundamental understanding of the impact of structure on reactivity is a general concept in coordination chemistry and is of importance for the optimization of specific reactions,[14] but there is a range of examples in the area of ferryl-based oxidation reactions for which reactivity trends are not understood on a fundamental basis.[15–17] Three recent examples are due to our bispidine-based systems (see Scheme 1 for the ligands discussed herein), where the adamantane-derived rigid ligand backbone enforces well-defined structural properties; ligands L^1 are tetradentate and, when coordinated to a hexacoordinate metal ion M (for example, Fe^{II} or $Fe^{IV}{=}O$), the complexes have two coligands X and Y, where the bond to X (*trans* to N3) generally is shorter and stronger than that to Y (*trans* to N7); complexes of the pentadentate ligands L^2 and L^3 have only one coligand, and with the two isomers L^2 and L^{3a} this is enforced to the positions X and Y, respectively. The L^2/L^3-based isomerism has implications on the reactivity of the ferryl complexes, and this has been observed and described but not well enough understood.[15,18–20] In a series of ferryl oxidants with pentadentate amine-pyridine ligands, also including the two isomeric L^2- and L^{3a}-based systems, the reactivities did or did not correlate with $Fe^{IV/III}$ redox potentials, depending on the type of reaction (oxygen atom transfer [OAT] or C–H activation [HAT]) and substrate, and this is still not understood on a fundamental basis.[15] Here, we report the reactivities and redox potentials of the ferryl complexes of all ligands from Scheme 1;[21] particular attention in terms of a quantitative understanding of the structure–activity correlation is given to the L^2- and L^{3a}-based ferryl complexes, in particular in HAT with cyclohexane as substrate.

Three approaches have been described to measure redox potentials, cyclic voltammetry,[24–26] spectropotentiometric titrations,[15,27] and titrations of ferryl complexes with ferrocene derivatives.[16,25,28] Cyclic voltammetry (in H_2O or wet MeCN) has been shown to be inappropriate for the measurement of the $Fe^{IV/III}$ potential, at least for bispidin–ferryl complexes,[29] the other two methods lead to fundamentally different parameters (spectropotentiometry: H^+-coupled electron transfer, Fc titrations: pure electron transfer), and both are not undisputed. Herein, we concentrate primarily on potentials determined by titrations with ferrocene derivatives (see Table 1; also tabulated are the reorganization energies of the electron transfer reactions, determined on the basis of the Marcus theory of the adiabatic outer-sphere electron transfer; see Supporting Information for experimental details and the methods used to determine the various parameters, Eqs. S1–S4, Figures S3–S5). The potentials of the tetradentate ligand L^1-based ferryl complex is the highest measured to date (ca. 300 mV higher than those of two tetraaza-macrocycle-based systems),[16,25,28] and the H^+-coupled electron transfer potential of one of the isomers of the pentadentate bispidine-based systems (L^{3a}) is significantly higher than those of a range of other ferryl systems with pentadentate amine-pyridine ligands,[15,30] that is, the bispidine ligands enforce structures of ferryl complexes which are highly strained and therefore have a large driving force for reduction.[31]

With increasing electron density at the amine donors (reduction of the keto (and ester) groups, L^{1a} vs. $L^{1b,c}$; L^{3a} vs. L^{3b}), the ferryl species is stabilized and the reduction potential

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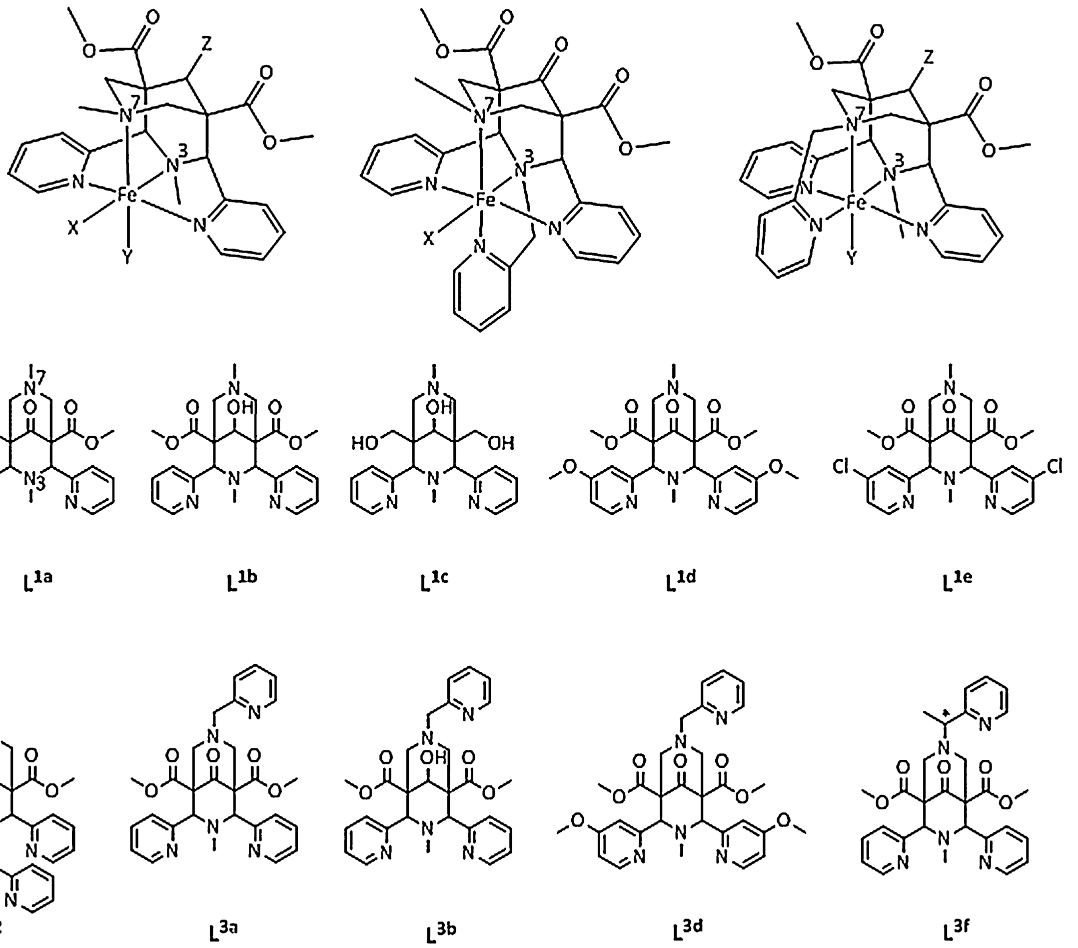
Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10.1002/anie.201605099.



Scheme 1. Bispidine ligands discussed herein.

Table 1: Redox potentials and reorganization energies of the $Fe^{IV/III}{=}O$ electron transfer with bispidine-type ligands.[a]

	$L^{1a[28]}$	L^{1b}	L^{1c}	L^{1d}	L^{1e}	L^{2}	L^{3a}	L^{3b}	L^{3d}	L^{3f}
redox potential [V]	0.73	0.63	0.61	0.62	0.61	0.40	0.42	0.37	0.44	0.51
reorganization energy [eV]	2.16	2.20	2.14	2.15	2.18	2.20	2.00	2.10	2.28	2.03
	(0.01)	(0.01)	(0.01)	(0.02)	(0.01)	(0.00)	(0.01)	(0.01)	(0.00)	(0.02)

[a] Potentials vs. SCE, in absolute acetonitrile, 25 °C, argon atmosphere. The estimated error limit of the redox potentials is ±0.01 V, the standard deviations of the reorganization energies are given in parentheses; see the Supporting Information for details.

therefore decreases. The effects observed with *para*-substitution of the pyridine groups are less straight forward, and this possibly is due to a combination of partially opposing factors. Interestingly, there is a large difference of the published potentials of the H^+-coupled electron transfer between the two isomeric forms of the pentadentate ligand L^2 and L^{3a}.[15] With the pure electron transfer (Table 1) the trend is the same, that is, the L^2-based ferryl complex is a less powerful oxidant but the difference is much smaller (20 vs. 250 mV), and it appears that much of the difference in reactivity may be due to differences in the thermodynamics of H^+ transfer and/or changes in the reorganization energy (see Table 1; note that the reorganization energies of the bispidine-based systems are significantly lower than those of other ferryl complexes, see Table 1 in comparison with published data, which are in the area of 2.40–2.75 eV[25]).

The reactivities of all ferryl complexes of the tetra- and pentadentate bispidines from Scheme 1 and Table 1 have been studied with a range of substrates for C–H activation reactions of alkanes, the epoxidation of alkenes and oxo-transfer reactions (Table 2 and Figure 1; see the Supporting Information for details). The observed rates span more than 8 orders of magnitude. From the data it emerges that there is a general trend involving the driving force of the oxidant, that is, the rates increase with an increase of redox potential (Figure 1). However, there is significant scattering, indicating that, as expected, various factors may influence the reactivities, for example, the thermodynamics of H^+ and electron transfer, the high-spin/intermediate-spin energy gap, σ- and π-channel pathways (see above). The most striking deviation from a simple correlation of the driving force with the reactivity is observed for the two isomeric systems based on

Table 2: Second-order reaction rate constants [$\mathrm{L\,mol^{-1}\,s^{-1}}$] from pseudo-first-order measurements.[a]

	Cyclohexane $\times 10^{-3}$	Benzyl alcohol $\times 10^{-1}$	Dihydroanthracene $\times 10^{-3}$	Diphenylcarbinol $\times 10^{-1}$	PPh_3 $\times 10^{3}$	Thioanisol	Cyclohexene $\times 10^{-1}$	*cis*-Cyclooctene $\times 10^{-3}$	*Z*-Stilbene $\times 10^{-3}$
L^{1a}		2.92 ± 0.14	8.00 ± 0.30				1.33 ± 0.05		647 ± 88
L^{1b}		1.56 ± 0.09	5.40 ± 0.30				1.30 ± 0.10		508 ± 64
L^{1c}		1.25 ± 0.09	4.90 ± 0.30				0.930 ± 0.020		254 ± 12
L^{1d}		12.6 ± 0.4	28.4 ± 4.2				4.16 ± 0.09		385 ± 18
L^{1d}		3.58 ± 0.08	8.50 ± 0.40				2.97 ± 0.04		808 ± 58
L^{2}	0.130 ± 0.003			0.220 ± 0.002	0.182 ± 0.003	5.65 ± 0.10		2.05 ± 0.06	1.15 ± 0.06
L^{3a}	4.91 ± 0.08			5.86 ± 0.07	11.3 ± 0.4	480 ± 2		94.1 ± 3.6	36.9 ± 0.6
L^{3b}	2.56 ± 0.05			4.34 ± 0.07	8.35 ± 0.15	129 ± 2		44.0 ± 1.5	18.5 ± 0.6
L^{3d}	5.59 ± 0.06			5.41 ± 0.11	15.3 ± 0.4	386 ± 12		108 ± 8	46.1 ± 1.1
L^{3f}	6.82 ± 0.09			7.37 ± 0.12	17.4 ± 0.4	548 ± 11		135 ± 4	50.3 ± 1.7

[a] Errors are standard deviations of the substrate concentration-dependent measurements; experiments carried out in absolute acetonitrile, argon atmosphere; tetradentate ligands $L^{1a\text{–}d}$: 0.5 mM $Fe^{IV}{=}O$, 238 K; pentadentate ligands $L^{2,3a,b,d,f}$: 1.0 mM $Fe^{IV}{=}O$, 298 K (triphenylphosphine 283 K).

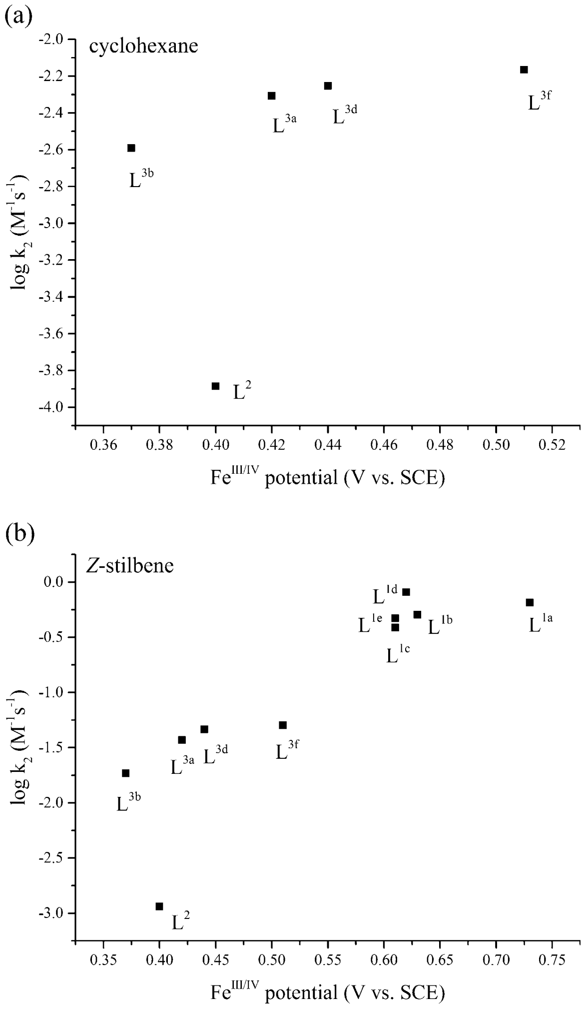


Figure 1. Plot of second-order rate constants for the reaction with a) cyclohexane ($L^{2,3a,b,d,f}$) and b) *Z*-stilbene ($L^{1a\text{–}e,2,3a,b,d,f}$) versus the corresponding $Fe^{IV/III}$ redox potentials (see Table 1 for the potentials and Table 2 for the rates).

the pentadentate bispidine ligands L^2 and L^{3a} that will be discussed separately below.

Plots of the observed rate constants as a function of the driving force (Supporting Information, Figures S6 and S7) are linear for the pentadentate ligand systems (with the expected deviation for the L^2-based system), and there is significant scattering for the tetradentate bispidine ferryl complexes. With substrates that are difficult to oxidize (cyclohexane, benzyl alcohol, cyclohexene) the electron transfer processes are strongly endergonic, with triphenylphosphine and thioanisole, which are easier to oxidize, the rates are well correlated with the driving force. For electron transfer activation in redox processes, both the redox potential and the reorganization are of importance, and a major reason for the deviations from linearity in the driving force vs. oxidation rate plots of the tetradentate bispidine systems may be due to the significantly lower reorganization energy of the corresponding ferryl complex (Supporting Information, Figure S6). An interesting observation is therefore that reduction of all bispidine-based complexes is accompanied by significantly smaller reorganization energies than observed with all other ferryl complexes with tetra- or pentadentate ligand systems (see above), and this is proposed to be the result of the rigid bispidine scaffold. In fact, with pentadentate ligand systems, the pure electron transfer potentials of the bispidine ligands discussed herein are not significantly larger than those of other ferryl systems,[25] while there are large differences in the potentials of the H^+-coupled electron transfer potentials.[15]

We now concentrate on the detailed analysis of the reactivity of the two isomeric ferryl complexes with the pentadentate bispidine ligands L^2 and L^{3a} towards oxidation of cyclohexane. As discussed above, there is a difference in the potential of the H^+ coupled redox potential of 250 mV[15] and of the pure electron transfer of 20 mV (coupled with a difference in the reorganization energy of 0.23 eV, see Table 1), indicating that the driving force of the L^{3a} based oxidant is significantly larger and the corresponding reaction rate indeed is about 40-fold faster (Figure 1 and Table 2; importantly, it emerges that $(L^{3a})Fe^{IV}{=}O$ is a more reactive oxidant than $(L^{2})Fe^{IV}{=}O$ in all reactions studied so far), and from published data it emerges that hydrogen atom abstraction is the rate determining step of the cyclohexane oxidation reaction (KIE of ca. 14, preference for tertiary alcohol formation, preference for alcohol vs. ketone product).[32,33]

The analysis of the HAT reaction profile with cyclohexane as substrate and (L^{2})Fe^{IV}=O compared to (L^{3a})Fe^{IV}=O as oxidant is based on a series of DFT calculations, including a thorough analysis of the theoretical setup (benchmarking of the functional, influence of solvation: PCM model with MeCN), and it also includes the computation of the intrinsic reaction coordinates, a comparison of computed and experimental activation barriers, an approximate computation of the distortion energy to the activation barriers, and structural variations of the transition states on the different spin surfaces, an analysis of the spin and charge distributions and an energy decomposition analysis (EDA; for details, see the Supporting Information, Table S9). Here, we concentrate on a comparison of the computed energies on the $S=1$ and $S=2$ spin surfaces of (L^{2})Fe^{IV}=O and (L^{3a})Fe^{IV}=O, the corresponding C−H activation transition states and the Fe^{III}−OH products (Figure 2; the transition states on the intermediate-spin surfaces are significantly higher in energy; see the Supporting Information, Table S2). The main result is that the C−H activation transition states and Fe^{III}−OH products of both isomers have very similar energies (those of the Fe^{III}−OH / organic radical products are relatively high owing to the instability of the radical species; see the Supporting Information, Table S2) and that the main difference between the two isomers is the stability of the ferryl oxidant: that of the more reactive L^{3a}-based system is approx. 13 kJ mol^{-1} less stable, and this translates quite well to the 40-fold reactivity increase, and the computed destabilization is also in excellent agreement with the observed thermodynamic difference, that is, with the redox potential (Supporting Information, Table S4). The only other remarkable difference between the two isomers is a reduction of the energy gap between the two spin states of the ferryl species from 18 kJ mol^{-1} for (L^{2})Fe^{IV}=O to 6 kJ mol^{-1} for (L^{3a})Fe^{IV}=O, that is, the high-spin states of the two oxidants also have very similar energies (Figure 2).

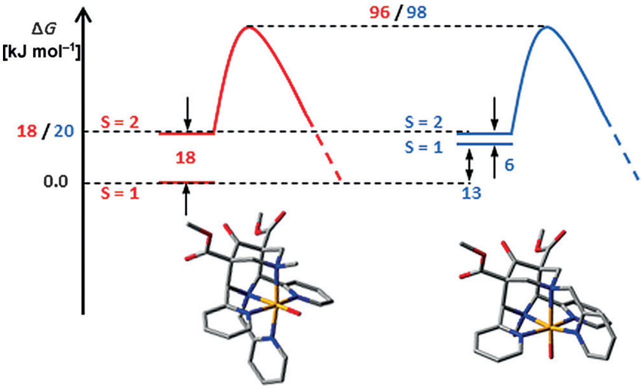


Figure 2. Computed free energy profile for the C−H abstraction from cyclohexane by (L^{2})Fe^{IV}=O (left) and (L^{3a})Fe^{IV}=O (right). Optimized solvent model structures (PCM, acetonitrile), B3LYP/def2TZVP level of theory (energies in kJ mol^{-1}).

Therefore, it appears that the enhanced C−H activation reactivity of (L^{3a})Fe^{IV}=O in comparison with (L^{2})Fe^{IV}=O is due to energization at the ferryl state, and this is therefore an interesting example of a catalyst in the entatic state.[34,35] The computational result of entasis (energization) of the (bispidine)Fe^{IV}=O oxidants, in particular of one over the other isomer, (L^{3a})Fe^{IV}=O vs. (L^{2})Fe^{IV}=O, is also emerging from the measurement of the corresponding complex stabilities with a series of divalent first-row transition metal ions: with Co^{II}, Ni^{II}, and Zn^{II} the stabilities with L^{2} are significantly larger (3 to 6 log units) than with L^{3a}; only with Cu^{II} is the stability order reversed (the L^{3a} complex is 3.5 log units more stable, and this is believed to be due to the Jahn–Teller lability of the d^{9} metal ion).[36] In analogy, it is expected that for steric reasons the intermediate-spin (L^{3a})Fe^{IV}=O complex is destabilized, that is, in an entatic state. The EDA analysis (Supporting Information, Table S9) supports the destabilization due to steric effects. The fact that in the high-spin transition state as well as in the high-spin state of the ferryl oxidant the steric destabilization is nearly entirely canceled (in the $S=2$ state the ferryl complexes and the C−H activation transition states of the L^{2} and L^{3a} isomers have close to identical energies; Figure 2, Supporting Information Table S2) is again due to electronic effects: in the high-spin state, a d^{4} system of tetragonal symmetry is pseudo-Jahn–Teller active with an electronic stabilization of the order of 10 kJ mol^{-1},[20,37] consistent with the computed energy profile in Figure 2.

In conclusion, we have presented an example of two isomeric $S=1$ (bispidine)Fe^{IV}=O oxidants which in all oxidation reactions, including oxygen transfer, C−H activation of alkanes, and epoxidation/dihydroxylation of alkenes, show a stark reactivity difference with up to two log units difference in the rates. Published stability constants as well as the redox potentials and extensive computational analyses presented herein show unambiguously that the reactivities reflect different amounts of energization of the oxidants, that is, the rate enhancements are primarily due to an increase in the driving force. This is an aspect which, in our view, has not been appreciated much enough so far and which has not been unambiguously pinpointed in any other example. Note, however, that clearly it is not appropriate to appreciate or assume the driving force as more than one of the important factors in determining reactivity of ferryl complexes. Moreover, a more general and accurate method for the determination of redox potentials of ferryl complexes is more needed than ever.

Acknowledgements

We are grateful for computational resources provided by the bwForCluster JUSTUS, funded by the Ministry of Science, Research and Arts and the Universities of the State of Baden-Württemberg, Germany, within the framework program bwHPC-C5. Financial support by the European Cooperation in Science and Technology (COST), the German Science Foundation (DFG), the Heidelberg Graduate School of Computational Methods for the Sciences (HGS), the Baden-Württemberg Stipendium (German-Japanese University Consortium HeKKSaGOn), JSPS (No. 16H02268, Japan), and the University of Heidelberg are gratefully acknowledged.

Keywords: coordination chemistry ·
density functional calculations · homogeneous catalysis ·
iron bispidine complexes · redox potentials

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 11129–11133
Angew. Chem. **2016**, *128*, 11295–11299

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Received: May 25, 2016
Revised: June 30, 2016