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Synthesis, Structure, and Spectroscopy of an Oxodiiron(II) Complex

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Diiron units with bridging oxygen ligands (i.e. O^{2-}, OH^-, or H_2O) are present in metalloenzymes such as methane monooxygenase, Δ^9-desaturase, and ribonucleotide reductase.[1] In these enzymes, the Fe_2 unit is bridged by one or two oxygen-based ligands.[1] As these enzymes activate O_2 and transfer oxygen atoms to various substrates, the iron centers pass through several oxidation states from $Fe^{II}Fe^{II}$ to $Fe^{IV}Fe^{IV}$.[1]

To better understand the mechanisms of these enzymes, chemists have synthesized oxo-bridged diiron complexes in a variety of oxidation states.[2,3] Oxodiiron(III) complexes are very common, while their reduced analogues (i.e. $Fe^{II}Fe^{III}$ or $Fe^{II}Fe^{II}$) are rare.[2] For example, there are only two isolable and fully characterized $Fe^{II}Fe^{III}$ oxo compounds.[4] Others have been inferred from electrochemical studies.[5] There is no published oxodiiron(II) compound that is stable under ambient conditions.[6] Here we report the synthesis, structure, and spectroscopic properties of $[L^{tBu}Fe]_2O$ (L^{tBu} = ArNC(^{t}Bu)CHC(^{t}Bu)Ar$^-$, where Ar = 2,6-diisopropylphenyl), an isolable oxo-bridged diferrous compound. Although the trigonal planar coordination of the iron atoms in this compound is different from the geometries in iron enzymes,[1] the ability to stabilize this unusual oxidation level is notable because it demonstrates a new direction in oxodiiron chemistry.

The reaction of equimolar amounts of $[L^{tBu}FeH]_2$[7] and H_2O in THF gives orange-red $[L^{tBu}Fe]_2O$ in 71% yield.[8] The same compound can also be accessed in 53% yield by adding 1 equiv of Me_3NO to $L^{tBu}FeNNFeL^{tBu}$.[9] The solid-state structure of $[L^{tBu}Fe]_2O$ is shown in Figure 1.[8] There is a crystallographically imposed C_2 axis that renders the two $L^{tBu}Fe$ units equivalent. The molecule is planar at iron (sum of bond angles = 359.4(1)°), as found in other three-coordinate iron diketiminate compounds.[7,9,10] The Fe−O−Fe angle of 167.55(14)° is only slightly bent, and the two diketiminate planes are nearly perpendicular (dihedral angle of 70.09(4)°).

The Fe−O distance of 1.7503(4) Å is difficult to put into context because the only iron(II) compounds with oxo ligands are part of mixed-valence dimers that do not have localized valence on the crystallographic time scale.[4] However, there are many examples of crystallographically characterized oxodiiron(III) compounds (Fe−O, av 1.774 Å, std dev 0.029 Å).[11] Because the ionic radius of Fe^{II} (0.77 Å) is substantially larger than that of Fe^{III} (0.63 Å),[12] it is noteworthy that the two Fe−O bonds in $[L^{tBu}Fe]_2O$ are as short as those observed for Fe(III)−oxo bridges. They are substantially shorter than the Fe−O distances in iron(II) hydroxides.[4b,c,13] Density-functional calculations show that reduction from the hypothetical diiron(III) complex $[L^{tBu}Fe]_2O^{2+}$ to diiron(II) places two electrons in d_{z^2} orbitals, where the z axes are oriented normal to the diketiminate planes. As these orbitals have nonbonding character with respect to the ligands, the Fe−O distances calculated for the diiron(II) species (Fe−O = 1.76 Å) are very close to those calculated for diiron(III) (Fe−O = 1.77 Å).

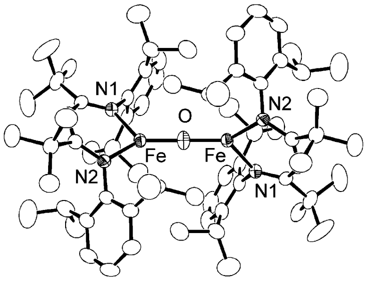

Figure 1. Thermal ellipsoid plot of $[L^{tBu}Fe]_2O{\cdot}OEt_2$ (50% probability ellipsoids), viewed along the C_2 axis. Hydrogen atoms and unassociated diethyl ether are omitted for clarity. Relevant distances (Å) and angles (deg): Fe−O 1.7503(4), Fe−N1 2.005(2), Fe−N2 1.966(2), Fe−O−Fe 167.55(14), N1−Fe−N2 98.22(7).

Solid-state FTIR spectra of $[L^{tBu}Fe]_2O$ show an intense band at 868 cm^{-1} that shifts to 833 cm^{-1} when $H_2{}^{18}O$ is used to prepare the oxo complex (Figure 2). The 35 cm^{-1} shift is consistent with that expected for an Fe−O harmonic oscillator. We assign this peak to the asymmetric stretching vibration of the Fe−O−Fe core, on the basis of the correlation between Fe−O−Fe stretching frequencies and Fe−O−Fe bond angles in oxodiiron(III) complexes.[14] No isotope-sensitive bands are observed in solution resonance Raman spectra, despite excitation into electronic absorptions at 380 and 560 nm.

The zero-field Mössbauer spectrum of solid $[L^{tBu}Fe]_2O$ at 4.2 K (Figure 3A) exhibits a quadrupole doublet with $\Delta E_Q = 1.42(2)$ mm/s and $\delta = 0.64(2)$ mm/s (vs Fe metal at 298 K). In frozen toluene solution we observe $\Delta E_Q = 1.44(2)$ mm/s and $\delta = 0.79(2)$ mm/s.[15] Given the low coordination numbers, the iron(II) sites are expected to be high-spin, like the three-coordinate Fe(II) diketiminate complexes reported previously.[16]

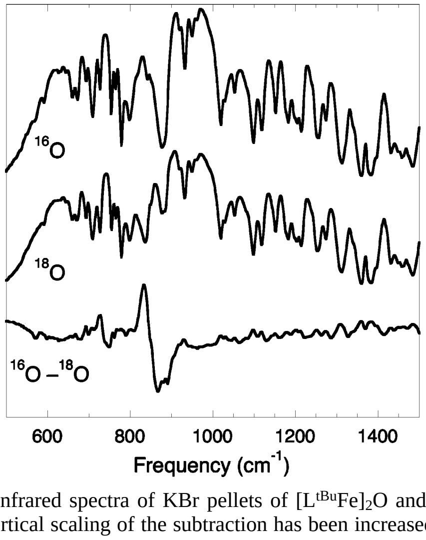

Figure 2. Infrared spectra of KBr pellets of $[L^{tBu}Fe]_2O$ and its ^{18}O isotopomer. Vertical scaling of the subtraction has been increased for clarity.

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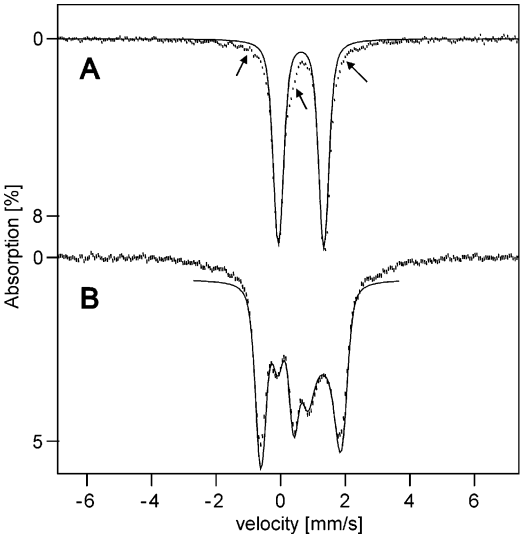

Figure 3. Mössbauer spectra of solid $[L^{tBu}Fe]_2O$ at 4.2 K, recorded in zero field (A) and a parallel applied field of 4.0 T (B). The solid line in (B) is a computer simulation for $\Delta E_Q = (eQV_{zz}/12)[(1 + (\eta^2/3)]^{1/2} = + 1.42$ mm/s, $\eta = 0$, $\delta = 0.64$ mm/s, and $B_{\mathrm{eff},x} = (1 + \alpha_x)B$ for $\alpha_x = 0.2$; details are given in the Supporting Information. Absorption from a contaminant with broad, unresolved features (ca. 20%) is indicated by arrows.[17]

We have recorded Mössbauer spectra for two solid samples and for a toluene sample at temperatures from 4.2 to 150 K and applied fields, **B**, up to 7.0 T. The applied-field spectra have shapes very similar to those observed for diamagnetic compounds.[18] However, at all temperatures and for all fields, in the solid as well as in the frozen solution, the magnetic splitting of the low-energy features is slightly larger than accounted for by the applied field (see Figure S-1, Supporting Information). The applied-field spectra yield $\Delta E_Q > 0$ and a small asymmetry parameter, $0 \leq \eta \leq 0.4$. Within the resolution, the splitting of the low-field features can be modeled by adding a *positive* magnetic hyperfine field, $\mathbf{B}_{\mathrm{int}}$, perpendicular to the largest component of the electric field gradient, V_{zz}. Our simulations reveal that $\mathbf{B}_{\mathrm{int}}$ is proportional to the applied field, $\mathbf{B}_{\mathrm{int}} = \alpha\mathbf{B}$, but independent of temperature up to 150 K. The simulation in Figure 3B assumes that the effective field along x is given by $B_{\mathrm{eff},x} = (1 + \alpha_x)B$, with $\alpha_x \approx +0.2$ and $\alpha_y = \alpha_z = 0$ (see Supporting Information for details). The observation of a positive and temperature-independent α_x suggests substantial unquenched orbital angular momentum, as observed by us in other three-coordinate iron(II) complexes.[16]

Room-temperature ^1H NMR spectra of $[L^{tBu}Fe]_2O$ in C_6D_6 exhibit only seven paramagnetically shifted resonances, with relative intensities as expected for the coordinated diketiminate ligands.[19] This shows that the diketiminate ligands are equivalent on the NMR time scale at room temperature, and the molecule has averaged D_{2h} or D_{2d} symmetry. The observation of equivalent Fe sites agrees with the single high-spin iron(II) environment seen by Mössbauer spectroscopy in frozen toluene solution.

In conclusion, we have synthesized and characterized a stable oxodiiron(II) complex. It contains two identical high-spin, three-coordinate Fe(II) centers supported by bulky diketiminate ligands. Further studies on the reactivity, electronic structure, and magnetic properties of this interesting complex are underway.

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Supporting Information Available: Synthetic, spectroscopic, and crystallographic data, and computational details (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Our samples are prepared in a glovebox, and the sample holders are sealed with a shrink fit cap (Delrin over brass). However, the intensity of the contaminant signals increases over weeks during storage in liquid N_2.

(18) Antiferromagnetic coupling of the ferrous ions in $[L^{tBu}Fe]_2O$ is supported by density functional theory calculations (see Supporting Information) that indicate an exchange coupling $J \approx 200-250$ cm^{-1} (with $\mathbf{H} = J\mathbf{S}_1\cdot\mathbf{S}_2$), in accord with a nearly linear Fe−O−Fe superexchange pathway.

(19) The two methyl groups of the ligand isopropyl groups are inequivalent due to hindered rotation of the aryl moiety. See ref 10f and Supporting Information.

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