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Coordination-Number Dependence of Reactivity in an Imidoiron(III) Complex**

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Mononuclear oxoiron species are postulated as intermediates in enzymatic oxidations, and have been characterized in heme systems and in the nonheme monoiron enzyme TauD.[1] Many of the differences in reactivity between the enzymatic intermediates are attributed to the spectator ligands.[2] Recently, the observation and isolation of synthetic iron oxo (L_nFeO)[3] and iron imido (L_nFeNR)[4] complexes has permitted the systematic variation of the ligand environment in species with Fe–O and Fe–N multiple bonds. The six-coordinate $[(tmc)(L)Fe(O)]^{2+}$ system (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) in particular has been amenable to variation of the ligand L.[3,5] In this context, it is important to understand how the number and identity of the spectator ligands modulate the reactivity of compounds with iron–ligand multiple bonds. As a part of this effort, this communication describes data that suggest the formation of a metastable three-coordinate iron(III) imido complex. Unexpectedly, coordination of a fourth ligand induces hydrogen-atom abstraction reactivity. These results contrast with the

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typical situation in which more unsaturated metals give higher reactivity. We also report electronic structure calculations that indicate possible reasons for this interesting phenomenon.

Addition of organic azides to low-valent metal precursors is a well-precedented tactic for introducing the imido ligand into late transition metal complexes.[4,6] We recently demonstrated that the diketiminate-supported dinitrogen complex [L^{Me}FeNNFeL^{Me}] is a source of the iron(I) fragment {L^{Me}Fe} (L^{Me} = 2,4-bis(2,6-diisopropylphenylimino)pent-3-yl).[7] Addition of adamantyl azide (AdN_3) to a blue solution of [L^{Me}FeNNFeL^{Me}] and 4-*tert*-butylpyridine (*t*BuPy, 2 equiv) gave effervescence and immediate formation of an orange-red solution.[8] The ^{1}H NMR and X-band EPR spectra of samples generated in this way are shown in Figure 1.

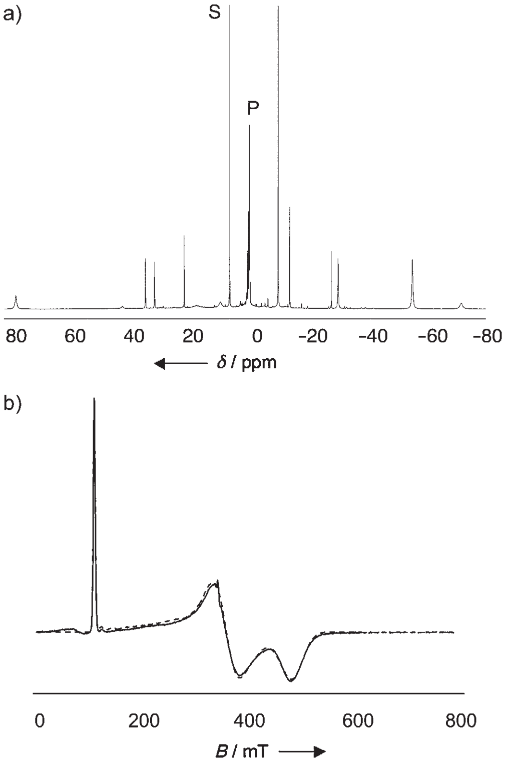


Figure 1. a) ^{1}H NMR spectrum of **A** in C_6D_6, generated from mixing [L^{Me}FeNNFeL^{Me}], 2 equiv AdN_3, and 2 equiv *t*BuPy. The solvent signal is indicated with S, and the *t*BuPy signal with P. b) Solid line: X-band EPR spectrum of **A** diluted to toluene/C_6D_6 (9:1). Conditions: 9.65 GHz, 0.75 mT modulation amplitude, 0.2 mW microwave power, $T = 7.5$ K. The dotted line shows the simulation that gave the values in the text.

The ^{1}H NMR spectra of the solution display resonances for a paramagnetic complex containing only L^{Me}, an adamantyl group, and perhaps *t*BuPy (Figure 1 a). The NMR-active species is formed in about 70 % yield. The X-band EPR spectrum (Figure 1 b) corresponds to an isolated Kramers doublet with $g_{\mathrm{eff}} = 6.12$, 1.94, and 1.42. The EPR spectrum is reminiscent of a spin quartet and can be simulated as an $S = 3/2$ species with $E/D = 0.33$, $g_x = 1.94$, $g_y = 2.20$, and $g_z = 1.94$. The temperature dependence of the signal shows that the ground Kramers doublet is well separated from the excited doublet ($|D| > 30\ \mathrm{cm^{-1}}$). Quantitation (by simulation or by double integration) of the observed signal yields a spin concentration of up to 73 % of the expected Fe concentration. Mössbauer spectra of samples at 150 K showed two quadrupole doublets in a 3:1 ratio with $\Delta E_Q = 0.98(4)\ \mathrm{mm\,s^{-1}}$ and $\delta = 0.47(2)\ \mathrm{mm\,s^{-1}}$ for the majority species (see Supporting Information). Thus, one major product is formed in roughly 70 % yield, and we label this majority species **A**.

We consider three assignments for **A** that are consistent with these combined data: the four-coordinate iron(I) azide complex [L^{Me}Fe(N_3Ad)(*t*BuPy)] (**1**), the three-coordinate iron(III) imido complex [L^{Me}FeNAd] (**2**), and the four-coordinate iron(III) imido complex [L^{Me}Fe(NAd)(*t*BuPy)] (**3**). A dinuclear structure is disfavored for steric reasons, and is difficult to reconcile with an $S = 3/2$ spin state. Known transition-metal azide complexes present an intense band around 2100 $\mathrm{cm^{-1}}$, but solution FT-IR spectra of **A** showed no bands between 1600 and 3000 $\mathrm{cm^{-1}}$.[9] As shown below, kinetic evidence is also inconsistent with this assignment. Therefore possibility **1** is unlikely. We infer that **A** is an iron(III) imido complex in an unusual intermediate-spin electronic configuration.

To help distinguish between assignments **2** and **3**, hybrid QM/MM computations were carried out on full models with density-functional treatment of the metal core and molecular mechanics treatment of the aryl and adamantyl (excepting the carbon bonded to the imido nitrogen) groups.[10] In model **2**, the $S = 3/2$ electronic state is lowest in energy by 10 kcal $\mathrm{mol^{-1}}$. Model **3** has a calculated $S = 5/2$ ground state with a low-lying $S = 3/2$ excited state 4 $\mathrm{kcal\,mol^{-1}}$ higher in energy. The experimental observation of a single ground spin state up to 40 K by EPR, and no sign of an $S = 5/2$ signal, implicate [L^{Me}FeNAd] (**2**) as the most reasonable assignment for **A**. Consistent with this idea, the experimental Mössbauer isomer shift ($\delta = 0.47(4)\ \mathrm{mm\,s^{-1}}$) is closer to that calculated for quartet **2** ($\delta = 0.40\ \mathrm{mm\,s^{-1}}$) than that calculated for quartet **3** ($\delta = 0.62\ \mathrm{mm\,s^{-1}}$).[10]

In the $S = 3/2$ ground state of computational model **2**, the Fe=N−C unit is nearly linear, with an Fe−N distance of 1.68 Å and Fe-N-C angle of 174.1°. The ordering of the d orbitals is similar to that for other three-coordinate iron-diketiminate complexes (Figure 2).[11] In the plane of the diketiminate, the d_{yz} orbital is high in energy from σ antibonding interactions with the diketiminate nitrogen atoms and π antibonding interactions with the imido group. The inability to occupy this orbital explains the stability of the quartet spin state. There is near degeneracy of the doubly occupied d_{xy} orbital and the singly occupied $d_{x^2-y^2}$ orbital,[11] and spin–orbit coupling between these orbitals rationalizes the large zero-field splitting.

We have not been able to isolate **A** because it converts to a purple high-spin iron(III) complex (**B**) over a few hours at room temperature. X-ray crystallography identifies **B** as a neutral, high-spin iron(III) adamantylamido complex with coordinated *t*BuPy (Figure 3 a). There is a C−C bond between the erstwhile isopropyl group of the diketiminate and a carbon atom of the diketiminate backbone, rendering it a dianionic ligand. The Fe−N distances of 1.905(3) Å and 1.925(3) Å in the new ligand are similar to the Fe−N(ada-

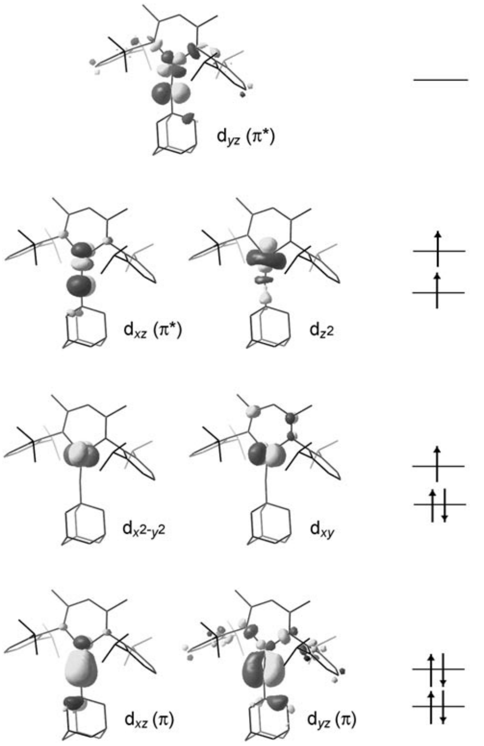
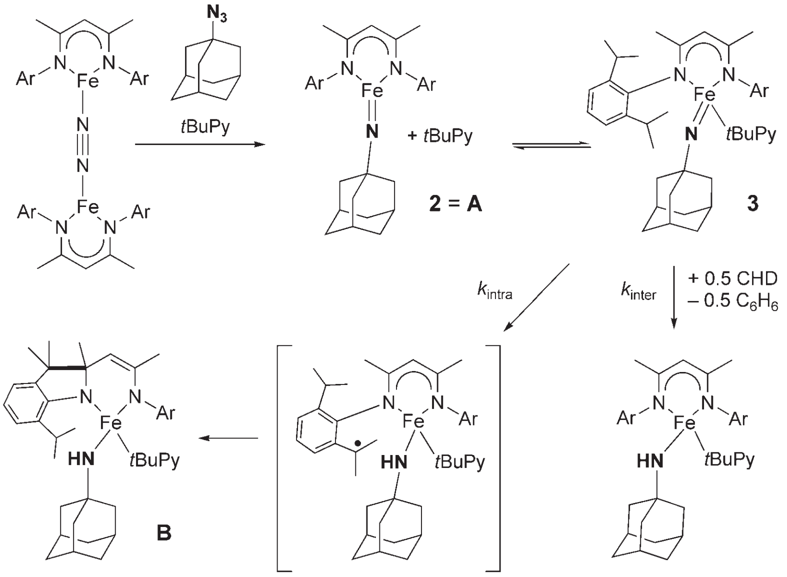


Figure 2. Qualitative ligand-field orbital-splitting diagram for [L^{Me}FeNAd] (**2**) obtained from density functional calculations.



Scheme 1. Proposed assignments for the discussed compounds. *t*BuPy = 4-*tert*-butylpyridine.

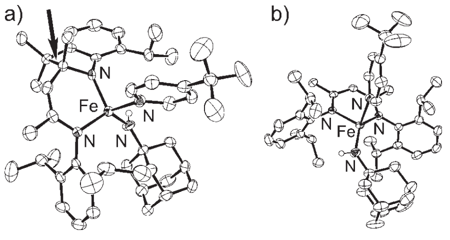


Figure 3. Plots of the X-ray crystal structures of a) **B** and b) [L^{Me}Fe-(NHAd)(*t*BuPy)] showing 50% probability ellipsoids. In **B**, the new C–C bond is indicated with an arrow. Hydrogen atoms are omitted for clarity.

mantylamido) distance of 1.882(3) Å, and to the Fe–N(arylamido) distance of 1.880(2) Å in [L^{Me}Fe(NHdipp)(OTf)] (dipp = 2,6-diisopropylphenyl, Tf = trifluoromethanesulfonyl).[12] Hydrogen-atom abstraction (HAA) by an iron-imido intermediate accounts for the formation of **B** (Scheme 1). The key hydrogen-atom abstraction step of this reaction is similar to those attributed to inferred iron(IV) imido species, and isolated nickel(III) and cobalt(III) imido complexes.[6,13]

The HAA reaction was examined through kinetic studies in which disappearance of **A** was monitored by ^{1}H NMR spectroscopy at 31(1) °C.[14] The observed rate constants show a first-order dependence on [*t*BuPy] with an intercept near zero, suggesting that a pyridine adduct of **A** is the only species undergoing intramolecular HAA. Addition of 10 equiv (based on [L^{Me}FeNNFeL^{Me}]) of 1,4-cyclohexadiene (CHD) to **A** in C_6D_6 leads to rapid formation of [L^{Me}Fe(NHAd)-(*t*BuPy)], isolated in 91% yield (Figure 3b). This intermolecular HAA reaction is much faster than the intramolecular HAA reaction to form **B**. The observed pseudo-first-order rate constant has a first-order dependence on [CHD] at −51(1) °C in [D$_8$]toluene, showing that the *t*BuPy adduct of **A** reacts directly with CHD. This observation is inconsistent with identifying **A** as the potential azide complex **1** or another compound that irreversibly forms the imido complex. The combined spectroscopic and kinetic results are most readily explained using the reaction manifold depicted in Scheme 1.

In the presence of *t*BuPy, **A** also reacts rapidly with indene at low temperature, but does not react with 9,10-dihydroanthracene (DHA) even at room temperature before intramolecular conversion to **B**. We attribute this large difference to a steric effect, because the three substrates have similar C–H bond energies (CHD 76(1) kcal mol^{-1}, indene 79(1) kcal mol^{-1}, DHA 78(1) kcal mol^{-1}).[15] The lack of reactivity with DHA argues against HAA by free radicals.

The QM/MM calculations indicate some differences between three-coordinate (**2**) and four-coordinate (**3**) iron(III) imido complexes that might explain the higher reactivity of the latter. In **3**, the geometry at iron is pseudotetrahedral, which results in a smaller splitting of the ligand-field orbitals (despite the increased coordination number) and hence an $S = 5/2$ ground state. (Because no such species is evident in EPR spectra, we suspect that the active species is present in extremely low concentration and is not observed.) As a result of populating the second π* orbital in the high-spin state of four-coordinate **3**, the Fe–N bond is lengthened to 1.74 Å (compared to 1.68 Å for the quartet state of three-coordinate **2**). Binding of pyridine also causes substantial bending of the imido ligand (Fe-N-C 155.1°). Finally, the nitrogen atom has much more spin density in four-coordinate **3** (0.82 e$^-$) than in three-coordinate **2** (0.23 e$^-$).

In conclusion, we have presented spectroscopic studies on an observable species **A** with an $S = 3/2$ ground state. Considering that **A** is the majority species, that its ground state is consistent with that calculated for [L^{Me}FeNAd], that it reacts directly with hydrogen-atom donors when pyridine is added, and can undergo an intramolecular reaction with the ligand isopropyl groups in the presence of pyridine, it is most reasonable to assign **A** as a three-coordinate iron(III) imido complex with an intermediate-spin electronic configuration. While other formulations of **A** that can rapidly interconvert with an imido complex are also compatible with the data, they are unnecessarily complicated.

Given this interpretation, it appears that the three-coordinate imido complex becomes active for HAA only upon addition of a fourth ligand. Calculations suggest that the ligand-induced change in reactivity is accompanied by 1) a weaker ligand field at iron, which has been observed to increase hydrogen-atom abstraction reactivity in octahedral iron(IV) oxo complexes;[5] 2) a weaker Fe–N bond and a more bent Fe-N-C angle, which decreases the reorganization energy for proton-coupled electron transfer;[16] and 3) a possible spin-state change that leads to enhanced radical reactivity at the imido nitrogen atom, which echoes the two-state reactivity proposed for cytochrome P450 enzymes.[17] The ability to modulate the reactivity of the imido complex through addition of a fourth ligand suggests that this diketiminate system will be useful for elucidating the effects of ligand field strength and geometry on the reactions of metal–nitrogen multiple bonds.

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