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Iron–Sulfur Clusters

Isolation and Characterization of Stable Iron(I) Sulfide Complexes**

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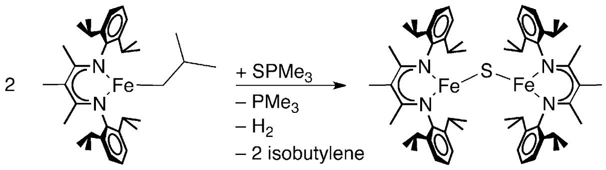
Iron–sulfur clusters are widespread in metalloproteins, where they most often function to transfer electrons but also can act as sites for catalysis.[1] In known iron–sulfide clusters, the iron ions are in the +2 and +3 oxidation states.[2,3] Even in synthetic chemistry, with a much broader range of supporting ligands, the iron ions in iron sulfide complexes are always Fe^{2+} or Fe^{3+}. Synthetic all-Fe^{2+} clusters using cyanide or *N*-heterocyclic carbene ligands are a recent advance.[4] However, there are no reports of iron sulfide compounds in which iron ions are reduced to the Fe^{1+} level.[5] Herein, we describe the first examples of isolable iron(I) sulfide compounds, which establishes that iron(I) is a feasible oxidation state in iron sulfide chemistry.

The progenitor of the new compounds is the previously reported μ-sulfidodiiron(II) compound $[\{L^{Me}Fe\}_2(\mu\text{-}S)]$ (**1-H**), $L^{Me} = HC[C(Me)N(2,6\text{-}i\text{Pr}_2C_6H_3)]_2$.[6] This molecule is the only crystallographically characterized iron sulfide with a three-coordinate iron atom. The work reported herein used a close variant of this compound, $[^{Me}L^{Me}Fe]_2(\mu\text{-}S)$ (**1-Me**), $^{Me}L^{Me} = MeC[C(Me)N(2,6\text{-}i\text{Pr}_2C_6H_3)]_2$, in which the supporting ligand contains an additional methyl group. $[\{^{Me}L^{Me}Fe\}_2(\mu\text{-}S)]$ (**1-Me**) is spectroscopically similar to its L^{Me} analogue (**1-H**).

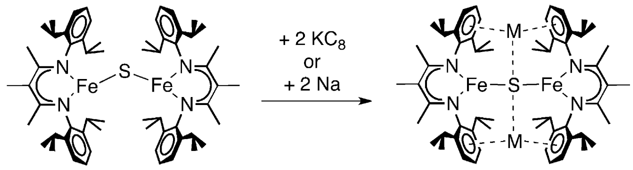
We also developed a novel organometallic route to the μ-sulfidodiiron(II) complexes. This strategy takes advantage of rapid, clean β-hydride elimination from low-coordinate alkyl complexes,[7] and the ability of low-coordinate iron(II) hydride complexes to reductively eliminate H_2 upon addition of coordinating ligands.[8] Thus, L^{Me}Fe(*iso*-butyl) or $^{Me}L^{Me}$Fe(*iso*-butyl) were mixed with PMe_3S and heated to 100 °C in toluene overnight to give the diiron(II) sulfides **1-H** or **1-Me** (Scheme 1 shows **1-Me**). All of the byproducts PMe_3, H_2, and isobutylene were conveniently removed by evaporation. The products were isolated in 65 % and 73 % yield, respectively.



1-Me

Scheme 1. Synthesis of the diiron(II) sulfide complex **1-Me**.

A red solution of **1-Me** in diethyl ether reacted with two molar equivalents of potassium graphite (KC_8) to give a color change to green. The product, $[K^{Me}L^{Me}Fe]_2(\mu\text{-}S)$ (**2-Me**) (Scheme 2), was isolated in 62 % yield and crystallographically characterized. **1-Me** can instead be reacted with excess metallic sodium in THF to give $[Na^{Me}L^{Me}Fe]_2(\mu\text{-}S)$ (**3-Me**) in 56 % yield. Compounds **2-Me** and **3-Me** had similar ^{1}H NMR spectra, and had half-lives of ca. 80 hours at 60 °C in C_6D_6 (Supporting Information, Figures S6, S7).



1-Me

2-Me; M = K
3-Me; M = Na

Scheme 2. Synthesis of the diiron(I) sulfide complexes.

X-ray diffraction studies showed the solid-state structures of **2-Me** and **3-Me** (Figure 1 and Supporting Information). The Fe–S bond lengths in **2-Me** and **3-Me** are 2.1745(13) Å and 2.1957(3) Å, respectively. These Fe–S bond distances are typical for μ_2-S atoms in diiron compounds (2.22(3) Å).[9] However, the Fe–S distances in **2-Me** and **3-Me** are significantly longer than the 2.102(2) Å for a three-coordinate iron(II) atom to a bridging sulfide in $L^{Me}Fe(\mu\text{-}S)Fe(NCCH_3)L^{Me}$.[6] The longer Fe–S bonds suggest that the iron is in a lower oxidation state, and charge counting in the structure suggests a diiron(I) formulation. This hypothesis is addressed below using spectroscopic and computational evidence.

In $[\{K^{Me}L^{Me}Fe\}_2(\mu\text{-}S)]$ (**2-Me**) and $[\{Na^{Me}L^{Me}Fe\}_2(\mu\text{-}S)]$ (**3-Me**), the μ-sulfido bridges are linear (Fe-S-Fe angles of 179.70(4)° and 180°, respectively). Linear sulfide bridges are

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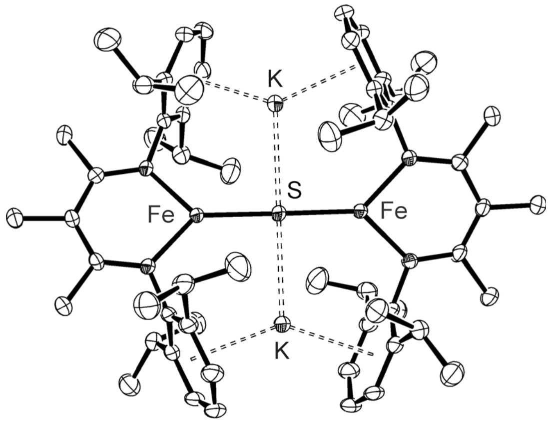

Figure 1. Thermal-ellipsoid plot of $[\{K^{Me}L^{Me}Fe\}_2(\mu\text{-}S)]$ (**2-Me**). Ellipsoids are set at 50% probability; hydrogen atoms omitted for clarity. The sodium analogue **3-Me** has also been crystallographically characterized, and is shown in the Supporting Information.

uncommon, and the average Fe-S-Fe bond angle for diiron complexes with a single bridging sulfur atom is 126(24)°.[9] The next most linear Fe-S-Fe bond angle is 167.0(2)°, in a five-coordinate iron complex with a bulky salen ligand.[10] Linear sulfido bridges have been seen in complexes of other transition metals, such as V, Mo, Co, Ni, and Cu.[11–14]

In the crystal structures of **2-Me** and **3-Me**, the alkali metal cations are sandwiched between the aryl groups of the β-diketiminate ligands, as found in formally iron(I) hydride and dinitrogen complexes.[15] Geometric restraints from the cation–π interactions may play a role in enforcing the linear sulfide bridge, though there are literature examples of linear sulfide bridges without such restraints.[11–13] The K–S distances in **2-Me** of 2.932(2) Å and 2.936(2) Å are the shortest known.[9] The next shortest K–S bond is 3.039(2) Å in a compound where the K^+ ion also has a cation–π interaction.[16] The Na–S distance in **3-Me** is 2.6994(7) Å, which is only slightly shorter than the average Na–S bond of 2.9(2) Å.[9] Other parameters from the crystal structures of **2-Me** and **3-Me** are similar, and thus no major structural differences arise from the choice of alkali metal cation.

The ability to exchange the alkali metals was evaluated using NMR spectroscopy. The ^1H NMR spectra of **2-Me** and **3-Me** were consistent with D_{2d} or D_{2h} symmetry in solution, with seven paramagnetically shifted resonances. Mixing **2-Me** with **3-Me** resulted in the growth of a third set of resonances in the ^1H NMR spectrum with a shift pattern similar to the reactants (Supporting Information). We assign the new peaks to the mixed-cation complex $[\{NaK^{Me}L^{Me}Fe\}_2(\mu\text{-}S)]$ (**4-Me**). This reaction reached an equilibrium in which all 3 species (**2-Me**, **3-Me**, **4-Me**) were present, requiring 24 h in C_6D_6 and 6 h in Et_2O. To further support the exchange of cations, Na^+ and K^+ sources (1 equiv of $NaBAr^F_4$ or KOTf, where Ar^F indicates 3,5-bis(trifluoromethyl)phenyl and OTf indicates trifluoromethanesulfonate) were added to **2-Me** and to **3-Me** in Et_2O solution. When the alkali salts matched (for example, addition of KOTf to **2-Me**), no reaction was seen, but the mixed alkali-metal experiments produced **4-Me**, as shown by ^1H NMR spectroscopy. These results demonstrate that the potassium and sodium cations can exchange between the aryl rings on the β-diketiminate ligands. However, the compounds are not stable without the alkali metal cations (see below).

We next turned to spectroscopic studies to support the oxidation state assignment as iron(I). The Mössbauer spectrum of solid **2-Me** showed a single quadrupole doublet for the two equivalent iron atoms, with isomer shift $\delta = 0.67\ \mathrm{mm\,s^{-1}}$ and quadrupole splitting $|\Delta E_Q| = 2.17\ \mathrm{mm\,s^{-1}}$ that was temperature independent from 4.2 to 80 K (Figure 2a. The zero-field Mössbauer spectrum of **3-Me** was similar, with an isomer shift $\delta = 0.64\ \mathrm{mm\,s^{-1}}$ and quadrupole splitting of $|\Delta E_Q| = 2.28\ \mathrm{mm\,s^{-1}}$ at 80 K. For comparison, the Mössbauer spectrum of the diiron(II) sulfide complex **1-Me** had distinctly different parameters of $\delta = 0.59\ \mathrm{mm\,s^{-1}}$ and $|\Delta E_Q| = 0.89\ \mathrm{mm\,s^{-1}}$. The increase in isomer shift upon reduction supports the hypothesis that reduction has occurred at the iron centers. The isomer shifts observed for **2-Me** and **3-**

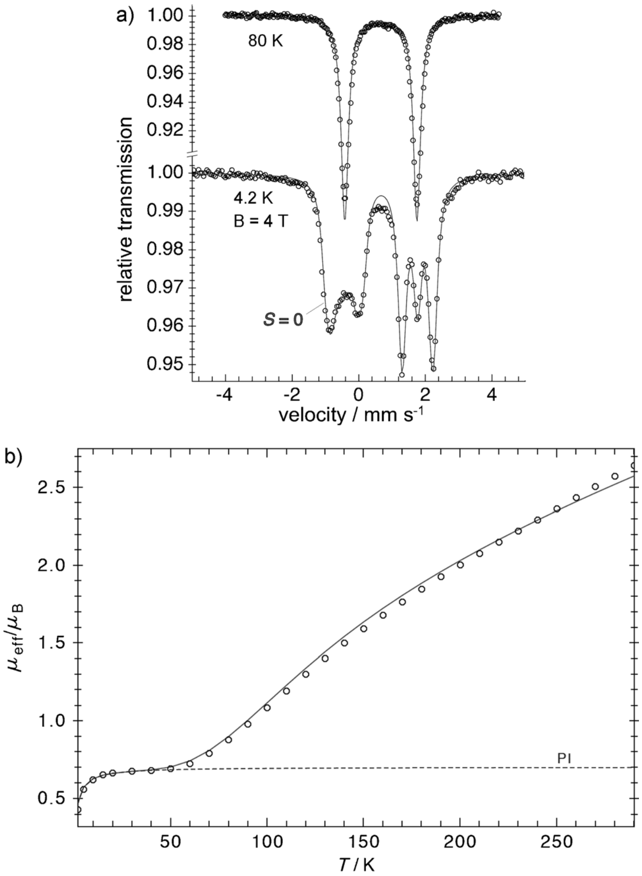

Figure 2. a) Mössbauer spectrum of **2-Me** at 80 K (top) and at 4.2 K with a 4 T field perpendicular to the gamma rays (bottom). The solid lines are fits for $\delta = 0.67\ \mathrm{mm\,s^{-1}}$ and $|\Delta E_Q| = 2.17\ \mathrm{mm\,s^{-1}}$. The magnetic simulation reveals $S = 0$ at 4.2 K, $V_{zz} = -2.17\ \mathrm{mm\,s^{-1}}$, and $\eta = 0.3$. b) Solid-state variable-temperature magnetic susceptibility of **2-Me**. The solid line is a fit where both iron centers have a spin state of $S_i = 3/2$ and antiferromagnetic coupling with $J = -123\ \mathrm{cm^{-1}}$ ($H = -2J S_1 \cdot S_2 + g\mu_B(S_1 + S_2) \cdot B$). The dashed line represents a 1.4% paramagnetic impurity (PI) with $S = 5/2$, which was necessary to account for the offset below 50 K.

Me also resemble those for thioether-supported iron(I) complexes ($\delta = 0.62$–$0.76\ \mathrm{mm\,s^{-1}}$),[17] and a phosphine-supported iron(I) complex ($\delta = 0.57\ \mathrm{mm\,s^{-1}}$).[18]

Applied-field Mössbauer measurements on **2-Me** revealed an energetically well-isolated diamagnetic ($S_{\mathrm{total}} = 0$) ground state for the dimer, and a positive sign of the electric field gradient with small asymmetry $\eta = 0.3$. Solid-state magnetic susceptibility studies (Figure 2b) also indicated antiferromagnetic coupling of two paramagnetic iron subsites to give a regular spin ladder with an $S_{\mathrm{total}} = 0$ ground state, as expected for strong exchange interaction that dominates the single-ion zero-field splitting (zfs). The data fit to a fundamental model where each iron(I) ion is high-spin ($S_{\mathrm{Fe}} = 3/2$) and $J = -123 \pm 8\ \mathrm{cm^{-1}}$ quantifies the antiferromagnetic coupling. Interestingly, this system does not have the strong first-order orbital moment that was observed for a related mononuclear iron(I) complex.[19] We estimate that $D = (0 \pm 30)\ \mathrm{cm^{-1}}$; the simulations are not particularly sensitive to zfs in such a dinuclear system where a spin singlet is the ground state.

The spectroscopic studies were supplemented with calculations on the full molecule with density-functional theory (DFT) using the crystallographic coordinates. The functional and basis set were varied to find the best match to the geometry, the Mössbauer parameters and the J value.[15b] The electronic structure description of **2-Me** derived from the best-fit (broken-symmetry calculations with TPSSh functional and TZVP basis set) calculations showed two antiferromagnetically coupled high-spin iron(I) centers with $J = -170\ \mathrm{cm^{-1}}$ (Figure 3). The β-diketiminates showed no compelling evidence for "redox non-innocent" sharing of spin density from the metals. There is slight π backbonding from the iron(I) centers to the unoccupied β-diketiminate orbitals, suggesting that the electronic properties of the supporting ligand may play a role in stabilizing the low oxidation state of iron(I). However, the interaction between the iron atoms and the π system of the β-diketiminates is small.

The role of the alkali metal in stabilizing the low iron oxidation state was evaluated experimentally by studying the diiron(I) sulfide in the presence of solvents and additives that have the ability to remove the alkali metal cation. In C_6D_6, **2-Me** and **3-Me** were stable for about 5 days at 60 °C, whereas under the same conditions in $[D_8]$THF they were stable for less than 2 h. This result suggests that THF may pull the alkali metal cations away from the Fe/S core, destabilizing **2-Me** and **3-Me**. In a more muscular test of this hypothesis, the potassium chelators [18]crown-6 or cryptand-222 were added to solutions of **2-Me** under argon or N_2, which led to immediate decomposition. Electrochemical reduction of **1-Me** in Et_2O indicated a one-electron wave at −2.7 V (vs. $\mathrm{Fc^{+/0}}$), thus also supporting the idea that two-electron reduction is not possible without the alkali metal cations. All of these results indicate that the cation plays a significant role in stabilizing the iron(I) complexes, most likely by the close interactions between cations and the negatively charged core of the molecule.

In conclusion, diiron(I) sulfide compounds can be isolated, and their characterization as bona fide iron(I) complexes is supported by crystallography, spectroscopy, magnetism, and computations. The unprecedented stability of an iron sulfide complex in this oxidation state is enabled by steric contributions (bulky ligands that protect the Fe-S-Fe core) and electronic contributions (especially close interactions between cations and the anionic core).

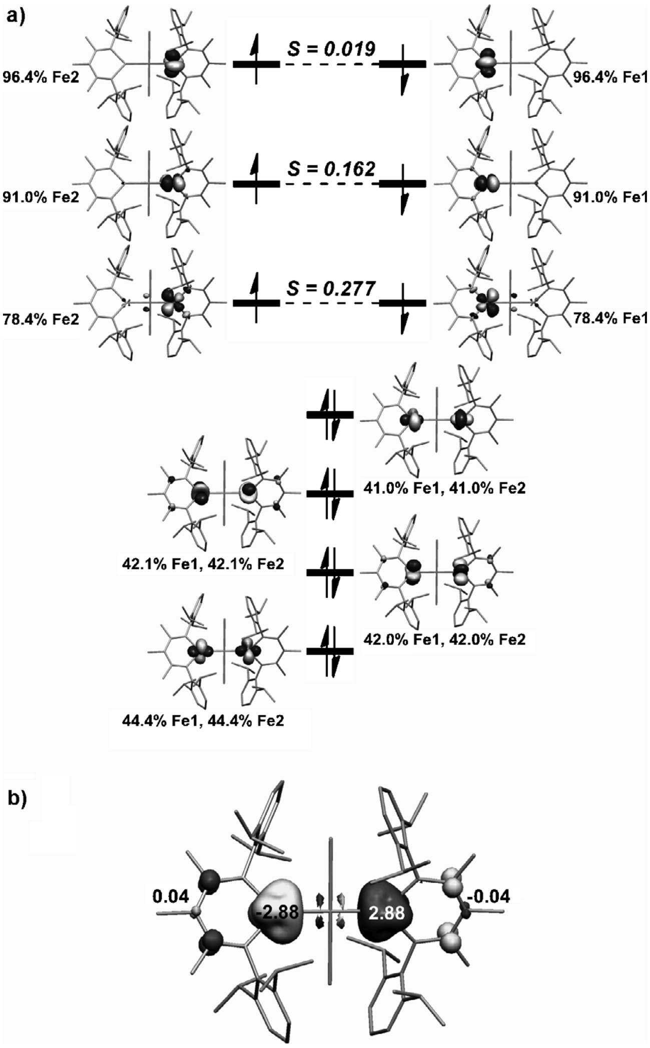

Figure 3. a) d orbitals from the computational model of **2-Me**. The Fe character is shown for each orbital, and the S values give the overlap between pairs of corresponding orbitals. This picture indicates two high-spin d^7 centers, with antiferromagnetic coupling mediated by sulfur p orbitals. b) Spin-density plot for **2-Me**; as there is little spin on the supporting ligands, they are redox-innocent.

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Iron–Sulfur Clusters

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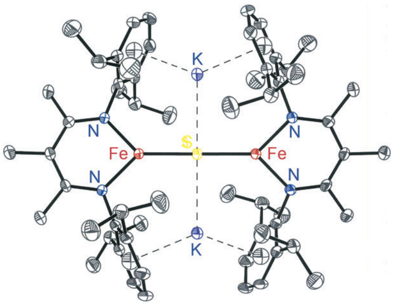
Isolation and Characterization of Stable Iron(I) Sulfide Complexes



The first examples of iron(I) sulfide complexes are presented, in contrast with the +2 and +3 oxidation states that are well-known in synthetic and biological systems. Spectroscopic and computational studies show a high-spin d^7 configuration at the metal. Alkali metal cations play a key role in supporting the unusually low oxidation state.