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High-Valent Iron

Observing the Formation and the Reactivity of an Octahedral Iron(V) Nitrido Complex in Real Time[**]

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Molecular species containing iron at extraordinarily high oxidation states are considered as key catalytic centers in a number of important chemical and biochemical transformations. For example, a ferryl-oxo species, $Fe^{IV}=O$, is at the heart of the hydroxylation of hydrocarbons by oxygen-activating heme enzymes like cytochrome P-450.[1] Similarly, oxoiron(IV) and oxoiron(V) intermediates have been invoked in the catalytic cycles of several non-heme enzymes[2] including those catalyzing the conversion of methane into methanol[3] or the dihydroxylation of aromatic compounds.[4] This relevance to fundamental questions related to the enzymatic oxidation has fueled research devoted to the preparation and isolation of compounds containing highly oxidized iron centers, to studying their chemical reactivities, and to understanding their electronic structure by means of advanced spectroscopic and theoretical methods. Particularly intriguing high-valent iron compounds are those in which the iron forms multiple bonds to nitrogen because transition-metal nitrides may be implicated in the catalytic reduction of N_2 to ammonia.[5]

Such nitrido iron complexes, $[L_nFe\equiv N]$, can be divided formally into two classes, which differ in the number or the denticity, n, of the ligands, L, that are used to stabilize the iron–nitrogen multiple bond by occupying the residual coordination sites at the metal center.[6] With $n=3$, a threefold symmetrical coordination motif is provided in which the highly oxidized iron center is embedded in the center of a trigonal pyramid that features the terminal nitrido ligand at its apex and the auxiliary ligands at its base. With iron in the oxidation state $+4$, such pseudo-tetrahedral complexes turn out to be very stable even at room temperature and could be prepared first as a transient species using tris(phosphine)borate ligands,[7] then isolated in an inert atmosphere using a tris(carbene)borate ligand,[8] and finally even isolated as an air-stable product using a tris(carbene)amine ligand.[9] Because of this tremendous stability, a $[L_3Fe^{IV}\equiv N]$ complex could recently be exploited in a simple one-electron oxidation as a precursor for a species containing iron in the oxidation state $+5$.[10] The resulting Fe^V complex in turn was sufficiently stable at room temperature, which facilitated an examination of its molecular and electronic structure by means of X-ray crystallography as well as by Mössbauer, EPR, and optical spectroscopy.

With $n=4$ or 5, a fourfold symmetrical coordination geometry is imposed around the metal center. The formation of a square-pyramidal nitrido iron(V) species upon irradiation of thin films of an azido iron(III) porphyrin complex under cryogenic conditions has been deduced from resonance Raman-spectroscopy.[11] Photochemical dinitrogen elimination by heterolytic N–N bond cleavage of an azido iron(III) precursor was also applied to access a pseudo-octahedral nitrido iron(V) species, $[L_5Fe^V\equiv N]$, containing an acetate-functionalized cyclam moiety as the pentadentate ligand L_5.[12] Research on the chemistry of octahedrally coordinated high-valent iron complexes eventually culminated in the preparation of a first species (other than the well-known ferrate dianion) that contains the metal center at the oxidation state $+6$.[13] This was achieved through an initial electrochemical one-electron oxidation of an $[L_5Fe^{III}-N_3]$ complex at low temperature and subsequent photolysis of the resulting $[L_5Fe^{IV}-N_3]$ intermediate in a frozen acetonitrile matrix at 77 K. The $[L_5Fe^{VI}\equiv N]$ complex was then cryogenically characterized by EXAFS and Mössbauer spectroscopy supplemented by density functional theory to verify the genuine hexavalent nature of the iron center.[13]

However, in stark contrast to their pseudo-tetrahedral counterparts, all fourfold symmetrical nitrido iron complexes are thermally highly unstable. Thus, an X-ray crystallographic analysis of square-pyramidal or octahedral complexes of the types, $[L_nFe^V\equiv N]$ and $[L_nFe^{VI}\equiv N]$, has not been conducted to date. More importantly, all spectroscopic studies of these systems have been restricted to cryogenic temperatures and the very existence of a fourfold symmetrical high-valent iron nitride at physiologically or technologically relevant temperatures still requires an unambiguous experimental verification.

To accomplish this feat we have focused on the photo-induced generation of an $[L_5Fe^V\equiv N]$ species from an $[L_5Fe^{III}-N_3]$ precursor complex at room temperature in liquid solution, which we investigated experimentally through laser flash photolysis combined with time-resolved Fourier-transform infrared spectroscopy (TR-FTIR). This experimental technique is capable of monitoring structural changes in real time and with high temporal and spectral resolution. As a precursor we chose the complex *trans*-$[(cyclam)Fe^{III}(N_3)_2]PF_6$ (**1**-PF_6, cyclam = 1,4,8,11-tetraazacyclotetradecane, cf. Figure 1),

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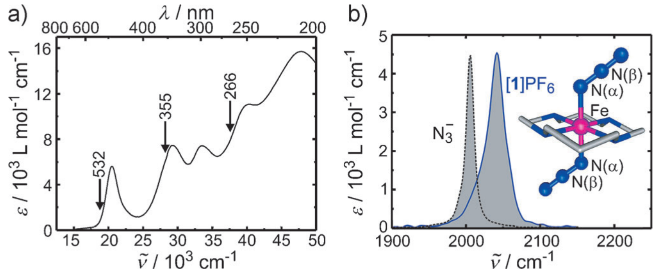


Figure 1. a) UV/Vis absorption spectrum of **1**-PF_6 in acetonitrile solution at room temperature. The photolysis wavelengths that were used are indicated by the vertical arrows. b) The IR spectrum of **1**-PF_6 (blue) and of free azide anions (black) in CH_3CN at $T = 298$ K in the azido stretching region. The molecular structure of **1**-PF_6 is also shown (Fe magenta, N blue, C gray). H-atoms are hidden for clarity.

which has two axial azido ligands rather than only one.[14] This structure has the unique benefit that upon the desired light-triggered elimination of an N_2 molecule, the resultant high-valent product still retains an azide ligand. In turn, this remaining N_3 moiety can be exploited as an internal probe of the electronic and structural changes associated with the metal center upon its photochemical conversion. We emphasize that all spectral data reported herein were obtained from liquid solutions of **1**-PF_6 at room temperature using acetonitrile as the solvent.

The electronic absorption spectrum of **1**-PF_6 (Figure 1 a) exhibits several bands in the visible and near ultraviolet regions that can readily be excited with the second, third, and fourth harmonic pulses of a Q-switched Nd:YAG laser at 532, 355, and 266 nm, respectively. Furthermore, the stationary FTIR spectrum of **1**-PF_6 (Figure 1 b) features a characteristic absorption band at 2042 cm^{-1} that arises from the in-phase and out-of-phase linear combinations of the two asymmetric N_3-stretching vibrations of the cationic complex. Importantly, the asymmetric stretching resonance of the free azide anion in the same solvent is located at 2006 cm^{-1}, that is, markedly shifted to lower frequency with respect to the starting complex. Because **1** has two azide ligands, the band integral over its N_3-resonance is exactly twice as large as the band integral over the free azide resonance. Nonetheless, their peak extinction coefficients are almost identical, which allows the N_3-resonance to be used not only as a structural reporter but also as an internal calibrant to quickly and reliably determine photochemical quantum yields (see below).

Representative time-resolved FTIR-spectra of an argon-purged solution of **1**-PF_6 in CH_3CN are shown in Figure 2 for the two excitation wavelengths, 355 and 266 nm. Within the signal-to-noise ratio, the data obtained for the photolysis wavelength of 532 nm are identical to those obtained at 355 nm. The observable in these spectra is the differential optical density (ΔOD as function of time and wavenumber), that is, the change of the sample's absorbance induced by the photolysis pulse. Focusing first on the data obtained with 355 nm photolysis light, a negative differential optical density at 2042 cm^{-1} can be detected, that is, exactly at the frequency of the azide asymmetric stretching mode of **1**. A negative signal indicates an increased transmission of the sample owing to a net loss of absorbers and hence, loss of the complex cations **1** as a result of a chemical conversion induced by the photolysis pulse. At the same time, a positive ΔOD is seen at 2006 cm^{-1}, that is, exactly at the frequency of the asymmetric stretching mode of free N_3^- ions. A positive signal indicates a decreased transmission of the sample owing to a net gain of absorbers and hence, a gain of free N_3^- ions formed upon 355 nm irradiation of **1** according to Equation (1).

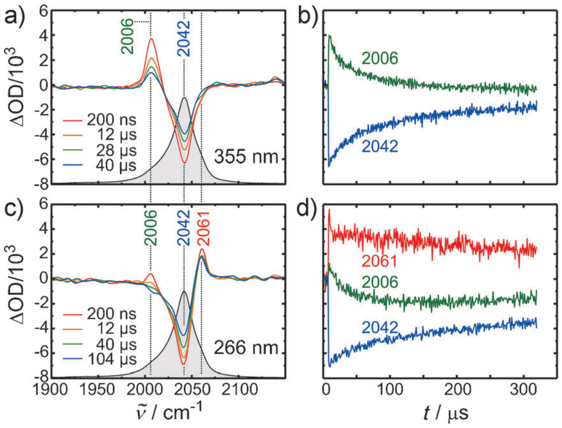
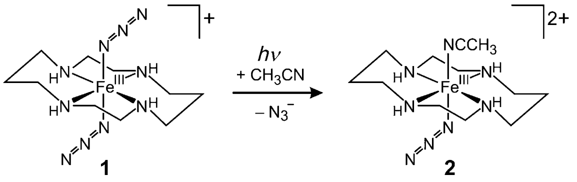


Figure 2. Time-resolved FTIR spectra (left) and kinetic traces (right) following laser photolysis of **1**-PF_6 in CH_3CN at $T = 298$ K using pulses at 355 nm (a, b) and 266 nm (c, d). The kinetic traces were recorded at the center of the parent bleach (blue, 2042 cm^{-1}), at the center of the free azide anion absorption (green, 2006 cm^{-1}), and at the center of the putative nitrido iron(V) product (red, 2061 cm^{-1}). The stationary FTIR spectrum of **1**-PF_6 is also included as the gray-shaded spectrum.

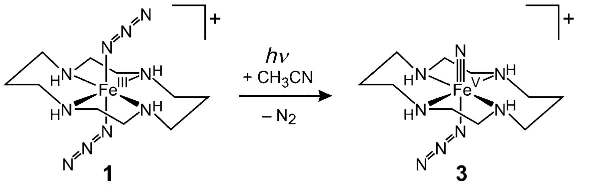


(1)

A N_3^- ion departing from the parent complex leaves behind a vacant coordination site at the metal center that is likely (but not necessarily) filled by a solvent molecule, in this case forming the acetonitrile complex, **2**. As we have discussed in previous publications,[15] the mechanism of such a photoreaction may either be direct or it may involve a primary photo-reduction of iron(III) to iron(II) with formation of azide radicals followed by an electron transfer from Fe^{II} to $N_3^{\cdot}$ with formation of **2** and N_3^-. However, azide radicals whose asymmetric stretching vibration absorbs at 1660 cm^{-1} have not been detected in this work on time scales ranging from 200 ns up to several milliseconds.

Inspecting the kinetic traces (Figure 2 b), it can be seen that the azide anion absorption decays within approximately 200 μs while the parent **1** recovers from bleaching on exactly the same time scale. This indicates that the parent complex **1** is replenished upon direct recombination of N_3^- with **2**. Since **2** still contains an axial azide ligand, it must also contribute to the TR-FTIR spectra somewhere in the azido stretching region. The question therefore arises as to where exactly the product complex **2** absorbs. A crude inspection of the spectra in Figure 2a shows that the induced absorption is spectrally about as broad as the induced bleach. However, from Figure 1b) we have learned that the linear FTIR band of the free azide ion is twice as narrow as that of the parent compound, which leads us to suspect that the induced absorption at 2006 cm^{-1} contains more than just the asymmetric stretching vibration of the free N_3^-. To follow up on this idea, a careful spectral decomposition of the data shown in Figure 2a was carried out (see Supporting Information), which revealed that the rather broad induced absorption around 2006 cm^{-1} is in fact the result of two overlapping transitions. One of which corresponds indeed to the free azide anion absorption centered at 2006 cm^{-1} while the other is centered at 2013 cm^{-1}, which we assign to the N_3-stretching mode of the product complex **2**. The spectral analysis retrieves a photochemical quantum yield for the above reaction of approximately 70% at the photolysis wavelength of 355 nm. The fate of the remaining 30% of photo-excited parent complexes remains unclear at this stage. However, the spectral decomposition (see Supporting Information) already reveals that upon 355 nm irradiation, an additional minor product is formed, which absorbs at 2061 cm^{-1}, that is, shifted to higher frequency with respect to the parent complex.

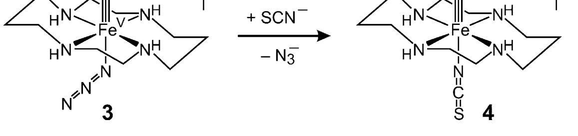
Focusing on the data displayed in Figure 2c,d, it can be seen that at a photolysis wavelength of 266 nm, this induced signal at 2061 cm^{-1} is now the dominant absorptive component to the TR-FTIR spectrum and that the signal shifted to low frequency arising from the azide anions is visible only at the earliest times. Thus, another reaction channel must exist that efficiently competes with the azide-ion dissociation discussed so far. Calculations of band integrals from the 200 ns data of Figure 2c indicate that the area under the bleaching band is more than four times as large as the sum of the areas under the two (high and low frequency shifted) absorption bands. Therefore, it must be concluded that the competing decay channel does not conserve the total number of azide absorbers. However, since, a metal complex is formed that continues to absorb in the azide stretching region (namely at 2061 cm^{-1}), we deduce that in this alternative channel the metal center has lost only one of its azide ligands. Since azide radicals have not been detected, we are left to presume that the desired high-valent nitrido iron(V) complex, **3** is indeed formed through the heterolytic N–N bond cleavage and simultaneous photo-oxidation of the metal center according to Equation (2).



(2)

We locate the asymmetric stretching vibration of the highly oxidized product at 2061 cm^{-1}. To corroborate such an interpretation, DFT electronic structure calculations have been conducted (see Supporting Information). These studies reveal that the nitrido iron(V) complex **3** is indeed a local minimum structure, its electronic ground configuration corresponds to the doublet state, and the doublet–quartet and doublet–sextet energy gaps are roughly 4800 cm^{-1} (58 $kJ\,mol^{-1}$) and 9700 cm^{-1} (116 $kJ\,mol^{-1}$), respectively. The thermal reaction **1**→**3** on the doublet surface turns out to be weakly endoenergetic by 5400 cm^{-1} corresponding to an energy of only 65 $kJ\,mol^{-1}$. A relaxed scan of the doublet potential-energy surface of the parent complex along the N(α)–N(β) bond length indicates that the thermal decomposition into the nitrido complex **3** and dinitrogen is kinetically inhibited by a relatively high energy barrier of 16130 cm^{-1} (or equivalently, 193 $kJ\,mol^{-1}$). Yet, the energies of the 532, 355, and 266 nm photons are more than enough to initiate the photo-oxidation of the parent complex. The spectral decomposition analysis yields a photochemical quantum yield for the formation of complex **3** of roughly 80%. Note that the nitrido iron(V) complex **3** has already been identified by EPR and Mössbauer spectroscopy but only in a frozen matrix at 77 K where it appears to be trapped in its quartet state.[14]

Having verified that the photo-oxidation is energetically feasible, we are still confronted with the task of unambiguously verifying the highly oxidized nature of the metal center in the product of the 266 nm photolysis. In principle, this could be achieved by directly observing its Fe–N stretching vibration in the TR-FTIR spectra. However, the frequency of this mode[6a,9,11,16] is expected to be under 1000 cm^{-1}, that is, in a spectral region where the solvent is no longer transparent. To circumvent this problem, we can explore the reactivity of the putative nitrido iron(V) complex. A kinetic trace recorded at the peak of the 2061 cm^{-1} absorption shows that it has a lifetime of approximately 350 μs under our experimental conditions. Therefore, and in agreement with conclusions drawn from previous studies on fourfold symmetrical $[L_5Fe^V{\equiv}N]$ complexes in cryogenic matrices, the octahedral complex **3** is also fleeting in nature. It lives however long enough to be detected in our experiment and to study its reactivity. Thus, several quenching experiments were conducted using various reagents (see Supporting Information for details). For example, when an argon-purged solution of **1**-PF_6 is photolyzed at 266 nm in the presence of an equimolar amount of potassium thiocyanate, the TR-FTIR spectra change markedly (Figure 3a,b). It can be seen that within 150 μs, the 2061 cm^{-1} band of complex **3** decays and gradually turns over into a net bleach. This behavior clearly indicates the concurrent consumption of **3** and SCN^- ions whose stretching mode happens to absorb at a nearby frequency of 2059 cm^{-1}. At the same time, an absorption from a surplus of free azide anions grows in at 2006 cm^{-1}, which is an unquestionable sign that complex **3** loses its remaining azide ligand upon reaction with SCN^- [Eq. (3)].



(3)

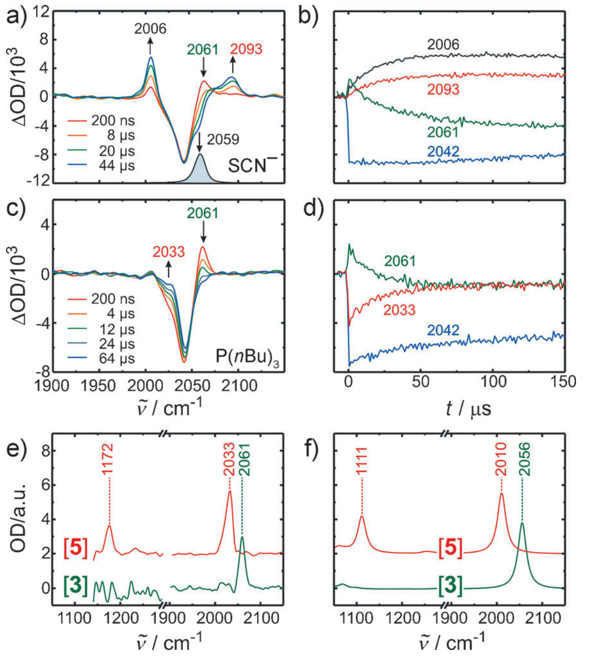
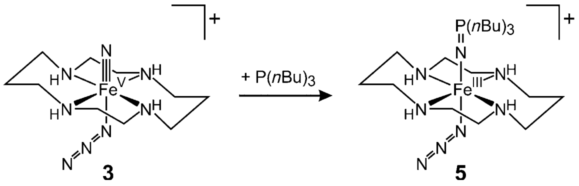


Figure 3. Time-resolved FTIR spectra (a,c) and kinetic traces (b,d) after 266 nm laser photolysis of **1**-PF_6 in CH_3CN at $T=298$ K in the presence of thiocyanate ions (a, b) and of tri-*n*-butylphosphane (c, d). The stationary FTIR spectrum of SCN^- ions is also included in (a) as the gray-shaded spectrum. e) Experimental IR spectra of the nitrido iron(V) complex **3** (green) and of the iron(III) phosphoraniminato complex **5** (red). f) Corresponding theoretical (DFT) spectra of **3** ($S={}^1\!/_2$) and of the trimethylphosphoraniminato analogue of **5** ($S={}^5\!/_2$).

The TR-FTIR-spectra precisely track the formation of the isothiocyanato iron(V) product complex **4** through the build-up of a new characteristic vibrational band centered at 2093 cm^{-1}, whose kinetics perfectly match the combined decay of complex **3** and SCN^- as measured at 2061 cm^{-1} (cf. Figure 3b).

The stable threefold symmetric nitrido iron(IV) complexes have been shown to react as electrophiles enabling them to transfer their nitrogen atom to phosphorous(III) nucleophiles under formation of iron(II) phosphoraniminato species.[6c,8,10] To test whether or not this reactivity applies equally to the elusive octahedral nitrido iron(V) species **3** according to Equation (4) the 266 nm photolysis of **1**-PF_6 was carried out in the presence of 0.5 equivalents of tri-*n*-butylphosphane, $P(nBu)_3$ (see Figure 3c,d).



(4)

Once again, the TR-FTIR spectra confirm that the presumed $\{Fe^V\equiv N\}$ species **3** is successfully converted because its characteristic band at 2061 cm^{-1} disappears completely within 50 μs. Simultaneously, the bleaching band of the starting complex, **1**, is partially recovered at its low-frequency edge on exactly the same time scale. This result can only be rationalized by the appearance of a new azido-stretching absorption in this spectral region, which must originate from a product that has inherited the N_3 ligand from complex **3** through its reaction with $P(nBu)_3$. More quantitative information about the reactant and product IR-spectra can be obtained from a spectral decomposition of the time-resolved data (Figure 3e). It can be seen that the product exhibits two distinctive vibrational bands, one of which is located at 2033 cm^{-1} and is responsible for the partial parent bleach recovery in the azido-stretching region. Another band is located in the fingerprint region at 1172 cm^{-1}. This second feature displays the same kinetics as the 2033 cm^{-1} band and it can be assigned to the stretching vibration of the P=N bond of a newly formed iron(III) phosphoraniminato complex. This assignment is also fully in line with DFT calculations on complexes **3** and **5** (cf. Figure 3 f). Therefore, the observation of a P=N stretching vibration in the quenching experiments with $P(nBu)_3$ represents an undeniable piece of evidence that the presumed octahedral azido iron(V) nitride **3** is indeed formed upon 266 nm laser photolysis of the diazidoiron(III) precursor **1**.

The kinetic analysis of the time-resolved IR data demonstrates that the reactivity of the octahedral iron(V) nitride is enormous with rate constants of the order of $10^7\,L\,mol^{-1}\,s^{-1}$ (for ligand exchange) up to the diffusion limit of approximately $10^9\,L\,mol^{-1}\,s^{-1}$ (for N-atom transfer, see Supporting Information for details). Thus, we can conclude that fourfold symmetrical iron(V) nitrido compounds can indeed exist in liquid solution at room temperature albeit, in this work, only as a transient species on a time scale of several hundred microseconds. Moreover, the fourfold symmetrical iron(V) nitrido complex seen herein has a strong propensity to exchange its axial azide ligand with anionic nucleophiles but, just like its thermally stable threefold symmetrical iron(IV) counterparts, it can engage in two-electron nitrogen-atom transfer reactions. In the future, we will further explore the reactivity of these intriguing highly oxidized octahedral iron species using a variety of other quencher substrates, such as for example, alkenes and carbenes.

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