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Aqueous $Fe^{IV}{=}O$: Spectroscopic Identification and Oxo-Group Exchange**

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An aqua oxoiron(IV) species is believed to play important roles in environmental and catalytic chemistry, and has been proposed by some researchers as an alternative to $HO^{\bullet}$ as the Fenton oxidant, that is, the intermediate produced in the reaction between Fe^{2+}_{aq} and H_2O_2 in aqueous solution.[1–8] The existence of a ferryl intermediate, most probably $[(H_2O)_5Fe^{IV}{=}O]^{2+}$, has not been established independently in acidic and neutral solutions. Such a complex is, however, believed to be generated in the $[Fe(H_2O)_6{}^{2+}]$/ozone reaction,[9–11] which simultaneously yields one equivalent of O_2,[10] a fact that rules out the description of the intermediate as an ozonide complex. The ozone-generated transient species decays exponentially ($\tau \approx 10$ s in acidic aqueous solution),[10,11] bears a 2+ charge,[11] and oxidizes organic and inorganic substrates.[11,12] All of these findings support the formulation of $[(H_2O)_5Fe^{IV}{=}O]^{2+}$, but the decisive spectroscopic data have not been available until now.

The species of interest, which we call **Z**, was generated at pH 1 in aqueous solution from $[Fe(H_2O)_6]^{2+}$ and O_3[10,11] [Eq. (1)]

$$[Fe(H_2O)_6]^{2+} + O_3 \rightarrow [(H_2O)_5Fe^{IV}{=}O]^{2+}\ (\mathbf{Z}) + O_2 + H_2O \qquad (1)$$

The sample preparation for Mössbauer spectroscopy and other experimental details are described in the Supporting Information. In addition to **Z**, the samples also contained up

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to 50 % $[Fe(H_2O)_6]^{3+}$, produced mainly by the decomposition of **Z** during sample preparation and handling (see Supporting Information).

Figure 1 shows the Mössbauer spectra recorded at 4.2 K in magnetic fields applied parallel to the observed γ-radiation.

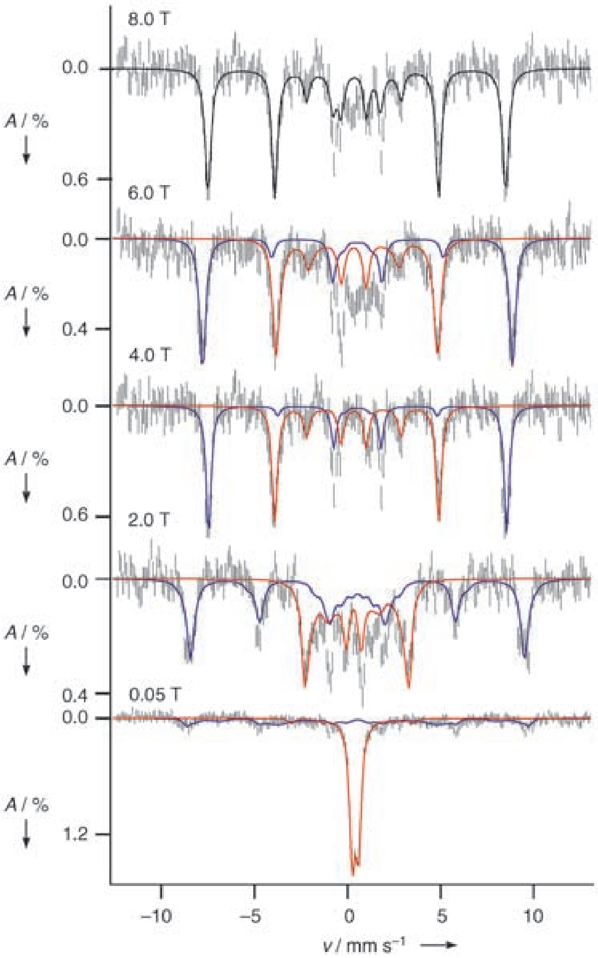


Figure 1. Mössbauer spectra of a sample at 4.2 K containing 250 μM **Z**, prepared by the rapid freeze–quench technique (see Supporting Information). The solid lines (red for **Z**, representing ca. 50% of total Fe) are simulations based on Equation (2). The contribution from $[Fe(H_2O)_6]^{3+}$ is shown in blue. We found the following parameters for **Z**: $D = 9.7(7)$ cm^{-1}, $A_x/g_n\beta_n = A_y/g_n\beta_n = -20.3(3)$ T, $\Delta E_Q = -0.33(3)$ mm s^{-1}, $\delta = 0.38(2)$ mm s^{-1}. For the 8.0-T spectrum, the theoretical curves for **Z** and $[Fe(H_2O)_6]^{3+}$ were added (black).

The spectra shown have contributions from two species: a paramagnetic complex (**Z**) with integer electron spin and a high-spin ferric species with parameters identical to those reported for $[Fe(H_2O)_6]^{3+}$.[13] The most prominent feature in the 0.05-T spectrum is a doublet with quadrupole splitting of $\Delta E_Q = 0.33(3)$ mm s^{-1} and isomer shift of $\delta = 0.38(2)$ mm s^{-1}, relative to Fe metal at 298 K. This doublet represents the reactive species **Z** and, as expected, was absent in a sample that was allowed to age for several minutes at room temperature before freezing. The solid lines drawn through the data are spectral simulations (red for **Z**, blue for $[Fe(H_2O)_6]^{3+}$) based on the spin Hamiltonian H, where H_Q describes the quadrupole interactions [Eq. (2)].

$$H = D[(\boldsymbol{S}_z^2 - S(S+1)/3] + E(\boldsymbol{S}_x^2 - \boldsymbol{S}_y^2) + 2\beta \boldsymbol{S}\cdot\boldsymbol{B} + S\boldsymbol{A}\cdot\boldsymbol{I} - g_n\beta_n\boldsymbol{B}\cdot\boldsymbol{I} + H_Q \tag{2}$$

The spectra of **Z** in the presence of applied fields exhibit paramagnetic hyperfine structure. The internal magnetic field, $\boldsymbol{B}_{int} = -\langle\boldsymbol{S}\rangle\cdot\boldsymbol{A}/g_n\beta_n$, is negative (namely, opposed to the applied field $\boldsymbol{B}$), and increases with increasing applied field $\boldsymbol{B}$. The outermost absorption lines of the spectrum of **Z** are remarkably sharp, thus showing that $\boldsymbol{B}_{int}$ is axial, and implying that $E \approx 0$ and $A_x \approx A_y$ in Equation (2). The Mössbauer spectra measured at 12 K (see Supporting Information) show that the fluctuation of the electronic spin of **Z** is slow. In the slow-fluctuation limit, the 0.05-T Mössbauer spectrum of a mononuclear ferric complex (a Kramers system) must exhibit (in the same way as $[Fe(H_2O)_6]^{3+}$ in Figure 1) paramagnetic hyperfine structure, whereas non-Kramers systems (such as Fe^{IV} complexes) usually exhibit quadrupole doublets. Our data thus imply that **Z** has integer spin, and suggest that it is (formally) an Fe^{IV}–oxo complex. The theoretical curves (red) for **Z** are spectral simulations generated for $S = 2$ by using the parameters quoted in the caption to Figure 1. The Mössbauer spectra show that **Z** is a pure species and rule out an equilibrium mixture of two forms, such as $\{Fe^{IV}{=}O\}^{2+}/\{Fe^{IV}(OH)_2\}^{2+}$. The paramagnetic states of Fe^{IV} have spins of either $S = 2$ or $S = 1$. The latter spin can be ruled out because Equation (2) would yield $A_x = A_y \approx -38$ T, which is substantially larger than the largest A values reported for any Fe^{IV}–oxo complex (−25 T).[14,15] The parameters obtained for **Z** are similar to those for the $S = 2$ $\{Fe^{IV}{=}O\}$ intermediate of *E. coli* taurine: α-ketoglutarate dioxygenase (TauD);[16] $D = 10.5$ cm^{-1}, $A_x/g_n\beta_n = A_y/g_n\beta_n = -18.0$ T, $\Delta E_Q = -0.88$ mm s^{-1}, $\delta = 0.31$ mm s^{-1}. Most plausibly, **Z** is formulated as $[(H_2O)_5Fe^{IV}{=}O]^{2+}$.

X-ray absorption spectroscopy was carried out on two samples for which Mössbauer spectroscopy established $\mathbf{Z}/[Fe(H_2O)_6]^{3+}$ ratios of 50/50 and 58/42. Figure 2 shows the

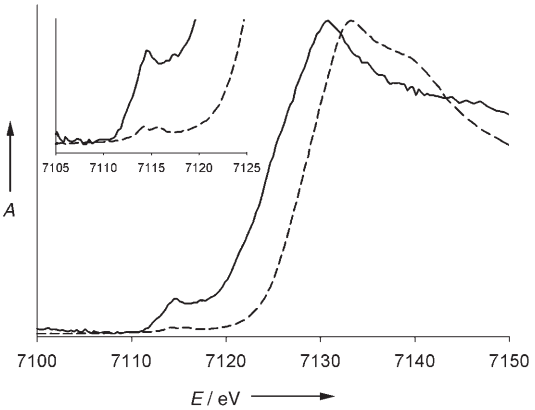


Figure 2. Normalized XANES spectra (Fe K-edge) of **Z** (solid line) and $[Fe(H_2O)_6]^{3+}$ (dashed line). The spectrum of **Z** was obtained by subtraction of 50% of the spectrum of $[Fe(H_2O)_6]^{3+}$ from the spectrum of the 1:1 $\mathbf{Z}/[Fe(H_2O)_6]^{3+}$ sample. The inset shows a magnification of the 1s→3d region.

X-ray absorption near-edge structures (XANES) of $[Fe(H_2O)_6]^{3+}$ (dashed line) and **Z** (solid line). The edge energy for $[Fe(H_2O)_6]^{3+}$ was found to be 7129 eV. In contrast, Fe^{III} complexes with N/O coordination have edges around 7123 eV.[17] On the basis of density functional theory (DFT) calculations (see Supporting Information) we attribute the higher-energy edge of $[Fe(H_2O)_6]^{3+}$ to its high ionic character.[13] Notably, the edge energy of **Z**, at 7126 eV, is midway between that for $[Fe(H_2O)_6]^{3+}$ and the range reported for non-heme $\{Fe^{IV}{=}O\}$ complexes (7123 eV for the high-spin intermediate of the enzyme TauD,[18] and 7124–7125 eV for the synthetic non-heme low-spin complexes[15,17]). The reduction in the edge energy of **Z** relative to that of $[Fe(H_2O)_6]^{3+}$ arises from the strong covalent bonding interaction with the terminal oxo group[19] (see Supporting Information).

Another notable feature in the XANES spectrum of **Z** is its pronounced 1s→3d transition (Figure 2). The intensity of this feature reflects the deviation of the metal center from centrosymmetric geometry; the intensity generally increases upon conversion from octahedral into tetrahedral geometry[20] or upon the introduction of an oxo ligand into a six-coordinate complex.[15,17] The pre-edge feature of $[Fe(H_2O)_6]^{3+}$ has a measured area of eight units, which is typical of nearly centrosymmetric, six-coordinate complexes. For the spectrum of **Z** we found an area of 60–70 units, which is the highest area yet for an iron center. This value is distinctly larger than those observed for known six-coordinate oxoiron(IV) species (25 to 38 units)[15,17] and suggests an oxoiron(IV) center with substantial deviation from centrosymmetric geometry.

DFT calculations were performed on **Z** as an $[(H_2O)_5Fe^{IV}{=}O]^{2+}$ species (see Supporting Information). The results can be summarized as follows: 1) Geometry optimization (Figure 3) yields an Fe=O bond length of 1.62 Å, which is similar to the Fe=O bond lengths in other non-heme oxoiron(IV) complexes[14]. 2) DFT calculations yield a ground state with $S=2$, which is in agreement with the Mössbauer analysis. 3) The hyperfine parameters are equal to those obtained from the Mössbauer spectra. 4) The zero-field splitting of the $S=2$ ground state is correctly predicted on the basis of electronic excitation energies involving an $(S=1)/(S=2)$ spin-mixing mechanism similar to that functioning in the $S=1$ complex $[Fe^{IV}(O)(tmc)(MeCN)]^{2+}$ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane). 5) The experimental values for δ, ΔE_Q, and the contact contribution to the A-tensor A_c are different for $[Fe^{IV}(O)(tmc)(MeCN)]^{2+}$ and **Z** in ways that the theory predicts if the equatorial sites in tmc are replaced by aqua ligands (see Supporting Information), that is, $\delta(\text{tmc}) < \delta(\mathbf{Z})$, $\Delta E_Q(\text{tmc}) > 0 > \Delta E_Q(\mathbf{Z})$, and $|A_c(\text{tmc})| < |A_c(\mathbf{Z})|$. 6) DFT analysis of the K-edge energy supports the $[(H_2O)_5Fe^{IV}{=}O]^{2+}$ formulation for **Z**.

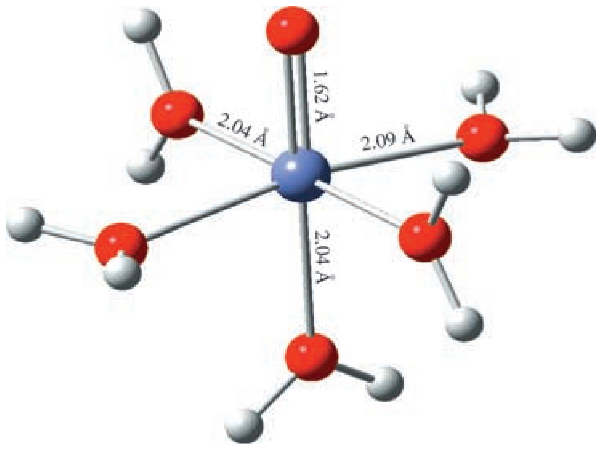
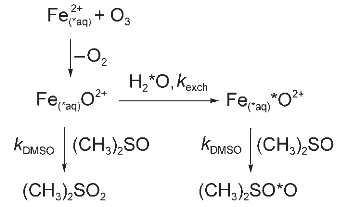


Figure 3. Proposed structure for **Z**, $[(H_2O)_5Fe^{IV}{=}O]^{2+}$, calculated with the B3LYP functionial and the 6-311G basis set with C_{2v} symmetry.

The reaction between $[(H_2O)_5Fe^{IV}{=}O]^{2+}$ (0.10 mM) and an excess (6–470 mM) of $(CH_3)_2SO$ or $(CH_3)(p\text{-tolyl})SO$ in 0.10 M aqueous $HClO_4$ produced the corresponding sulfone and regenerated $[Fe(H_2O)_6]^{2+}$ quantitatively. The combination of this oxygen-atom-transfer step and the $O_3/[Fe(H_2O)_6]^{2+}$ reaction constitutes a catalytic cycle for the oxidation of $(CH_3)_2SO$ by ozone.

The catalytic oxidation was carried out in $H_2{}^{18}O$ (97% ^{18}O enrichment, pH 1) and utilized 0.4–7 mM $[Fe(H_2{}^{18}O)_6]^{2+}$ as catalyst under continuous bubbling with $^{16}O_3$ until approximately 30% of the $(CH_3)_2S^{16}O$ (initial concentration 0.1 M) was oxidized. The direct oxidation of $(CH_3)_2SO$ by O_3 under these conditions contributes $\ll 1\%$ to the overall process. The products, identified and quantified by GC-MS, were $(CH_3)_2S^{16}O_2$ (88%) and $(CH_3)_2S^{16}O^{18}O$ (12%), irrespective of the concentration of $[Fe(H_2O)_6]^{2+}$. With a substrate concentration of 0.010 M, the proportion of $(CH_3)_2S^{16}O^{18}O$ increased to 48%, which is as expected if the intermediate $[(H_2O)_5Fe^{IV}{=}O]^{2+}$ undergoes both reaction with the substrate and oxygen exchange with water (Scheme 1). The data at the two concentrations of $(CH_3)_2SO$ were fitted to an equation for competition kinetics (see Supporting Information) and provided an estimate for the rate constant for oxygen exchange as $k_{\text{exch}} \approx 10^3\ s^{-1}$.

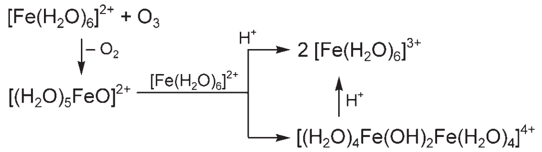


Scheme 1.

The nearly quantitative yield of $(CH_3)_2S^{16}O_2$ at high concentrations of $(CH_3)_2SO$ confirms the presence of one unique oxygen atom in the reactive form of the catalyst, which is most consistent with the $[(H_2O)_nFe^{IV}{=}O]^{2+}$ formulation. Other possible formulations, such as $[(H_2O)_mFe^{IV}(OH)_2]^{2+}$, in which at least one of the two hydroxo groups would have to be derived from the ^{18}O-labeled water, would permit the incorporation of at most 50% ^{16}O into the product sulfone, and is thus ruled out by our observations. These conclusions are in accord with the Mössbauer data, which show that only one major Fe^{IV} species is present in our samples.

With the identification of **Z** as $[(H_2O)_5Fe^{IV}{=}O]^{2+}$, the question of its participation in Fenton chemistry was addressed by studying the kinetic patterns and products for three substrates, namely $[Fe(H_2O)_6]^{2+}$, $(CH_3)_2SO$, and (CH_3)(*p*-tolyl)SO, in the Fenton reaction and in the reaction with $[(H_2O)_5Fe^{IV}{=}O]^{2+}$ under identical and carefully selected conditions.

Stopped-flow mixing of O_3 (0.25 mM) and a large excess of $[Fe(H_2O)_6]^{2+}$ (0.10 M) in $HClO_4$ (0.090 M) produced, within the mixing time ($k = 4.3 \times 10^4\,M^{-1}\,s^{-1}$),[11] a mixture of $[Fe(H_2O)_6]^{3+}$ (84% of total Fe^{III}) and the hydrolytic dimer, $[(H_2O)_4Fe(\mu\text{-}OH)_2Fe(H_2O)_4]^{4+}$ (16%), followed by hydrolysis of the dimer[21] to $[Fe(H_2O)_6]^{3+}$ with $k = 0.76\,s^{-1}$[11] (Scheme 2).



Scheme 2.

In an otherwise identical experiment with H_2O_2 in place of O_3, no dimer was produced, thus ruling out $[(H_2O)_5Fe^{IV}{=}O]^{2+}$ as a reactive intermediate in the Fenton reaction (see Supporting Information).

The sole products of the oxidation of $(CH_3)_2SO$ and (CH_3)(*p*-tolyl)SO by $[(H_2O)_5Fe^{IV}{=}O]^{2+}$ in both acidic and neutral solutions were the corresponding sulfones (see Supporting Information). The Fenton reaction with $(CH_3)_2SO$ under air-free conditions yielded mostly ethane, methylsulfinic acid, and small amounts of methane and dimethyl sulfone, that is, products known to be derived from OH radicals.[22,23] The yields of all the products decreased in the presence of O_2, and no sulfone was detected.

In summary, we have generated $[(H_2O)_5Fe^{IV}{=}O]^{2+}$, characterized it spectroscopically, theoretically, and chemically, and developed criteria that made it possible to distinguish between hydroxyl radicals and aqueous ferryl-oxo species. These criteria have allowed us to settle a long-standing debate and unambiguously rule out $[(H_2O)_5Fe^{IV}{=}O]^{2+}$ as a crucial Fenton intermediate in acidic and neutral aqueous solutions.[24]

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Keywords: Fenton reaction · iron · Mössbauer spectroscopy · oxygen · X-ray absorption spectroscopy

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