Electronic Structure and Magnetic Anisotropy of an Unsatuated Cyclopentadienyl Iron(I) Complex with 15 Valence Electrons

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Dedicating to Professor Evamarie Hey-Hawkins on the occasion of her 60th birthday

Abstract: The 15 valence-electron iron(I) complex \([\text{Cp}^*\text{Fe}-(\text{IIiPr}_2\text{Me}_2)]\) \(1, \text{Cp}^* = C_5(H)\text{C}_5(\text{H})\text{C}_5(\text{H})\text{C}_5(\text{H})\text{C}_5(\text{H})\) was synthesized in high yield from the \(\text{Fe}^{II}\) precursor \([\text{Cp}^*\text{Fe}(\text{μ-Bri})]_2\). \(^{57}\text{Fe}\) Mössbauer and EPR spectroscopic data, magnetic measurements, and ab initio ligand-field calculations indicate an \(S = 3/2\) ground state with a large negative zero-field splitting. As a consequence, \(1\) features magnetic anisotropy with an effective spin-reversal barrier of \(U_{\text{eff}} \approx -64\, \text{cm}^{-1}\). Moreover, \(1\) catalyzes the dehydrogenation of \(N,N\text{-dimethylamine–borane}\), affording \(\text{tetramethyl-1,3-diaz}-2,4\text{-diboretan}\) under mild conditions.

Decades after cyclopentadienyl iron compounds entered the spotlight,[1,2] this extensive class of compounds continues to fascinate owing to new fundamental insight[3,4] and widening applications in catalysis and materials science.[5,6] Countless examples make use of ferrocene derivatives.[7]

Mononuclear cyclopentadienyl iron(I) compounds \([\text{CpFe}(\text{L})]\) \((\text{L}\) being a two-electron donor) are scarce.[8] One example is the \([\text{Cp}^*\text{Fe(dppe)}]\) radical \((\text{A}, \text{Cp}^* = \eta^5\text{C}_5\text{Me}_5, \text{dppe} = 1,2\text{-bis(diphenylphosphino)ethane})\); Figure 1.[9] While this complex is stable at room temperature as a monomer, related carbonyl complexes \([\text{Cp}^R\text{Fe(CO)}_2]_2\) \((\text{B}, \text{Cp}^R = \eta^5\text{C}_5\text{H}_5, \text{B} = \eta^5\text{C}_5\text{Me}_5)\) usually dimerize very rapidly to carbonyl-bridged complexes \([\text{Cp}^R\text{Fe(CO)}_2]_2\).[10,11] Monomer–dimer equilibria were observed even with rather bulky pentaaryl-substituted cyclopentadienyl ligands \([\text{Cp}^R = \eta^5\text{C}_5\text{Ph}_5, \eta^5\text{C}_5\text{Ph}_5(p\text{-tolyl}), \text{and } \eta^5\text{C}_5(H)\text{C}_5(\text{H})\text{C}_5(\text{H})\text{C}_5(\text{H})\text{C}_5(\text{H})\text{C}_5(\text{H})\)\).[10,12] The penta-isopropyl-substituted complex \([\text{Cp}^R(\text{IIiPr}_2\text{Me}_2)\text{Fe(CO)}_2]_2\) is a monomer in solution, but forms a carbonyl-bridged dimer in the solid state.[10]

Stable 15 valence electron (VE) iron(I) species of the type \([\text{Cp}^*\text{Fe}(\text{L})]\) appear to be unknown.[11] IR spectroscopic studies suggested the formation of a triply bonded species \(([\text{Cp}^*\text{Fe})\text{Fe} = \text{Fe(CO)}_2]_2\) by stepwise decarbonylation \([\text{Cp}^*\text{Fe} = \text{Fe(CO)}_2]_2\) in a 3-methylpentane matrix at 98 K,[13] while prolonged heating of \([\text{Cp}^*\text{Fe} = \text{Fe(CO)}_2]_2\) in xylene led to the tetrahedral cluster \([\text{Cp}^*\text{Fe} = \text{Fe(CO)}_2]_4\).[14] Herein, we report the synthesis of a 15 VE cyclopentadienyl iron(I) complex \([\text{Cp}^*\text{Fe} = \text{IIiPr}_2\text{Me}_2]_2\) \((\text{I}, \text{IIiPr}_2\text{Me}_2 = 1,3\text{-disopropyl-4,5-dimethylimidazol}-2\text{-ylidene})\). Spectroscopic studies, magnetic measurements, and quantum-chemical calculations revealed...
a pronounced magnetic anisotropy for 1, a property required for single-molecule magnets (SMMs). [17–19]

Complex 1 was isolated in 78% yield by reducing [Cp*FeBr(IPrMe2)] (2), which had been prepared in situ from [Cp*Fe(μ-Br)]3, [3, Cp* = C5(C5H4-4-Et)5] and IPrMe2 (Scheme 1), with potassium graphite in benzene over two days. [20] Broad 1H NMR resonances were observed in CD8 solution between −36 and 61 ppm (Figure S1 in the Supporting Information). Single-crystal X-ray diffraction revealed the slightly bent “pogo-stick” structure of 1 (Figure 1) with an η1-coordinated CpFe ligand and CpFe(centroid)-C carbene angles of 162.11(8)° and 171.19(8)° for two crystallographically independent molecules in the unit cell. The Fe-Cpe(centroid) distance [1.851(1) and 1.847(1) Å] is shorter than in 2 [2.038(1) and 2.020(1) Å for two crystallographically independent molecules]. The Fe–C carbene bonds (1.992(2) and 1.996(2) Å) are similar in length to the Fe–C carbene bond of 2.014(2) Å for two-coordinate [(IPr)Fe{(3)SiMe3}Dipp)] (Dipp = C5H4-2,6-iPr) [21] and the Fe–C carbene bond of 2.110(3) and 2.128(3) Å observed for FeII complex 2. Dark-yellow 1 is paramagnetic, thermally stable, and air-sensitive as a solid. A magnetic moment of μeff = 5.4(1) μB was determined in C6D6 solution using the Evans method.

Linear two-coordinate FeII (d5) and FeI (d6) complexes possess η6 and η5 electronic ground states and therefore have unquenched orbital moments. [22–27] Spin–orbit coupling leads to orbital moment contributions to the S = 2 and S = 3/2 spins. Therefore, some orientations of the magnetic moment will be strongly preferred (magnetic anisotropy). We were keen to study how the unsymmetric structure that arises from the specific ligand set of 1 affects the electronic structure and the magnetic behavior.

Temperature-dependent magnetic susceptibility and variable-temperature/variable-field (VT/VH) magnetization measurements (Figure S12) support an S = 3/2 spin ground state, with best fits values of g∥ = g⊥ = 2.18, g∥ = 2.52, D = −33.4 cm−1, and E(D) = 0. The large negative zero-field splitting parameter D indicates that at low temperatures, only the Kramers doublet with m∥ = ± 3/2 is populated, which is a prerequisite for FeI-based SMMs.

A first indication for the SMM-type behavior of 1 came from Mössbauer spectra (Figure S16), which are in line with a large unquenched orbital magnetic moment at low temperature. The spectrum at 80 K is unsymmetrically broadened, indicating the onset of slow paramagnetic relaxation on the Mössbauer time scale (ca. 10−5 s). [28] At 7 K, this leads to a sharp octet, which could be simulated with a spin Hamiltonian calculation for an effective spin of S = 3/2 and a uniaxial internal magnetic field on the iron nucleus of Hint = 16.1 T.

Alternating current (AC) magnetic susceptibility measurements in the absence of a direct current (DC) magnetic field (Figure S13) revealed a characteristic out-of-phase signal even though the characteristic maxima in the imaginary part (χ″) were not observed, which is presumably due to barrierless quantum tunneling of magnetization enabled by the bent structure of 1. The application of DC fields of ≥1000 Oe (Figure S14), which suppress quantum tunneling, led to the clear observation of frequency-dependent maxima of χ″ (Figure 2). Analysis of the temperature-dependent χ″ data (Figure S15) taking into account Raman and Orbach relaxation mechanisms [42] revealed an energy barrier of Ueff = 63.6 cm−1 and a characteristic relaxation time of τ0 = 6.8 × 10−18 s. The calculated Ueff parameter (63.6 cm−1) is in good agreement with the value estimated from DC susceptibility measurements (|2D| = 67 cm−1).

To probe the electronic structure and the magnetic properties of 1, we carried out complete active space self-consistent field (CASSCF) and n electron valence state perturbation theory to second order (NEVPT2) calculations on the crystallographically determined molecular structure (see the Supporting Information). By using the recently developed ab initio ligand field theory (AILFT), [29] the Racah parameters B and C and the spin–orbit coupling parameter ζ were calculated. The CpFe and N-heterocyclic carbene (NHC) donors and the considerable tilting of the cyclopentadienyl ligand (Cp–Fe–C angle 166.8°) lead to a modification of the electronic structure (Figure 3a) compared with an ideal linear MX3 complex:

i) The NHC ligand features out-of-plane electrons that are available for π-bonding but no such electrons in the ligand plane. This π-anisotropy leads to a splitting of the dπ, dπ, orbital pair, which would otherwise be degenerate.

ii) Bending of the Cp–Fe–C vector from linearity induces a splitting of the 3dπ, 3dπ, orbitals parallel owing to indirect (via their mixing with 3dπ, 3dπ, 3dπ, 3dπ, 3dπ, 3dπ, 3dπ, 3dπ), which becomes non-zero for C–Fe–C deviating from linearity.
This is due to metal–ligand signal should depend only Kramers D 2017 following-CT and the tetrahedral complex of m and [Fe = = impurity (y expected g g = j S in 1 = < 4 (see the Supporting Information). The orbitals dₓ and dᵧ which are singly occupied in both states, were computed at 1979 cm⁻¹ and are not shown.

iii) Large 3d–4s mixing is evident from the very low energy of the MO of dₓ character. This is due to metal–ligand interactions, which place this MO just above the 3dᵧ, MO.

iv) The low symmetry induces extensive 3d MO mixing.

Taken together, these effects (i–iv) lead to an unusual configuration of the 3d orbitals in the (non-relativistic, spin-free) ground state. In addition, interelectronic repulsion energetically favors a non-aufbau electron distribution in the ground state as shown in Figure 3b for complex 1 following the holohedral symmetry Cᵥᵥ (see the Supporting Information for details regarding the procedure). The aufbau occupation dₓ, dᵧ, d₉, dₓ, dᵧ, d₉ corresponds to an excited state that is disfavored in energy by 12.8 = 8664 cm⁻¹ (B = 722 cm⁻¹) with respect to the 4Δ ground state. This large energy by far exceeds the dₓ−dᵧ−d₉ orbital energy difference of Δₓ = 751 cm⁻¹.

The S = 3/2 ground state additionally splits into two separate Kramers doublets, |mₓ| = ±1/2 and |±3/2), through spin–orbit coupling. The |mₓ| = ±3/2) Kramers doublet is the magnetic ground state owing to the negative zero-field splitting parameters D = −42 cm⁻¹ and E = −0.50 cm⁻¹. The experimental value (D = −33.4 cm⁻¹, see above) is somewhat smaller, presumably owing to vibronic coupling. Large orbital contributions to the effective magnetic moment are apparent from the calculated effective g-tensor values with dominant axial (Ising-type) anisotropy for the ground-state Kramers doublet (gₓ, gᵧ, g₉ = 8.362, 0.075, 0.075) and easy plane anisotropy for the excited Kramers doublet (gₓ, gᵧ, g₉ = 2.955, 4.056, 4.182). These can be compared with the computed intrinsic spin Hamiltonian values of gₓ, gᵧ, g₉ = 2.802, 2.080, 2.067.

The results of the calculations are consistent with our EPR spectroscopic data for 1. The Δmₓ = 3 transition within the magnetic |mₓ| = ±3/2) ground-state doublet is formally forbidden, and hence associated with a very weak EPR signal intensity. Accordingly, X-band EPR measurements at 30 K using a microwave power of about 1 mW merely showed the signals of a minor S = 1/2 impurity (< 0.1% of the total Fe concentration according to spin integration measurements, see Figure S17). Only in spectra recorded with a higher microwave power (200 mW) and at a lower temperature (8 K), a derivative signal consisting of a single, relatively sharp low-field peak at g_eff = 7.76 became visible (Figure S18), which corresponds to the main S = 3/2 species. This signal can be assigned to the resonance stemming from the z-component of the very anisotropic g_eff = ±3/2) tensor of the ±3/2) Kramers doublet. With a sufficiently large zero-field splitting relative to the microwave energy (hν ≈ 0.3 cm⁻¹ for X-band), the effective g-value (g_eff) of the g_eff = ±3/2) signal should depend only on the rhombicity parameter E/D and the real g-value of the S = 3/2 species.⁴⁰ The deviation of the measured effective g-value from the expected value of six thus shows that the g-tensor of the S = 3/2 system indeed has a z-component that is significantly larger than two. Based on the near-zero rhombicity parameter (E/D ≈ 0) found by the magnetic measurements and the calculations, a reasonable value of g_eff ≈ 2.55 can be estimated from spectral simulations, thus reproducing the position of the experimentally observed EPR signal at g_eff = 7.76. This value compares well with the value of g_eff = 2.6 reported for [(nacnac)Fe⁵(AdNNNA)⁴] [nacnac = HC-(C(Me)N(C₆H₄-2,6-Pr₂)]), which also has an S = 3/2 ground state with a large negative zero-field splitting, D < 0.⁴⁰

The SMM-type behavior of 1 is unusual given the unsymmetric, non-linear molecular structure.¹⁷,²¹–²⁷ Several linear Fe⁴ and Fe³ complexes have been reported to feature large unquenched orbital contributions to the magnetic moment.²¹⁻²⁷,²⁹⁻₃¹,³⁴⁻⁴⁷ A few of these have SMM properties. For example, the Fe³ complex [(C₆H₄Pr₃)Fe(C₆H₄-2,6-Pr₂)], which has a linear structure, does not show slow magnetic relaxation in the absence of an applied field owing to fast quantum tunneling of magnetization,⁴⁵ but a spin-reversal barrier of U_eff = 28.1 cm⁻¹ was determined in a DC field of 750 Oe. Similar spin-reversal barriers were determined for linear Fe⁴ species, for example, [K(L)][Fe⁴[N(SiMe₃)₃]₂] (L = [18]crown-6 and [2.2.2.]crypt, U_eff = 43 and 64 cm⁻¹);³⁵ trigonal-planar [(CAAC)₂FeĈ] (U_eff = 22.4 cm⁻¹);³⁴ [Fe⁴[N-SiMe₃]₃(PCy)₂] (26.3 cm⁻¹);³² and the tetrahedral complex [(PnP)Fe⁴Cl₄] (PnP = N[2-P(CHMe₃)₂] 4-methylphenyl)]. U_eff = 32–26 cm⁻¹.²⁸ Significantly, the highest spin-reversal barrier reported for any Fe-based SMM was observed for [K(crypt-222)][Fe⁴(C₅SiMe₃)₂] (D, U_eff = 264 cm⁻¹), which has axial Dₓ symmetry and a ¹E ground state.⁴⁰ As a consequence, D shows magnetic hysteresis and blocking of the magnetization at temperatures below 4.5 K.

Why is the spin-reversal barrier in 1 smaller than that in D? To address this question, we performed calculations on the model complex [Fe₄(CH₃)₆] (see the Supporting Information), which has a Dₓ symmetric structure. Compared to 1, D has higher ground-state anisotropy (g_eff = 10 in [Fe₄(CH₃)₆]) and a larger energy separation between the ground and the lowest excited Kramers doublet (224 cm⁻¹ in [Fe₄(CH₃)₆]), 84 cm⁻¹ in 1). However, the most striking difference is the direct relaxation pathway predicted to be available in 1. As shown by Figure 4, the transitions from the ground state to the excited states are accompanied by sizable horizontal pathways (usually referred to as quantum tunnel-
In summary, we have synthesized the first 15 VE cyclopentadienyl iron(I) complex 1, which is a rare organometallic iron complex with a heteroeliptic structure and the properties of a single-molecule magnet.\textsuperscript{17,18} The basis for the SMM behavior is the unusual electronic structure, where extensive metal–ligand interactions and 3d–4s mixing that are due to the bent structure produce a nearly orbitally degenerate ground state. As a consequence, 1 shows slow relaxation of the magnetization in the presence and even in the absence of an external magnetic field. Furthermore, 1 catalyzes dimethylamine–borane dehydrogenation, a reaction for which only a few other iron catalysts are known.\textsuperscript{19–48} This initial result bodes well for the future development of further synthetic and catalytic applications of 1 and related cyclopentadienyl iron(I) complexes.

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Conflict of interest

The authors declare no conflict of interest.

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indicating the high sensitivity of the


