A high-spin square-planar Fe(II) complex stabilized by a trianionic pincer-type ligand and conclusive evidence for retention of geometry and spin state in solution†

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Square-planar high-spin Fe(II) molecular compounds are rare and the only three non-macrocyclic or sterically-driven examples reported share a common FeO₄ core. Using an easily modifiable pincer-type ligand, the successful synthesis of the first compound of this type that breaks the FeO₄ motif was achieved. In addition, we present the first evidence that geometry and spin state persist in solution. Extensive characterization includes the first high-field EPR and variable field/temperature Mössbauer spectra for this class of compounds. Analysis of the spectroscopic data indicates this complex exhibits a large and positive zero-field splitting tensor. Furthermore, the unusually small ΔE₀ value determined for this compound is rationalized on the basis of DFT calculations.

Chemistry students learn that inorganic complexes adopt predictable geometries and electronic structures depending on the identity of the ligands, the metal ion, and its oxidation state. Examples of inorganic dogma are ubiquitous d⁸ square-planar Pd(II) and Pt(II) complexes that are predictably low-spin, unusual geometries and electronic structures is important to stimulate curiosity. Convincing metal ions to adopt metals.

Extended [2,3] that are most informative and stimulate curiosity. Convincing metal ions to adopt unusual geometries and electronic structures is important to realizing new chemistry. More specifically, it is appealing to expand the scope of iron chemistry because of its low toxicity, abundance, and therefore low cost relative to the noble metals. In particular, square-planar Fe(II) complexes are abundant and virtually all adopt an S = 1 intermediate-spin state; classic examples are Fe(II) porphyrins. Gillespie (BaFeSi₄O₁₆), a mineral discovered in 1922, deviates from this norm and contains Fe(II) in a square-planar geometry with a high-spin S = 2 state; though the geometry may be due to constraint within the crystal lattice rather than an inherent electronic stabilization. The conditions that promote a high-spin square-planar geometry are: (1) charge from anionic ligands to prevent higher coordination numbers, (2) alkali metal counter cations to stabilize the anionic charge, (3) strong π-donor ligands to destabilize the sterically preferred tetrahedral geometry, and (4) weak σ-donating ligands to minimize the anti-bonding character of the dₓ²−y²/C₀z² field splitting tensor. Furthermore, the unusually small ΔE₀ value determined for this compound is rationalized on the basis of DFT calculations.

† Electronic supplementary information (ESI) available: Detailed experimental conditions, elemental analysis, ¹H-NMR spectroscopy, magnetic susceptibility data and fitting, Mössbauer spectroscopy, high-field EPR spectroscopy of 2, and DFT calculations. CCDC 1006581. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4sc02634a
the first evidence that the geometry and spin state are retained in solution, highlighting that the stability of this compound is driven by electronic factors rather than constraints from the crystal lattice.

A striking feature common to the previously reported molecular species and Gillespie is the FeO₆ core. An important advance is to employ alternative donor motifs and to install a site for functionalization. Pincer ligands provide a convenient starting point for expanding square-planar $S = 2$ Fe(II) complexes beyond the FeO₆ unit. In particular, trionic pincer ligands⁷ provide the requisite anionic charge to maintain a low coordination number and are easily modified. The tunability of trionic pincer ligands opens the possibility of selectively accessing the $S = 1$ and $S = 2$ states for potential application as spin-crossover materials.⁸

Our group recently reported the trionic pincer-type ligand precursor 2,2′-(azanediylbis(2,1-phenylene))bis[1,1,1,3,3,3-hexafluoropropan-2-ol] ([(CF₃ONO)H₃ 1]) and its coordination chemistry with W(VI) and Ta(V).⁹ Deprotonation of 1 using 3 equivalents of Li[N(SiMe)₃]₂ in THF, followed by subsequent addition to a slurry of FeCl₃(THF)₃⁹ in THF results in an immediate color change from yellow to brown. Stirring the reaction mixture for 3 h, and removing all volatiles provides 2 as an analytically pure brown microcrystalline powder in 43.6% yield (Scheme 1).

Dissolving 2 in diethyl ether and cooling to $-35$ °C produces red crystals suitable for single crystal X-ray diffraction analysis. Fig. 1 depicts the molecular structure of 2. In the solid state, the molecule is pseudo-$C₂$-symmetric (disregarding solvent molecules bound to the Li⁺ counterions) and features an Fe(II) center in a square-planar environment consisting of the [CF₃ONO]⁻⁻ pincer-type ligand and a chloride. The complex is disordered in the lattice and was refined in two parts (A and B) with site occupation factors of 0.742(1) and 0.258(1). Both partitions are similar, but the less populated conformation distorts from an ideal square-plane, as revealed by the larger $\tau_4$ value (0.056 vs. 0.115). The $\tau_4$ parameter is an index of the distortion from a square-planar ($\tau_4 = 0$) to a tetrahedral geometry ($\tau_4 = 1$), thus the slightly higher value of 0.115 is still representative of a square-plane. These $\tau_4$ values are comparable to the other three reported examples (0.0–0.214).¹²–¹⁴ The [CF₃ONO]⁻⁻ pincer O–Fe–O bite angles of 176.34(7)° (A) and 168.83(11)° (B) are nearly linear and much larger than observed within known Ta(V) (155.79(9)°–164.70(7)°)¹⁸ and W(VI) (147.39(8)°–147.80(7)°) complexes,¹⁰ highlighting that the preference for a square-planar geometry is not enforced solely by the ligand.

Scheme 1 Synthesis of the square-planar $S = 2$ complex 2. Sv: THF, Et₂O

Fe1–Cl1 distances of 2.3888(9) Å (A) and 2.338(3) Å (B) are longer than those typically observed for four-coordinate Fe(II) complexes,¹²–¹⁶ mainly due to the strong trans influence of the amido N-atom of the pincer (N1–Fe1 = 1.9704(19) Å (A) and 1.960(2) Å (B)). For partition A, the Fe1–O1 and Fe1–O2 distances of 1.9261(19) Å and 2.0174(18) Å fall within the range reported for the three molecular Fe(II) $S = 2$ square-planar compounds (1.959(2)–2.0275(19) Å).¹⁴ In contrast, the Fe–O bond lengths in B are just outside this range: 2.113(2) Å and 1.848(2) Å, respectively.

DFT calculations of 2 at the B3LYP/LANL2DZ level of theory¹⁷,¹⁸ yield bond lengths that differ by less than 0.05 Å with respect to the X-ray structure, except for the 0.16 Å longer Fe1–Cl1 bond. Calculations using a different basis set (6-311G) also result in an overly elongated Fe1–Cl1 bond. Removing the solvent molecules from the calculation causes even further elongation of this bond (0.38 Å) and removing the Li⁺ counterions results in a large distortion towards a tetrahedral geometry ($\tau_4 = 0.657$). Interestingly, coplanar alkali counterions are also present in the molecular structures of the previously reported compounds and are clearly important in stabilizing the square-planar geometry.¹²–¹⁴ However, examples of tetrahedral Fe(II) complexes with closely bound Li atoms are known²⁹,³⁰ and imply that the presence of alkali counterions alone do not impose the square-planar geometry.

SQUID measurements of microcrystalline brown 2 (Fig. 2) reveal a room temperature $\chi_MT$ value of 3.16 cm$^3$ K mol$^{-1}$,
which confirms its $S = 2$ state. The room temperature value is higher than the spin only ($g = 2$) value of 3.00 cm$^3$ K mol$^{-1}$ expected for a high-spin complex due to spin–orbit coupling. The $\chi_M T$ value steadily decreases with decreasing temperature, reaching 1.25 cm$^3$ K mol$^{-1}$ at 5 K. A good fit to the susceptibility data in the 300–5 K range can be obtained with $|D| = 20.9(4)$ cm$^{-1}$, $g = 2.05(3)$, $\Theta = 0.8$ K, and no TIP term using eqn (S1) (see ESI†). The fitting parameters are similar to those reported by Doerr and coworkers. The room temperature magnetic susceptibility value is also consistent with the solution value of 3.01 cm$^3$ K mol$^{-1}$. SQUID measurements performed on recrystallized red 2 reflect the two partitions within the crystal lattice and a reasonable fit was accomplished, see ESI† for more details.

High-field, high-frequency EPR measurements on powder samples establish the magnitude of both the zero-field splitting (ZFS) and the $g$ tensor of the quintet ground state of 2. Fig. 3 exhibits two representative 5 K EPR spectra recorded for 2 at 416.0 (top) and 203.2 GHz (bottom). The entire data set is summarized in Fig. 4 and was analysed in the framework of a standard $S = 2$ spin-Hamiltonian (see ESI eqn (S3)†). By using $g_x = 2.19$, $g_y = 2.18$, $g_z = 2.04$, $D = 17.4$ cm$^{-1}$ and $E/D = 0.14$ it is possible to not only simulate the individual spectra (Fig. 3), but also reproduce the field and frequency-dependent behaviour of the observed resonances (Fig. 4). In agreement with the results of the crystallographic investigation and of the Mössbauer data analysis the EPR spectra recorded on samples of recrystallized 2 as ground red crystals exhibit two distinct spectral components. While one of the components is essentially identical to that observed for microcrystalline brown 2 the other exhibits a more complicated behaviour, see ESI†.

Fig. 3. High-field EPR spectra recorded at 5 K for 2 brown, at 416.0 (top) and 203.2 GHz (bottom). The solid red traces are simulations obtained for a $S = 2$ with $D = 17.4$ cm$^{-1}$, $E/D = 0.14$, $g_x = 2.19$, $g_y = 2.18$ and $g_z = 2.04$. The features marked by (+) account for the molecular O$_2$(g) adsorbed on the surface of the sample containers. The resonance marked by (*) appears at $g = 2.0023$ and arises from a radical contaminant.

Fig. 4. Black dots mark the field and frequency dependencies of the prominent resonances observed for the low-temperature, high-field EPR spectra of microcrystalline brown 2. The solid lines account for the ground state resonances and the dotted lines account for the excited state resonances. The red, blue and green colors mark the $z$, $y$ and $x$ molecular orientations, respectively.

Fig. 5. Field and temperature dependent $^{57}$Fe Mössbauer spectra recorded for 2 brown. The red solid lines are spectral simulations obtained for a $S = 2$ using eqn (S5).† For these simulations we used the ZFS and $g$ tensors determined from high-field EPR and $A_x/g_x \beta_\mu = -17(1) \text{T}$, $A_y/g_x \beta_\mu = -13(1) \text{T}$, $A_z/g_x \beta_\mu = -30(2) \text{T}$, $\delta = 0.82$ mm s$^{-1}$, $\Delta E_G = -0.45$ mm s$^{-1}$, $\eta = 0.62(2)$, $\alpha_{EFG} = 0^\circ$, $\beta_{EFG} = 90^\circ$, $\gamma = 90^\circ$, see ESI†.
At 4.2 K, the zero-field Mössbauer spectrum of 2 consist of a sharp quadrupole doublet with an isomer shift $\delta = 0.83(1)$ mm s$^{-1}$ and quadrupole splitting $\Delta E_Q = \pm 0.45(1)$ mm s$^{-1}$ (Fig. 5). While the observed $\delta$ is typical of high-spin Fe$^{II}$ ions, the $\Delta E_Q$ is unusually small. Interestingly, this low value is similar to the only other reported data for a square-planar high-spin Fe$^{II}$ species. We propose that this unusually small $\Delta E_Q$ is a signature of this class of compounds. The DFT-predicted values at the UB3LYP/6-311G level of theory, $\delta^{\text{DFT}} = 0.67$ mm s$^{-1}$ and $\Delta E_Q^{\text{DFT}} = -0.55$ mm s$^{-1}$, are in good agreement with the experimental data. Furthermore, the small quadrupole splitting can be rationalized on the basis of a large ligand contribution to the electric field gradient (EFG) that essentially quenches the large valence contribution expected for a $d^6$ electron configuration (see Table S8†). Interestingly, this result is a consequence of fitting a high-spin ferrous ion with a doubly occupied $d_z^2$ orbital ground state in a square-planar coordination geometry (Fig. 6).\textsuperscript{21}

The uniquely small $\Delta E_Q$ offers an opportunity to examine if the square-planar geometry and spin state are retained in solution. Indeed, the zero-field spectrum recorded at 4.2 K for a $^{57}$Fe enriched toluene solution of 2 exhibits two distinct quadrupole doublets (Fig. 7). More than 70% of the iron exhibits a quadrupole doublet that is essentially identical to that observed for 2 in the solid state. The remaining iron amount can be assigned to a high-spin ferrous species that in 0 T displays a broad quadrupole doublet characterized by $\delta = 1.1(1)$ mm s$^{-1}$, $\Delta E_Q = 2.9(1)$ mm s$^{-1}$, and $I = 0.6$ mm s$^{-1}$. The second species is tentatively assigned as an Fe(u) five-coordinate complex in which residual THF binds to the Fe center in solution. Support for this assignment comes from the fact that purposely increasing the amount of THF shifts the ratio of the two species. Consequently, this observation suggests that dissolving 2 in toluene does not lead to a loss of the square-planar geometry and that the electronic structure of the iron site is conserved.

Analysis of the variable-field, variable-temperature Mössbauer spectra recorded for 2 reveals the presence of an anisotropic $^{57}$Fe hyperfine coupling tensor $A$ that exhibits two relatively small components. Furthermore, investigation of the high-field, high-temperature data indicate that $\Delta E_Q < 0$ and that the EFG asymmetry parameter $\eta \approx 0.6$ (see ESI†). The $A_z$, ZFS, and $g$ tensors are overall consistent and suggest the presence of two large, spin–orbit coupling induced, orbital contributions along their $x$ and $y$ directions.

The field-dependent spectra recorded for recrystallized 2 as red crystals exhibit two distinct spectral components. While one component is identical to 2 prior to recrystallization, the other can be understood only by considering axial ZFS and $A$ tensors ($E \equiv 0; A_x \approx A_y \approx A_z$). Since in zero-field these two components exhibit identical quadrupole doublets they must originate from two distinct conformation of the same chemical species.\textsuperscript{22} Typically, an axial ZFS tensor entails a symmetric structure and thus we speculate that while the $E \equiv 0$ component is associated with partition A, the $E/D = 0.14$ component of 2 is associated with partition B of the crystal structure. We propose the two partitions arise from variable solvent (THF/Et$_2$O) substitution at each Li$^+$ site within the lattice.

**Conclusions**

This work extends the set of known Fe(u) square-planar high-spin compounds beyond the limited FeO$_4$ motif, and presents the first high-field EPR and variable field/temperature Mössbauer characterization of this class of compounds. Moreover, the $^{57}$Fe enriched solution phase Mössbauer confirms for the first time that the square-planar geometry is retained in solution. The results also indicate ligand 1 satisfies the prerequisites for stabilizing a square-planar high-spin Fe(u): (1) it provides three negatively charged donors, (2) it preferentially
binds three meridional positions, (3) the amido and alkoxides are weak-field ligands that provide π-donation, and (4) the heavily fluorinated alkoxides are relatively weak σ-donors. We are currently analyzing approaches to modify the ligand to optimize the energy difference between the \( S = 2 \) and \( S = 1 \) states to prepare and isolate molecular spin crossover complexes.

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Notes and references