Low-Coordinate Metal Centers | Hot Paper

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Two-Coordinate Iron(I) Complex $[Fe\{N(SiMe_3)_2\}_2]^-$: Synthesis, Properties, and Redox Activity**

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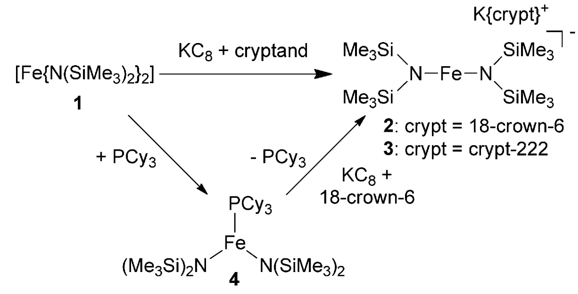
Abstract: *First-row two-coordinate complexes are attracting much interest. Herein, we report the high-yield isolation of the linear two-coordinate iron(I) complex salt $[K(L)][Fe\{N(SiMe_3)_2\}_2]$ (L = 18-crown-6 or crypt-222) through the reduction of either $[Fe\{N(SiMe_3)_2\}_2]$ or its three-coordinate phosphine adduct $[Fe\{N(SiMe_3)_2\}_2(PCy_3)]$. Detailed characterization is gained through X-ray diffraction, variable-temperature NMR spectroscopy, and magnetic susceptibility studies. One- and two-electron oxidation through reaction with I_2 is further found to afford the corresponding iodo iron(II) and diiodo iron(III) complexes.*

The replacement of noble-metal-based transformations by iron systems is currently under intense scrutiny.[1] It is thus desirable to expand the scope of well-defined and highly reactive iron complexes. The choice of a suitable metal precursor is a key parameter to induce a rich coordination chemistry. As a parallel to our extensive studies in ruthenium chemistry,[2] but keeping in mind the differences in redox properties within Group 8, we launched a program aimed at developing related iron species. The iron complex $[Fe\{N(SiMe_3)_2\}_2]$ (**1**)[3,4] was identified as a good precursor, since the amido ligands have been shown to be easily displaced. Moreover, first-row two-coordinate metal complexes represent a promising class of compounds for coordination chemistry. This field was recently reviewed by Philip Power.[5] In the case of iron, a number of two-coordinate iron(II) complexes have been synthesized, and it has been demonstrated that linear structures present very interesting magnetic properties.[6] Starting from a linear iron(II) precursor, Long et al. further disclosed the isolation of the first linear two-coordinate iron(I) complex salt $[K(crypt\text{-}222)][Fe\{C(SiMe_3)_3\}_2]$, featuring a $S = 3/2$ ground state, and exhibiting a record high barrier to magnetic relaxation of $226\ cm^{-1}$ under zero applied field.[7] Although complexes featuring an iron(I) oxidation state are often invoked in enzyme transformations and catalysis, their isolation and reactivity remain much less explored than for the more common iron(II) and iron(III) oxidation states.[8,9]

We found that addition of KC_8 to a diethylether solution of $[Fe\{N(SiMe_3)_2\}_2]$ (**1**) in the presence of the crown ether 18-crown-6 led to an immediate color change to an intense bronze color. After filtration, pentane layering of the solution afforded green crystals of $[K(18\text{-crown-}6)][Fe\{N(SiMe_3)_2\}_2]$ (**2**) in nearly quantitative yield (Scheme 1). Complex **2** is highly sensitive towards air or moisture, but is stable in the solid state at −30 °C for months under an inert atmosphere and can be prepared on a gram scale. The X-ray analysis of **2** (Figure 1) shows that the metal is located on an inversion center of symmetry, leading to a linear N-Fe-N arrangement



Scheme 1. Reduction of complexes **1** and **4** into complexes **2** and **3**.

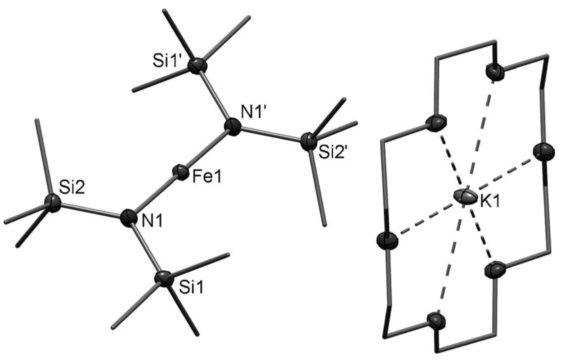


Figure 1. X-ray diffraction structure of compound **2**. All hydrogen atoms are omitted for clarity.

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with the two $N(SiMe_3)_2$ groups eclipsed, as found for the complex [K(crypt-222)][$Fe\{C(SiMe_3)_3\}_2$].[7a] The Fe–N bond length of 1.9213(6) Å is in the range of iron complexes with $Fe-N(SiMe_3)_2$ units. For comparison, the recently reported $[Fe\{N(Dipp)(SiMe_3)\}_2]^-$, shows a slightly bent structure (N-Fe-N angle of 172.65(6)°) and Fe–N bonds of approximately 1.91 Å.[8c] The potassium counter ion, trapped in the mean plane of the oxygen atoms of the crown ether, is separated from the metal center by 6.4566(2) Å. The shortest distance between two iron atoms in the lattice is 9.5765(2) Å. The same synthesis conducted with crypt-222 affords the corresponding complex salt [K(crypt-222)][$Fe\{N(SiMe_3)_2\}_2$] (**3**, Figure S28 in the Supporting Information), which has a similar linear structure and a comparable Fe–N distance (1.9219(17) Å), a longer Fe···K distance (7.4656(4) Å), as expected for the more encapsulating cryptand, and a slightly shorter Fe···Fe distance (8.8514(3) Å).

Most monomeric two-coordinate iron(II) complexes feature bulky ligands that prevent dimerization and reduce the reactivity towards Lewis bases.[10] However, complex **1**, a monomer in the gas phase and in toluene solution at room temperature, dimerizes easily at lower temperature (80% dimer at −40 °C). In the solid state, its dimeric structure with two bridging $N(SiMe_3)_2$ groups was demonstrated by X-ray diffraction.[3b] In addition, **1** reacts readily with various Lewis bases to form trigonal iron complexes.[3b,11] We thus attempted the reduction of the phosphine trigonal adduct [$Fe\{N(SiMe_3)_2\}_2(PCy_3)$] (**4**),[11c,12] and were pleased to see that upon reaction with KC_8 in the presence of 18-crown-6, complex **2** could also be isolated in good yield. The phosphine is released from **4** and the geometry of the iron center changes from trigonal to linear. No further reaction of **2** with PCy_3 (1–5 equiv) or $P(OEt)_3$ was observed. The strategy used to isolate compounds **2** and **3** is markedly different to the one used for the synthesis of the only other two-coordinate anionic iron(I) complexes reported to date, $[Fe\{C(SiMe_3)_3\}_2]^{-[7]}$ and $[Fe\{N(Dipp)(SiMe_3)\}_2]^-$.[8c] We show herein, that a two-coordinate geometry of the iron(II) precursor is not mandatory to isolate a two-coordinate iron(I) complex.

The solution-state characterization of compounds **2** and **3** was performed by ^1H NMR spectroscopy (Figure 2, and Figures S1,S2 and S9,S10). At 298 K, in [D_8]THF, the signals for the $SiMe_3$ groups resonate upfield, at around $\delta = -17.6$ ($w_{1/2} \approx 900$ Hz). The counterion signals are highly shifted, with one signal at $\delta = -1.5$ ppm ($w_{1/2} = 54$ Hz) for the crown-ether of **2** and three signals at $\delta = -0.84$ ppm ($w_{1/2} = 40$ Hz), −1.04 ppm ($w_{1/2} = 45$ Hz), and −1.50 ppm ($w_{1/2} = 30$ Hz) for crypt-222 of **3** (for comparison, standard values are around $\delta = 4.0$ ppm for 18-crown-6 and $\delta = = 2.5$–4.0 ppm for crypt-222).[13] Upon cooling to 178 K, the $SiMe_3$ proton signals of **2** and **3** significantly broadened and shifted to $\delta = -28$ ppm. The signals associated with the cryptands were also shifted by several ppm. Moreover, a splitting into two signals was observed for **2** at $\delta = -8.6$ ($w_{1/2} \approx 400$ Hz) and −12.3 ppm ($w_{1/2} \approx 800$ Hz) and into at least four signals between $\delta = -4$ and −9 ppm for **3**. The paramagnetic metal center has thus a strong influence on the protons of the cryptands. A differentiation of the protons is even observed, a phenomenon not, to our knowledge, reported to date for paramagnetic compounds.

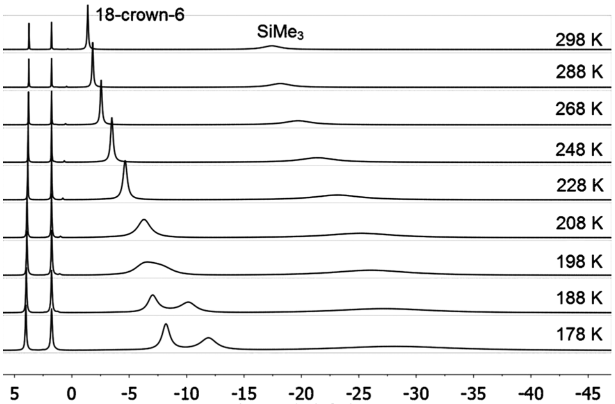


Figure 2. Variable-temperature NMR spectra of compound **2** in [D_8]THF (50 mM).

A cyclovoltammetric measurement of **2** in THF shows an irreversible oxidation event at −1.98 V (vs. Fc/Fc^+; Fc = [$(\eta\text{-}C_5H_5)_2Fe$]) comparable to the value of −1.82 V for [K(crypt-222)][$Fe\{C(SiMe_3)_3\}_2$], with the latter being a reversible event.[7a,14] Compound **2** was further characterized as containing an iron(I) center by ^{57}Fe Mössbauer spectroscopy. The spectra reveal at 4 K a sharp sextet with a fit yielding an internal field of $H_{int} = 55.85(3)$ T, an isomer shift of $\delta = 0.365(5)$ mm s^{-1}, and a quadrupole shift of $\varepsilon = -1.189(5)$ mm s^{-1} (Figure S7).[15] Upon increasing the temperature to 100 K, the sextet collapsed, whereas no absorption could be detected at room temperature, which may be due to decomposition. These data are similar to that reported for [K(crypt-222)][$Fe\{C(SiMe_3)_3\}_2$].[7a]

The determination of the magnetic moment by the Evans method gave at ambient temperature $\mu_{eff} = 5.12$ and 5.14 μ_B (3.28 and 3.30 cm^3 K mol^{-1}) for compounds **2** and **3**, respectively. Such values are significantly higher than the spin-only value expected for a high-spin Fe^+ ion ($S = 3/2$, $\mu_{S.O.} = 3.87$ μ_B) and close to the free ion value (d^7, 5.19 μ_B) indicating a large magnetic contribution from unquenched orbital angular momentum. As such contributions can lead to large magnetic anisotropy, we conducted further magnetic measurements. Variable-temperature dc magnetic susceptibility data were obtained under an applied field of 1 T.[16] The $\chi_M T$ values at room temperature, 3.89 and 3.78 cm^3 K mol^{-1} for compounds **2** and **3**, respectively, are significantly greater than the value of 1.875 cm^3 K mol^{-1} expected for an $S = 3/2$ system, in good agreement with the Evans measurements. Both complexes show a temperature dependence of $\chi_M T$ at low temperatures that is indicative of magnetic anisotropy. Below 6 K, there is a dramatic drop in $\chi_M T$, which can be a signature of magnetic blocking. However, performing field-cooled and zero-field-cooled dc susceptibility measurements at these temperatures did not show any magnetic blocking, in contrast to the case for [K(crypt-222)][$Fe\{C(SiMe_3)_3\}_2$].[7a]

Variable-frequency, variable-temperature ac magnetic susceptibility measurements were carried out to assess the magnetization dynamics of compounds **2** and **3**. Both compounds display peaks in the out-of-phase susceptibility

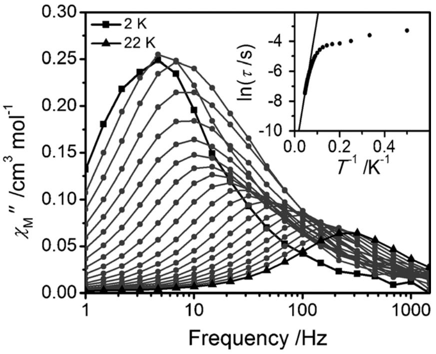
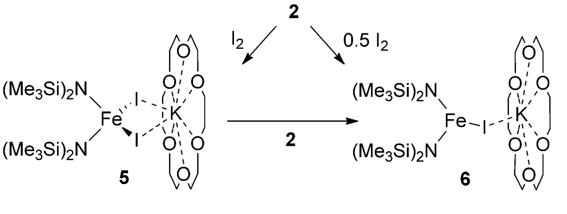


Figure 3. Out-of-phase (χ_M'') component from variable-temperature, variable frequency ac molar magnetic susceptibility measurements on **3** from 2 to 22 K (with intervals of 1 K) collected in the absence of an applied dc field. Inset: Arrhenius plot of the natural log of relaxation time versus inverse temperature.

(χ_M'') indicative of slow magnetic relaxation (Figure 3).[17] The data indicate effective barriers to magnetic relaxation of $U_{eff} = 43$ and 64 cm^{-1}, and attempt times of $\tau_0 = 4.9 \times 10^{-6}$ and 8.9×10^{-6} s for compounds **2** and **3**, respectively. The τ_0 values are slightly larger than what is normal for mononuclear single-molecule magnets (10^{-7}–10^{-10} s),[18] suggesting that through-barrier relaxation processes (e.g. Raman, quantum tunneling) may still be present.[19] The significantly smaller U_{eff} values for compounds **2** and **3** compared to [K{crypt-222}][Fe{C(SiMe$_3$)$_3$}$_2$] is related to the lower symmetry of the two-coordinate iron(I) complexes. This symmetry reduction and subsequent splitting of otherwise degenerate orbitals may quench orbital angular momentum, which in turn decreases magnetic anisotropy and accelerates magnetic relaxation.[6a,b]

The first two-coordinate iron(I) complex was reported in 2013,[7a] and the reactivity of this new class of compounds is virtually unexplored.[8a] Therefore, we started studying the behavior of compound **2** towards single- and double-electron transformations. Its reaction with 1 or 0.5 equivalents of I_2 at −30 °C afforded the compounds [K(18-crown-6)][Fe{N(SiMe$_3$)$_2$}$_2$I$_2$] (**5**) and [K(18-crown-6)][Fe{N(SiMe$_3$)$_2$}$_2$I] (**6**), respectively, which could be isolated in good yields (ca. 80 %) (Scheme 2). The structures of these compounds, as determined by X-ray diffraction analysis, show for **5** a distorted tetrahedral geometry, and for **6** a distorted trigonal-planar geometry (Figure S29 and S30). In both cases, the potassium counterion remains in the center of the crown ether, but interacts with the iodine ligands (I1···K1 = 3.9319(4) Å, I2···K1 = 3.6990(4) Å for **5**, and I1···K1 3.6212(2) Å for **6**). Determination of the magnetic moment and Mössbauer measurements support formulations as iron(III) and iron(II) species for **5** and **6**, respectively. The ^{1}H NMR spectrum of a [D$_8$]THF solution of complex **5** at room temperature exhibits one broad SiMe$_3$ signal at $\delta = 9$ ppm ($w_{1/2} = 710$ Hz) and one crown-ether signal as a sharp singlet at $\delta = 3.66$ ppm (Figure S18). In the case of **6**, the K(18-crown-6) signal appears at $\delta = 2.11$ ppm ($w_{1/2} = 18$ Hz) and the SiMe$_3$ groups resonate at $\delta = 1$ ppm ($w_{1/2} = 900$ Hz). Upon cooling to 178 K, the crown-ether signal in **6** is affected by the paramagnetic metal center (Figure S24) but to a much lesser extent than in compound **2**, whereas no significant shifting was observed in the case of **5**. Finally, it is worth noting that the iron(II) complex in **6** can be cleanly produced from the stoichiometric reaction of the iron(I) complex in **2** with the iron(III) complex in **5**.



Scheme 2. Oxidation of compounds **2** with I_2 into compounds **5** and **6**.

In conclusion, we have been able to isolate the linear iron(I) complex salts [K(L)][Fe{N(SiMe$_3$)$_2$}$_2$] (L = 18-crown-6 (**2**), crypt-222 (**3**)) featuring moderate bulky ligands by comparison to the very recently reported iron(I) compounds.[8] We show that the steric rules governing a two-coordinate geometry for iron(II) species are not mandatory in the case of anionic iron(I) compounds. Our alternative synthetic pathway from the phosphine complex [Fe{N(SiMe$_3$)$_2$}$_2$(PCy$_3$)] implies, upon reduction, a change of geometry from trigonal to linear with the concomitant release of the Lewis base. These findings broaden the scope of potential precursors for the design of attractive two-coordinate M(I) compounds. Compounds **2** and **3** exhibit single-molecule magnet (SMM) behavior. However, the observed U_{eff} relaxation barriers are smaller than that reported for [K(crypt-222)][Fe{C(SiMe$_3$)$_3$}$_2$] which may be explained by the lower symmetry. Our preliminary reactivity studies show an easy interplay between oxidation states involving iron(I), with controlled single and double oxidation processes. In addition, NMR spectroscopy allowed us to describe the strong influence of the paramagnetic iron center on the associated cryptands in compounds **2**, **3**, and **6**. Further experimental and computational work is underway to understand the differences in magnetic behavior, to evaluate the generality of our synthetic strategy in terms of first-row metals and ligand scope, as well as to study the reactivity of two-coordinate metal(I) species.

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Keywords: iron complexes · iron(I) · oxidation · single-molecule magnets · two-coordinate complexes

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[16] In the course of our study, we discovered that sample **2**, despite its isolation as large monocrystals showing good elemental analyses, could be contaminated by a non-molecular magnetic impurity. Multiple recrystallization steps were necessary to prevent this issue (see Supporting Information for more details).

[17] The frequencies, υ, of $\chi_{M''}$ peaks at a given temperature can be related to relaxation time, τ, by $\upsilon = (2\pi\tau)^{-1}$. If magnetic relaxation proceeds by thermal activation over a spin-reversal barrier, the magnetic relaxation times will follow an Arrhenius law and an effective barrier, U_{eff}, and attempt time, τ_0, can be extracted using $\tau = \tau_0 \exp(U_{\mathrm{eff}}/k_{\mathrm{B}}T)$ where k_{B} is the Boltzmann constant, see: R. L. Carlin *Magnetochemistry*, Springer, Amsterdam, **1986**. As can be seen in the Inset to Figure 3, the natural log of relaxation time does indeed exhibit a linear behavior versus inverse temperature at higher temperatures for compound **3** and a similar result is seen for **2** (Figure S15).

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[19] These through-barrier processes are certainly present at low temperatures, where relaxation time is largely temperature independent.[16,17] Considering these other active relaxation mechanisms, it is likely that the determined barriers are lower bounds for the true barriers.