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Spin state and reactivity of iron(IV)oxido complexes with tetradentate bispidine ligands†‡

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The iron(IV)oxido complex [(bispidine)Fe^{IV}=O(Cl)]⁺ is shown by experiment and high-level DLPNO-CCSD (T) quantum-chemical calculations to be an extremely short-lived and very reactive intermediate-spin (*S* = 1) species. At temperatures as low as −90 °C, it decays with a half-life of approx. two minutes, and this is the reason why, so far, it remained undetected and why it is extremely difficult to trap and fully characterize this interesting and extremely efficient oxidant. The large difference in reactivity between [(bispidine)Fe^{IV}=O(Cl)]⁺ and [(bispidine)Fe^{IV}=O(MeCN)]²⁺ (at least two orders of magnitude), while both oxido-iron(IV) complexes have very similar structures and an *S* = 1 electronic ground state, is presumably due to the large difference in the energy gap between the triplet and quintet electronic states. In presence of cyclohexane as substrate, [(bispidine)Fe^{IV}=O(Cl)]⁺ oxidizes cyclohexane with a rate that is approx. 25 times faster than the self-decay of the oxidant, and selectively leads to chlorocyclohexane in moderate yield. The *S* = 1 electronic ground state of [(bispidine)Fe^{IV}=O(Cl)]⁺ and a relatively low gap to the *S* = 2 state (approx. 6 kJ mol^{−1} vs. approx. 75 kJ mol^{−1} for [(bispidine)Fe^{IV}=O(MeCN)]²⁺) is also predicted by DLPNO-CCSD(T) quantum-chemical calculations. The method used was benchmarked with a set of six ferryl complexes with experimentally known electronic ground states.

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Introduction

Mononuclear non-heme iron centers have been described and thoroughly studied in enzymes and bioinspired low molecular weight complexes since the early 2000s. They play an important role in nature and are of interest in preparative chemistry and environmentally relevant processes – examples of the diverse reactions include hydroxylation and halogenation of unactivated alkanes (hydrogen atom transfer, HAT) and oxygen atom transfer (OAT) such as epoxidation and sulfoxidation.^{1–6} The reactivity of non-heme iron(IV)-oxido species is believed to depend on the spin state of the Fe^{IV}=O²⁺ core (high-spin, *S* = 2 vs. intermediate-spin, *S* = 1; low-spin is energetically barely accessible). The high-spin state is believed to be more reactive, and this is supported by theoretical considerations.^{7,8} All known enzyme sites are high-, while most model complexes

are intermediate-spin. Experimentally, the determination of the spin state is only trivial for the less reactive Fe^{IV}=O²⁺ complexes that can be isolated in pure form but spectroscopic analyses of trapped meta-stable intermediates have also allowed to characterize some of the more reactive and hence more interesting complexes – however, one needs to be cautious with indirect indications, as will be shown below. The quantum-chemical prediction of the spin ground state is also problematic, particularly with density functional theory (DFT), where the description of the wavefunction strongly depends on the functional,⁹ and this is particularly problematic for the energetics of the spin states of ferryl centers,^{10–13} where the ground state can often only be computed with empirical corrections,¹⁴ *i.e.* predictions have to be considered with great care.

We have extensively studied and reported on bispidine-iron(IV)-oxido chemistry with penta- and tetradentate bispidine ligands (the oxido complexes of the simplest tetradentate bispidine discussed here with Cl[−] or MeCN (acetonitrile) as monodentate co-ligand are shown in Chart 1). These ferryl complexes are among the most reactive Fe^{IV}=O species and have very high Fe^{IV/III} redox potentials.^{15–17} While the other well-characterized bispidine-iron(IV)-oxido complexes are known to have a triplet ground state (Mössbauer spectroscopy, electronic spectroscopy [dd transition in the 700–800 nm range], also supported by DFT calculations, and this includes the Fe^{IV}=O complex with the tetradentate ligand and MeCN as

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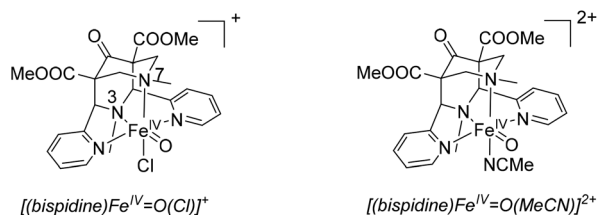


Chart 1 Structure of the bispidine-iron(IV)-oxido complexes with the tetradentate bispidine and a monodentate co-ligand (Cl^- or MeCN); only the more stable isomers with the oxido group trans to N3 are shown.

co-ligand), the hydroxido-, chlorido- and fluoro-ferryl complexes with the tetradentate bispidine were believed to have a quintet ground state.^{18–20} A simple ligand field analysis suggests that a weak co-ligand in the xy plane (also including the tertiary amine N7 [see Chart 1 for numbering] with a long metal-amine bond enforced by the bispidine platform, as well as the two pyridine donors with likewise sterically enforced relatively weak bonds) yields a relatively low energy $d_{x^2-y^2}$ orbital, resulting in a high-spin ground state, and this was supported by DFT calculations.^{18–20} Experimentally, the proposal of high-spin electronic configuration was corroborated by the absence of any dd transition in the area of 600–800 nm (while the corresponding MeCN complex features the expected transition at 768 nm). Moreover, with cyclohexane as substrate, $[(\text{bispidine})\text{Fe}^{\text{IV}}=\text{O}(\text{Cl})]^+$ was shown to produce chlorocyclohexane with no cyclohexanol or cyclohexanone side products, and an experimentally determined kinetic isotope effect (KIE) of 14 suggested that C–H abstraction is the rate determining step.^{20–22} These (and few other) experimental results were taken as supporting evidence for the qualitative ligand field analysis and the DFT calculations, *i.e.*, suggesting that, while the corresponding acetonitrile complex $[(\text{bispidine})\text{Fe}^{\text{IV}}=\text{O}(\text{MeCN})]^{2+}$ has the usual $S = 1$ ground state, the chlorido complex $[(\text{bispidine})\text{Fe}^{\text{IV}}=\text{O}(\text{Cl})]^+$ has a high-spin ($S = 2$) electronic configuration. This assignment is wrong.

Results and discussion

Experimental characterization

Cryo-stopped-flow experiments (MeCN, 238 K or lower) unambiguously show that, at low temperature, an extremely short-lived intermediate is formed that has escaped observation so far. Shown in Fig. 1 are the UV-vis-NIR spectra of the chlorido-oxido and the acetonitrile-oxido complexes – the former recorded in propionitrile (EtCN) at 183 K, the latter at 238 K in MeCN, both generated *in situ* from the bispidine- $\text{Fe}^{\text{II}}\text{Cl}_2$ or the bispidine- $\text{Fe}^{\text{II}}(\text{Otrif})_2$ precursors ($\text{Otrif}^- = \text{trifluoromethanesulfonate}$), respectively, using an excess of iodosylbenzene ($[\text{PhIO}] = 4 \text{ mM}$ vs. $[\text{Fe}^{\text{II}}] = 2 \text{ mM}$). The time-traces also shown in Fig. 1, recorded at the maxima of the near infrared dd transitions (768 nm or 850 nm for $[(\text{bispidine})\text{Fe}^{\text{IV}}=\text{O}(\text{MeCN})]^{2+}$ and $[(\text{bispidine})\text{Fe}^{\text{IV}}=\text{O}(\text{Cl})]^+$, respectively), show that the MeCN complex is moderately stable at 238 K, while the chlor-

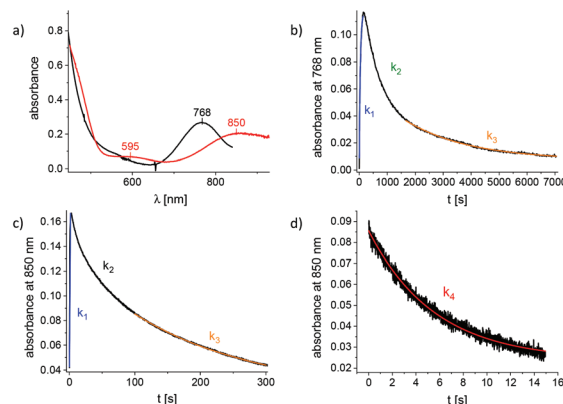


Fig. 1 (a) UV-vis-NIR spectra of *in situ* generated $[(\text{bispidine})\text{Fe}^{\text{IV}}=\text{O}(\text{Cl})]^+$ (red) in oxygen-free EtCN at 183 K and $[(\text{bispidine})\text{Fe}^{\text{IV}}=\text{O}(\text{MeCN})]^{2+}$ (black; approx. 2 mM each) in oxygen-free MeCN at 238 K; (b) time-trace of $[(\text{bispidine})\text{Fe}^{\text{IV}}=\text{O}(\text{MeCN})]^{2+}$ (conditions as above) (c) time-trace of $[(\text{bispidine})\text{Fe}^{\text{IV}}=\text{O}(\text{Cl})]^+$ (conditions as above); (d) time-trace of $[(\text{bispidine})\text{Fe}^{\text{IV}}=\text{O}(\text{Cl})]^+$ after addition of cyclohexane (15 mM), 3 seconds after *in situ* generation (maximum of the time-trace (c); 183 K); also shown in red is the fit to a pseudo-first-order reaction with $k_4 = 0.2 \text{ s}^{-1}$.

ido complex has an extremely short life-time, even at -90°C (the observed approx. rate constants for the formation (k_1) and decay (k_2, k_3) of the two complexes are $k_1^{\text{Cl}} = 1.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, $k_3^{\text{Cl}} = 5.5 \times 10^{-3} \text{ s}^{-1}$, $k_1^{\text{MeCN}} = 2.0 \text{ M}^{-1} \text{ s}^{-1}$, $k_3^{\text{MeCN}} = 4.1 \times 10^{-4} \text{ s}^{-1}$). Note that the rates were obtained in different solvents and at different temperatures (see above and caption to Fig. 1), and that the formation is a second order reaction while the decay includes more than one process.²³ The fact that, at -90°C , the chlorido-oxido complex is formed and decays with half-lives in the area of less than a second and approx. two minutes, respectively, explains why this extremely reactive species that we assume to be responsible for the very high halogenation and oxygen transfer reactivity, has not been observed before.^{16,19,20}

For the acetonitrile complex $[(\text{bispidine})\text{Fe}^{\text{IV}}=\text{O}(\text{MeCN})]^{2+}$ there are preliminary data from Mössbauer spectroscopy that support the assignment of an $S = 1$ ground state (see ESI†). For the chlorido complex, due to the extremely low stability, apart from the electronic spectra shown in Fig. 1, we have not yet been able to trap the $\text{Fe}^{\text{IV}}=\text{O}$ intermediate for spectroscopy. However, the observed dd transitions (see Fig. 1) are fully consistent with the assignment of an intermediate-spin ($S = 1$) electronic ground state of $[(\text{bispidine})\text{Fe}^{\text{IV}}=\text{O}(\text{Cl})]^+$. In accordance with elaborate optical spectroscopy (variable temperature UV-vis-NIR and MCD in combination with DFT calculations) of two model $S = 1$ $\text{Fe}^{\text{IV}}=\text{O}$ complexes with similar pseudo-tetragonal symmetry as the complexes discussed here,^{24,25} we assign the band observed at 850 nm to the $d_{xz/yz}, d_{xy} \rightarrow d_{x^2-y^2}$ transitions (in pseudo- D_{4h} symmetry, z -axis along $\text{Fe}^{\text{IV}}=\text{O}$), and the shoulder at approx. 592 nm to the $d_{xz/yz} \rightarrow d_{z^2}$ transition.^{26–30} This is an extremely low energy $d_{x^2-y^2}$ transition of an intermediate-spin ferryl species. A comparable very reactive pseudo-tetragonal $\text{Fe}^{\text{IV}}=\text{O}$ complex with an $S =$

1 ground state and a low ligand field is that with the tetradentate ligand Me₃NTB (Me₃NTB = tris[(1-methyl-benzimidazol-2-yl)methyl]amine) with the corresponding dd transition at 770 nm.³¹ The very low energy dd transition of [(bispidine)Fe^{IV}=O(Cl)]⁺ at 850 nm supports the earlier analysis that this complex has a very low in-plane ligand field, leading to a low energy gap between the d_{xz/yz}, d_{xy} and the d_{x²-y²} orbitals. However, in contrast to our earlier conclusion, the ground state is *S* = 1 and not *S* = 2.

Interestingly, the acetonitrile complex [(bispidine)Fe^{IV}=O(MeCN)]²⁺ is much less reactive (at least two orders of magnitude) than [(bispidine)Fe^{IV}=O(Cl)]⁺ (see Fig. 1b vs. 1c; note the different time axes). The second phase of the self-decay is a first-order process with a rate constant for the chlorido complex of $k_3^{\text{Cl}} = 5.5 \times 10^{-3} \text{ s}^{-1}$ (−90 °C, EtCN), that of the acetonitrile complex is $k_3^{\text{MeCN}} = 4.1 \times 10^{-4} \text{ s}^{-1}$ (−35 °C, MeCN). The approx. decay rate of [(bispidine)Fe^{IV}=O(Cl)]⁺ in presence of a 15-fold excess of cyclohexane is $k_4 = 0.2 \text{ s}^{-1}$ (EtCN, −90 °C, *i.e.* approx. 25 times faster than without substrate, see Fig. 1c vs. 1d), and this selectively leads to chlorocyclohexane (approx. 20% yield; slightly different experimental setup, ambient temperature).^{18–20} A full kinetic and mechanistic analysis of all pathways involved in the formation, self-decay and product formation processes is in progress but a preliminary qualitative interpretation of the striking difference in reactivity, based on the approx. rates of the two complexes with very similar molecular structures and a supposedly identical electronic ground state is appropriate.

According to quantum-chemical calculations at different levels of theory, generally and independently of the spin state of the ferryl complex, the oxidation of substrates occurs on the high-spin surface – the only known exception is the carbene-Fe^{IV}=O complex (NHC, see Chart 2 below).^{4,7,8,11,12,32–35} The concept of two-state-reactivity illustrates this observation,^{36,37} and that is supported by a large body of computational and experimental data.^{7,38} However, in only few of the studies spin-orbit coupling has been considered explicitly for the energetics of the spin crossover.^{39–43} It has been shown that the transmission coefficient κ_{SO} in the Eyring equation (eqn (1)) is directly related to the spin-orbit coupling matrix element, and spin-orbit coupling between the quintet and

triplet states strongly increases with a decreasing energy gap, *i.e.* the transmission coefficient κ_{SO} increases with decreasing energy difference of the high-spin and intermediate spin states.^{41–43}

$$k(T) = \kappa_{\text{SO}} (k_{\text{B}}T/h) \exp(-\Delta G_{\text{q}}/RT) \quad (1)$$

The observed large rate difference between the two intermediate-spin ferryl complexes [(bispidine)Fe^{IV}=O(Cl)]⁺ and [(bispidine)Fe^{IV}=O(MeCN)]²⁺ therefore suggests that the chlorido complex has a much lower energy gap than the acetonitrile complex, and this agrees with the qualitative ligand field analysis (see Introduction). Importantly, a thorough kinetic study of complexes with very similar structures but a wide variation of the energy gap should allow to obtain quantitative information on the triplet-quintet energy gap of ferryl complexes and therefore may help to tune quantum-chemical approaches for spin state energetics. With the bispidine-iron (iv)-oxido complexes discussed here (see Chart 1) and derivatives with substituted pyridine donors that are available (see also ESI[†]),^{16,44} a series of ferryl complexes with very similar structures are available to test these ideas.

Computational analysis

DFT models are known to over-stabilize high-spin configurations. Therefore, it is unsurprising that DFT does not describe the spin state energetics of Fe^{IV}=O complexes correctly.^{9–12} Coupled cluster calculations are known as the gold-standard for this type of problem^{45,46} but the computational cost of CCSD(T) is still too high for a general application. A number of methods based on multiconfigurational perturbation theory have been proposed, and the various approaches have been compared, specifically also for high-valent iron complexes.⁴⁶ The combination of CASPT2 calculations, with an error of approx. 40 kJ mol^{−1} with respect to CCSD(T), with simplified CCSD(T) methods (electron correlation for the transition metal (3s3p) semicore), CASPT2/CC, leads to a reduced error of about 9 kJ mol^{−1}.⁴⁶ The recently introduced DLPNO-CCSD(T) method provides a particularly interesting approach to this problem.^{47,48} Here we describe an extensive *ab initio* quantum-chemical analysis of a series of Fe^{IV}=O complexes with tetradentate ligands and experimentally known electronic ground states, also including the two bispidine complexes with Cl[−] and MeCN as co-ligands (see Chart 2) to benchmark the method used and to address the spin state problem discussed above, *i.e.* to reliably calculate the spin state energetics of [(bispidine)Fe^{IV}=O(Cl)]⁺.

The protocol used involves the optimization of the structure with B3LYP/def2-TZVP (PCM solvation, MeCN), followed by single point gas phase DLPNO-CCSD(T) calculations to determine the electronic ground state of the optimized geometries. Correlation consistent basis sets were used.^{52,53} These provide the advantages that it is relatively easy to extrapolate the energy to the complete basis set limit (CBS) and that they provide a large basis for the iron center. Moreover, HF orbitals were taken as starting point for the DLPNO-CCSD(T) calcu-

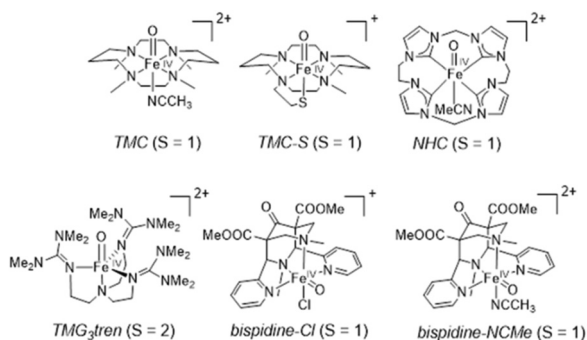


Chart 2 Complexes studied by DLPNO-CCSD(T).^{32,49–51}

Table 1 Quintet-triplet energy gap in kJ mol^{-1} (gas phase energies calculated by a single point calculation: $\Delta E_{\text{gas}} = E_{\text{quintet}} - E_{\text{triplet}}$, *i.e.* a negative entry indicates a quintet ground state, see ESI† for details). The CASPT2/CC values are taken from the literature⁵⁶

| Basis set | DFT (B3LYP) ^c | DLPNO-CCSD(T) | | | | CASPT2/CC ⁵⁶ |
|--|--------------------------|---------------|----------------------------|---------|---------|-------------------------|
| | def2-TZVP | cc-PVDZ | cc-PVTZ | cc-PVQZ | cc-PV5Z | |
| TMC ($S = 1$) | 10.3 | 48.3 | 40.2 | 41.0 | 42.0 | 42.7 |
| TMC-S ($S = 1$) | -16.3 | 21.0 | 17.0 ^a | 17.8 | — | 23.0 |
| NHC ($S = 1$) | 109.0 | 154.0 | 157.7 | 185.5 | — | 123.9 |
| TMG3tren ($S = 2$) | -96.5 | -137.3 | -109.0 | -107.6 | -114.4 | — |
| [(Bispidine)Fe ^{IV} =O(Cl)] ⁺ ($S = 1$) | -12.1 | 22.2 | 11.4 | 5.7 | 0.0 | — |
| [(Bispidine)Fe ^{IV} =O(MeCN)] ²⁺ ($S = 1$) | -2.6 | 22.7 | -29.3 (83.3 ^b) | 75.7 | — | — |

^a Loose criteria for the DLPNO-CCSD(T) calculation (the default criteria for the DLPNO-CCSD(T) calculation is NormalPNO). ^b cc-PVQZ basis set on Fe. ^c Optimization with the PCM solvent model (MeCN).

lations, and a well-established protocol was used for the extrapolation of the calculated energies to the energies at the complete basis set limit (CBS).⁵⁴ Coupled cluster calculations depend heavily on the size of the basis set, and care was taken to increase the size of the basis set such that convergence of the relative energies was reached (see Table 1 for the results and the ESI† for details of the protocol used as well as detailed results of the benchmarking; note that solvation effects are not included in the DLPNO-CCSD(T) calculations, and Table S1† also includes DFT gas phase calculations for comparison).

The DLPNO-CCSD(T) method used may give errors of up to $\sim 20 \text{ kJ mol}^{-1}$.⁵⁵ Therefore, it is necessary to evaluate the results very carefully. Importantly, it was possible to predict the experimentally determined spin state for all of the investigated complexes, specifically also for the two bispidine complexes, where the experimental data suggest a large difference of the quintet-triplet energy gap, and this also emerges from the calculations (see Table 1). It is not unexpected that the calculated energy gap strongly depends on the size of the basis set. The results for the cc-PVDZ, cc-PVTZ and cc-PVQZ basis sets in Table 1 indicate that a larger basis set on the iron center is of importance (as specifically observed in the case of [(bispidine)Fe^{IV}=O(MeCN)]²⁺). It appears that at least a quadruple quality basis set is needed to obtain accurate results. In addition, the choice of the PNO cutoff is very important. Due to their different orbital cutoffs the NormalPNO and the LoosePNO criteria lead to very different energies, especially in the case of the TMC-S complex. Also, the triple zeta basis set appears to be too small to describe the Fe-S bond accurately.

In a recent publication, a similar DLPNO-CCSD(T) approach was used to evaluate corrections for DFT calculations. Importantly, that study also involved CASPT2/CC calculations (see the last column in Table 1).⁵⁶ It appears, specifically for the two TMC complexes, that the DLPNO-CCSD(T) results with our protocol lead to similar spin state energies to those at the CASPT2/CC level, and this may indicate that the high quality starting orbitals and large basis sets used here assure accurate and consistent data. Specifically for [(bispidine)Fe^{IV}=O(Cl)]⁺ ($S = 1$) but also for all others, this is supported by the experimental data.

Experimental section

Materials and methods

All chemicals and reagents were purchased from commercial sources. Dry solvents were stored over molecular sieves and used without further purification. Preparation and handling of air-sensitive materials were carried out using either Schlenk techniques or in a glovebox. The bispidine-iron(II) complex and soluble iodosylbenzene (sPhIO) were synthesized according to literature procedures.^{20,57-60} The chlorido complex was prepared as follows: iron(II) chloride (0.8 g, 6.36 mmol) was added to a solution of the bispidine ligand (2.8 g, 6.36 mmol) in dry acetonitrile (60 mL) under nitrogen atmosphere. After one hour stirring at room temperature, the precipitated complex was filtered and dried under vacuum.

Cryo Stopped-Flow measurements were performed with a SFM-4000/S stopped flow mixer from Bio-Logic Science Instruments. The UV-vis spectra were recorded by using a Tidas MCS UV/NIR from J&M Analytik AG and the temperature was controlled by a Thermo Scientific Phoenix II cryostat.

The solution of the Fe(II) complex (4 mM) and the suspension of sPhIO (20 mM) in dry acetonitrile were prepared in a glovebox under argon atmosphere. The solutions were filtered through a syringe filter prior to insertion into the stopped flow. Mixing was performed in a 1 : 1 ratio with a dead time of 2.1 ms. The addition of cyclohexane was carried out in double-mixing mode. First, the iron(II) complex was oxidized with sPhIO in a delay line. After 3s the aged solution was mixed with cyclohexane in the UV/vis cuvette.

The stability measurements of [(bispidine)Fe^{IV}=O(MeCN)]²⁺ were recorded on an Agilent 8463 spectrophotometer with cryostat from Unisoku Scientific Instruments.

The rate constants were obtained either by fitting the data with the software OriginPro 2018G or *via* global analysis with the software ReactLab KINETICS.

Computational methods

The optimizations were carried out using the Gaussian16 (Rev. B.01)⁶¹ software package. All geometries were optimized with the UB3LYP functional^{62,63} and Ahlrich's def2-TZVP basis

set.^{64,65} Solvation effects were included with acetonitrile as model solvent (polarized continuum model, PCM).^{66,67} To verify minima on the potential energy surface, frequency calculations were carried out for all optimized structures. The structures were then used for DLPNO-CCSD(T) single point calculations with the correlation consistent basis sets of Dunning *et al.*,^{52,53} the TIGHTSCF criteria and the RJCOSX approximation^{68,69} The DLPNO-CCSD(T) calculations were carried out using the ORCA 4.0.1.2 program package.⁷⁰ CBS extrapolation was performed using the result of three different basis set calculations (*e.g.* double zeta, triple zeta and quadruple zeta) and a published implementation (eqn (2)).^{54,71}

$$E_X = E_{\text{CBS}} + B e^{-\alpha X} \quad (2)$$

Our DLPNO-CCSD(T) calculations are based on HF orbitals and generated by a previous HF calculation. These starting orbitals are therefore different from the UKS starting orbitals in reference.⁵⁶ Another important difference is the use of different basis sets. The comparison between the different DLPNO-CCSD(T) calculations indicate, that the HF orbitals might be a better starting point for the DLPNO-CCSD(T) procedure (see Table S1†). This is further supported by the low values for the T1 diagnostic (see Table S2†). The T1 diagnostic is an indicator for the quality of the CCSD(T) calculation and an empirical way to judge its reliability. A high T1 value indicates that there is a multireference problem that cannot be treated by CCSD(T), while a low number indicates an acceptable quality of the calculation. Note also that solvation (PCM model) in the DFT calculation results in a difference of ~ 5 kJ mol⁻¹ in comparison to the gas phase (single point on the solvent-optimized structure).

Conclusions

An important conclusion is that spin state energies can be calculated with high accuracy with DLPNO-CCSD(T), and this alleviates the problem of incorrect spin-state predictions from standard DFT calculations. While DFT fails to describe the correct spin state for TMC-S (see Table 1), the double zeta basis set DLPNO-CCSD(T) calculation can already correct this. As expected, it appears that optimization at the DFT level, followed by a DLPNO-CCSD(T) single point calculation, even with a moderately sized basis set, produces much more reliable spin state predictions than DFT. At least for the systems studied here, the quality of the starting orbitals is of importance, quadruple zeta basis sets seem to be a good balance between computational cost and accuracy, and the number of orbitals and the threshold for the PNO localization need to be selected carefully.

The other important conclusion is that, with bispidine ligands, so far there are no high-spin Fe^{IV}=O complexes available. However, the very small quintet-triplet energy gap for [(bispidine)Fe^{IV}=O(Cl)]⁺ with an *S* = 1 ground state leads to an extremely reactive oxidant, by far the most reactive ferryl

complex reported so far. Also, derivatives of the tetradentate bispidine with slightly smaller ligand fields are available, and it will be interesting to probe with more examples than those discussed here, how the gap between the spin states of ferryl complexes quantitatively influences the reactivity.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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References

- 1 C. Krebs, D. G. Fujimori, C. T. Walsh and J. M. Bollinger, Jr., *Acc. Chem. Res.*, 2007, **40**(7), 484–492.
- 2 W. Nam, *Acc. Chem. Res.*, 2015, **48**, 2415–2423.
- 3 W. Nam, Y.-M. Lee and S. Fukuzumi, *Acc. Chem. Res.*, 2014, **47**, 1146–1154.
- 4 E. I. Solomon, T. C. Brunold, M. I. Davis, J. N. Kensley, S.-K. Lee, N. Lehnert, F. Neese, A. J. Skulan, Y.-S. Yang and J. Zhou, *Chem. Rev.*, 2000, **100**, 235.
- 5 M. M. Abu-Omar, A. Loaiza and N. Hontzeas, *Chem. Rev.*, 2005, **105**, 2227–2252.
- 6 P. Comba, M. Kerscher, M. Krause and H. F. Schöler, *Environ. Chem.*, 2015, **12**, 381–395 <http://www.publish.csiro.au/en/EN14240>.
- 7 D. Usharani, D. Janardanan, C. Li and S. Shaik, *Acc. Chem. Res.*, 2012, **46**, 471–482.
- 8 M. Puri and L. Que Jr., *Acc. Chem. Res.*, 2015, **48**, 2443–2452.
- 9 M. Atanasov, P. Comba, B. Martin, V. Müller, G. Rajaraman, H. Rohwer and S. Wunderlich, *J. Comput. Chem.*, 2006, **27**, 1263, DOI: 10.1002/jcc.20412.
- 10 P. Verma, Z. Varga, J. E. M. N. Klein, C. J. Cramer, L. Que Jr. and D. G. Truhlar, *Phys. Chem. Chem. Phys.*, 2017, **19**, 13049–13069.
- 11 M. Swart and M. Gruden, *Acc. Chem. Res.*, 2016, **49**, 2690–2697.
- 12 F. Neese, *J. Inorg. Biochem.*, 2006, **100**(4), 716–726.
- 13 C. Geng, S. Ye and F. Neese, *Angew. Chem., Int. Ed.*, 2010, **49**(33), 5717–5720, DOI: 10.1002/anie.201001850.

- 14 F. Acuna-Parés, *Inorg. Chem.*, 2014, **53**(11), 5474–5485.
- 15 P. Comba, S. Fukuzumi, H. Kotani and S. Wunderlich, *Angew. Chem., Int. Ed.*, 2010, **49**, 2622–2625, DOI: 10.1002/anie.200904427.
- 16 P. Comba, S. Fukuzumi, C. Koke, A. M. Löhr and J. Straub, *Angew. Chem., Int. Ed.*, 2016, **55**, 11129–11133, DOI: 10.1002/ANIE.201605099.
- 17 D. Wang, K. Ray, M. J. Collins, E. R. Farquhar, J. R. Frisch, L. Gomez, T. A. Jackson, M. Kerscher, A. Waleska, P. Comba, M. Costas, E. Münck and L. Que Jr., *Chem. Sci.*, 2013, **4**, 282–291, DOI: 10.1039/c2sc21318d.
- 18 A. Anastasi, P. Comba, J. McGrady, A. Lienke and H. Rohwer, *Inorg. Chem.*, 2007, **46**, 6420–6426.
- 19 J. Bautz, P. Comba, C. Lopez de Laorden, M. Menzel and G. Rajaraman, *Angew. Chem., Int. Ed.*, 2007, **46**, 8067, DOI: 10.1002/anie.200701681.
- 20 P. Comba and S. Wunderlich, *Chem. – Eur. J.*, 2010, **16**, 7293–7299, DOI: 10.1002/chem.201000092.
- 21 P. Comba, M. Maurer and P. Vadivelu, *J. Phys. Chem. A*, 2008, **112**, 13028.
- 22 P. Comba, M. Maurer and P. Vadivelu, *Inorg. Chem.*, 2009, **48**, 10389–10396, DOI: 10.1021/ic901702s.
- 23 We assume that the first decay pathway of the ferryl complex (k_2 in Fig. 1) is a second order process that leads to oxido-bridged diiron(III) complexes. The half-life of this decay process is in the order of one minute under the conditions in Fig. 1c.
- 24 A. Decker, J. U. Rohde, L. Que Jr. and E. I. Solomon, *J. Am. Chem. Soc.*, 2004, **126**, 5378–5379.
- 25 A. Decker, J.-U. Rohde, E. J. Klinker, S. D. Wong, L. Que Jr. and E. I. Solomon, *J. Am. Chem. Soc.*, 2007, **129**, 15983–15996.
- 26 Note that, without any thorough assignment, the observation of an electronic transition in the 700–800 nm region was also used as evidence for ferryl species with $S = 2$ ground state.^{27–30} However, irrespective of whether these have octahedral or trigonal bipyramidal geometries, based on spin selection rules and the relative d orbital energies two transitions in the area of around 600 nm and 800 nm are only expected for an $S = 1$ species with pseudo tetragonal symmetry.
- 27 J. England, M. Martinho, E. R. Farquhar, J. R. Frisch, E. L. Bominaar, E. Münck and L. Que Jr., *Angew. Chem., Int. Ed.*, 2009, **48**, 3622–3626.
- 28 D. C. Lacy, R. Gupta, K. L. Stone, J. Greaves, J. W. Ziller, M. P. Hendrich and A. S. Borovik, *J. Am. Chem. Soc.*, 2010, **132**, 12188–12190.
- 29 J. P. Bigi, W. H. Harman, B. Lassalle-Kaiser, D. M. Robles, T. A. Stich, J. Yano, R. D. Britt and C. J. Chang, *J. Am. Chem. Soc.*, 2012, **134**, 1536–1542.
- 30 A. N. Biswas, M. Puri, K. K. Meier, W. N. Oloo, G. T. Rohde, E. L. Bominaar, E. Münck and L. Que Jr., *J. Am. Chem. Soc.*, 2015, **137**, 2428–2431.
- 31 S. Banerjee, W. Rasheed, R. Fan, A. Draksharapu, W. N. Oloo, Y. Guo and L. J. Que, *Chem. – Eur. J.*, 2019, **25**, 9608–9613.
- 32 S. Meyer, I. Klawitter, S. Demeshko, E. Bill and F. Meyer, *Angew. Chem., Int. Ed. Engl.*, 2013, **52**, 901–905.
- 33 S. Ye, C. Kupper, S. Meyer, E. Andris, R. Navratil, O. Krahe, B. Mondal, M. Atanasov, E. Bill, J. Roithov, F. Meyer and F. Neese, *J. Am. Chem. Soc.*, 2016, **138**, 14312–14325.
- 34 F. G. Cantu-Reinhard and S. P. De Visser, *Chem. – Eur. J.*, 2017, **23**, 2935–2944.
- 35 R. Kumar, A. Ansari and G. Rajaraman, *Chem. – Eur. J.*, 2018, **24**, 6818–6827.
- 36 S. Shaik, D. Danovich, A. Fiedler, D. Schröder and H. Schwarz, *Helv. Chim. Acta*, 1995, **78**, 1393–1407.
- 37 D. Schröder, S. Shaik and H. Schwarz, *Acc. Chem. Res.*, 2000, **33**, 139–145.
- 38 S. Shaik, H. Hirao and D. Kumar, *Acc. Chem. Res.*, 2007, **40**, 532–542.
- 39 M. Y. M. Pau, J. D. Lipscomb and E. I. Solomon, *Proc. Natl. Acad. Sci. U. S. A.*, 2007, **104**, 18361–18362.
- 40 Y. Shiota and K. Yoshizawa, *J. Chem. Phys.*, 2003, **118**, 5872–5879.
- 41 D. Danovich and S. Shaik, *J. Am. Chem. Soc.*, 1997, **119**, 1773–1789.
- 42 J. Harvey, *Phys. Chem. Chem. Phys.*, 2007, **9**, 331–349.
- 43 H. Hirao, L. Que Jr., W. Nam and S. Shaik, *Chem. – Eur. J.*, 2008, **14**, 1740–1756.
- 44 P. Comba, M. Morgen and H. Wadepohl, *Inorg. Chem.*, 2013, **52**, 6481–6501, DOI: 10.1021/ic4004214.
- 45 J. Řezáč and P. Hobza, *J. Chem. Theory Comput.*, 2013, **9**, 2151–2155.
- 46 Q. M. Phung, M. Feldt, J. N. Harvey and K. Pierloot, *J. Chem. Theory Comput.*, 2018, **14**, 2446–2455.
- 47 C. Riplinger, B. Sandhoefer, A. Hansen and F. Neese, *J. Chem. Phys.*, 2013, **139**, 134101.
- 48 C. Riplinger and F. Neese, *J. Chem. Phys.*, 2013, **138**, 034106.
- 49 J.-U. Rohde, J.-H. In, M. H. Lim, W. W. Brennessel, M. R. Bukowski, A. Stubna, E. Münck, W. Nam and L. Que Jr., *Science*, 2003, **299**, 1037–1039.
- 50 M. R. Bukowski, K. D. Koehntop, A. Stubna, E. L. Bominaar, J. A. Halfen, E. Münck, W. Nam and L. Que, *Science*, 2005, **310**, 1000–1002.
- 51 J. England, M. Martinho, E. R. Farquhar, J. R. Frisch, E. L. Bominaar, E. Münck and L. Que Jr., *Angew. Chem.*, 2009, **121**, 3676–3680.
- 52 T. H. Dunning Jr., *J. Chem. Phys.*, 1989, **90**, 1007–1023.
- 53 D. E. Woon and T. H. Dunning Jr., *J. Chem. Phys.*, 1993, **98**.
- 54 A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper and J. Olsen, *Chem. Phys. Lett.*, 1999, **302**, 437–446, DOI: 10.1016/S00092614(99)00179-7.
- 55 M. Feldt, Q. M. Phung, K. Pierloot, R. A. Mata and J. N. Harvey, *J. Chem. Theory Comput.*, 2019, **15**, 922–937.
- 56 Q. M. Phung, C. Martín-Fernández, J. N. Harvey and M. Feldt, *J. Chem. Theory Comput.*, 2019, **15**, 4297–4304.
- 57 H. Börzel, P. Comba, K. S. Hagen, M. Merz, Y. D. Lampeka, A. Lienke, G. Linti, H. Pritzkow and L. V. Tsymbal, *Inorg. Chim. Acta*, 2002, **337**, 407–419, DOI: 10.16/S0020-1693(1002)01100-01103.

- 58 B. V. Meprathu and J. D. Protasiewicz, *ARKIVOC*, 2003, **2003**(vi), 83–90.
- 59 S. E. Gibson, N. Guillo, A. J. P. White and D. J. Williams, *J. Chem. Soc., Perkin Trans.*, 1996, **1**, 2575–2581.
- 60 D. Macikenas, E. Skrzypczak-Jankun and J. D. Protasiewicz, *J. Am. Chem. Soc.*, 1999, **121**, 7164–7165.
- 61 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 16, Revision C.01*, Gaussian, Inc., Wallingford CT, 2016.
- 62 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789.
- 63 A. D. Becke, *J. Chem. Phys. B*, 1993, **98**, 5648–5652.
- 64 R. Ahlrichs and F. Weigand, *Phys. Chem.*, 2005, **7**, 3297–3305.
- 65 F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057–1065.
- 66 S. Miertus, E. Scrocco and J. Tomasi, *Chem. Phys.*, 1981, **55**, 117.
- 67 J. Tomasi and R. Cammi, *J. Comput. Chem.*, 1995, **16**, 1449.
- 68 R. Izsák and F. Neese, *J. Chem. Phys.*, 2011, **135**, 144105.
- 69 R. Izsák, F. Neese and W. Klopper, *J. Chem. Phys.*, 2013, **139**, 094111.
- 70 F. Neese, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2012, **2**, 73–78.
- 71 V. Vasilyev, *Comput. Theor. Chem.*, 2017, **1115**, 1–3.