Supplementary Information

Coordination Equilibria Between Seven- and Five-coordinate Iron(II) Complexes

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General

Manipulations of moisture- and oxygen-sensitive compounds were carried out under an inert atmosphere, on a vacuum line, using standard Schlenk or cannula techniques. Additionally, conventional nitrogen atmosphere glove boxes were used for the preparation of analytical and spectroscopic samples, as well as for the weighing and storage of air and moisture sensitive compounds.

¹H-, ¹⁹F-, ¹³C-, and 2D-NMR spectra were recorded using AC-400 MHz, DRX-400 MHz and AM-500 MHz spectrometers. Variable temperature (VT) ¹H- and ¹⁹F-NMR spectra were recorded using the DRX-400 MHz spectrometer. The ¹H- and ¹³C-NMR chemical shifts are indicated in parts per million (ppm) relative to the residual protio impurity of the deuterated solvent and ¹³C-NMR signal of the deuterated solvent, respectively. The ¹³C-NMR spectra were recorded with proton decoupling. ¹⁹F-NMR chemical shifts are referenced externally to CFCl₃ at 0 ppm. Coupling constants *J* are given in Hertz. The following abbreviations have been used to describe the multiplicites of the NMR signals: s (singlet), d (doublet), t (triplet), dd (double doublet), dt (double triplet), br (broad signal) and m (multiplet).

UV/Vis spectra were recorded using a Perkin-Elmer Lambda 20 spectrometer, which was equipped with a cryostat CoolSpeK UV USP-203-A from Unisoku Scientific Instruments to

record the UV/Vis spectra at different temperatures. The solutions had a concentration of 2-3 mM, either in acetonitrile of 1,2-dichloroethane and were recorded in the temperature range of 233 - 323 K and 233 - 333 K, respectively. The quartz cuvette used has a 1 mm path length and the data obtained were corrected for the change in density dependent on the temperature for the two solvents used. After the cuvette was inserted into the cryostat at room temperature, the cryostat was cooled to the lowest measured temperature (233 K) while a slow flow of nitrogen was passed through the instrument. Once the temperature was reached the system was kept at this temperature for 30 minutes until the first measurement was taken. Next, the temperature was increased at 10 K intervals and the system was cooled to room temperature, the cell taken out the cryostat and the nitrogen flow stopped.

Mass spectra were recorded by Mr. J. Barton at Imperial College London using either a VG Autospec or a VG Platform II spectrometer. Different methods such as electrospray (ESI), electron impact ionisation (EI) or liquid secondary ion mass spectrometry (LSIMS) were applied depending on the compound.

Element analyses were performed by Mr. S. Boyer at the London Metropolitan University.

X-ray diffraction analyses were carried out and solved by Dr. A. White at Imperial College London.

Magnetic susceptibilities in CD₃CN solutions were determined by the Evans' NMR Method.¹⁻ ⁵ A small quantity of complex (3-5 mg) was dissolved in deuterated acetonitrile (containing 5% v/v TMS), and the resulting solution placed in a stem coaxial insert - WGS-5BL. This insert was placed in a conventional NMR tube filled with the TMS/acetonitrile solution. A ¹H NMR spectrum was recorded at ambient temperature or, for VT measurements, at different set temperatures. Corrections for the change in solvent density with temperature were applied according to the data provided for CH₃CN,⁶ and an additional factor (0.844/0.786) was applied for the difference between the densities of CD₃CN (δ = 0.844 g/mL at 298 K) and CH₃CN (δ = 0.786 g/mL at 298 K). The chemical shift difference (Δf) in Hz for the tetramethylsilane protons between the inner and outer tubes was used to calculate the magnetic susceptibility, χ_m , according to eq. 1. The difference between the chemical shift of the reference compound in the inner and outer tubes is caused by the *pseudo*-contact shift interaction with the unpaired electrons at the metal centre. The effective magnetic moment is then determined by using eq. 2.

$$\chi_M = \frac{3\Delta f}{1000 f c} \tag{S1}$$

where,

 χ_M = molar susceptibility (m³/ mol) Δf = chemical shift difference (Hz) f = operating frequency of the spectrometer (Hz) c = concentration of the solution of complex (mol/ L)

The molar susceptibility of the complex is required to calculate the magnetic moment (μ_{eff}) of the metal centre in a complex, as described in eq. 5.

$$\mu_{eff} = \sqrt{\frac{3kT\chi_M}{N_A\mu_0\mu_B^2}} = 798\sqrt{T\chi_M}$$
(S2)

where,

 $\mu_{eff} = \text{effective magnetic moment (BM)}$ $k = \text{Boltzman constant} = 1.381 \text{ x } 10^{-23} \text{ J K}^{-1}$ T = temperature (K) $\chi_M = \text{molar susceptibility (m^3 \text{ mol}^{-1})}$ $N_A = \text{Avogadro's constant} = 6.022 \text{ x } 10^{23} \text{ mol}^{-1}$ $\mu_0 = \text{permeativity of a vacuum} = 1.257 \text{ x } 10^{-6} \text{ H m}^{-1}$ $\mu_B = \text{The Bohr Magneton} = 9.274 \text{ x } 10^{-24} \text{ J T}^{-1}$

The diamagnetic contributions of the ligand framework are neglected in the calculations of μ_{eff} since their contribution is in comparison very small. The theoretical spin-only value of μ_{eff} of a paramagnetic atom is given by eq. 3.

$$\mu_{eff} = \sqrt{n(n+2)} \tag{S3}$$

where,

 μ_{eff} = effective magnetic moment (BM)

n = number of unpaired electrons at the paramagnetic centre

X-Ray Crystallography

The X-ray crystal structure of [Fe(1)Br₂]

Crystal data for [Fe(1)Br₂]: C₂₁H₂₅Br₂FeN₅, M = 563.13, triclinic, P-1 (no. 2), a = 8.7168(3), b = 15.3336(6), c = 16.8358(7) Å, α = 85.049(3), β = 89.833(3), γ = 85.877(3)°, V = 2236.06(15) Å³, Z = 4 [two independent molecules], D_c = 1.673 g cm⁻³, μ (Mo-K α) = 4.266 mm⁻¹, T = 173 K, yellow platy needles, Oxford Diffraction Xcalibur 3 diffractometer; 15596 independent measured reflections (R_{int} = 0.0000), F² refinement,⁷ R₁(obs) = 0.0413, wR₂(all) = 0.0847, 9240 independent observed absorption-corrected reflections [|F_o| > 4 σ (|F_o|), 2 θ _{max} = 62°], 524 parameters. CCDC 887947.

The crystal that was studied was modelled as a two component twin in a ca. 90:10 ratio, with the two lattices related by the approximate twin law [1.00 0.00 0.00 0.25 -1.00 0.00 0.01 0.00 -1.00]. As a result of processing the data to account for this twinning, all of the reflections are treated as unique and so the R_{int} is zero.

The structure was found to contain two crystallographically independent molecules, $[Fe(1)Br_2]$ -A and $[Fe(1)Br_2]$ -B, in the asymmetric unit and the two complexes have essentially identical geometries, the r.m.s. fit of their non-hydrogen atoms being ca. 0.03 Å.

In the check cif file for [Fe(1)Br₂], a B-level alert appeared: PLAT021_ALERT_1_B Ratio Unique / Expected Reflections too High ... 1.082

This comes about because the crystal used was twinned, so the HKLF5 data file contains reflections from both components and thus there appear to be more data points than one would normally expect. The explanation of this alert given by the checkCIF hyperlink is: PLAT021 Type_4 Check Expected number of Reflections (Max = 1 Centro, 2 - non-centro) The expected number of reflections corresponds to that in the asymmetric unit of the Laue group. Expected ratio: less-or-equal 1 for centro symmetric structures and less than 2 for non-centrosymmetric structures.

Reasons to exceed those numbers can be:

- 1 Systematic extinctions not omitted from the observed data count.
- 2 Refinement with redundant (i.e. not merged/unique) data set.
- 3 SHELXL HKLF 5 Refinement

The refinement of $[Fe(1)Br_2]$ comes under section 3, and is therefore acceptable.

The X-ray crystal structure of [Fe(1)(CH₃CN)₂](ClO₄)₂

Crystal data for $[Fe(1)(CH_3CN)_2](ClO_4)_2$: $C_{25}H_{31}Cl_2FeN_7O_8$, M = 684.32, monoclinic, P2₁/c (no. 14), a = 18.3004(2), b = 12.48519(17), c = 13.43464(16) Å, β = 90.6391(11)°, V = 3069.41(6) Å³, Z = 4, D_c = 1.481 g cm⁻³, μ (Mo-K α) = 723 mm⁻¹, T = 173 K, pale yellow blocky needles, Oxford Diffraction Xcalibur 3 diffractometer; 10277 independent measured reflections (R_{int} = 0.0267), F² refinement,⁷ R₁(obs) = 0.0405, wR₂(all) = 0.1113, 8733 independent observed absorption-corrected reflections [|F_o| > 4 σ (|F_o|), 2 θ_{max} = 65°], 411 parameters. CCDC 887948.

The Cl(2)-based perchlorate anion was found to be disordered, and two orientations of ca. 84 and 16% occupancy were identified. The geometries of the two orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the major occupancy atoms were refined anisotropically (the remainder were refined isotropically).

The X-ray crystal structure of [Fe(1)](OTf)₂

Crystal data for [Fe(1)](OTf)₂: C₂₃H₂₅F₆FeN₅O₆S₂, M = 701.45, monoclinic, C2/c (no. 15), a = 22.4112(9), b = 10.5689(2), c = 15.0745(6) Å, β = 129.267(6)°, V = 2764.4(3) Å³, Z = 4 [C₂ symmetry], D_c = 1.685 g cm⁻³, μ (Mo-K α) = 0.787 mm⁻¹, T = 173 K, pale yellow tablets, Oxford Diffraction Xcalibur 3 diffractometer; 4741 independent measured reflections (R_{int} = 0.0169), F² refinement,⁷ R₁(obs) = 0.0526, wR₂(all) = 0.1409, 4436 independent observed absorption-corrected reflections [|F_o| > 4 σ (|F_o|), 2 θ_{max} = 65°], 196 parameters. CCDC 887949.

In the Check-cif file for $[Fe(1)](OTf)_2$, there is a B-level alert: PLAT434_ALERT_2_B Short Inter HL..HL Contact F23 ... F23 . 2.59 Ang.

The structure has no disorder, so this represents a real result and the quoted distance is entirely genuine.

Figures:



Fig. S1 The structure of one ($[Fe(1)Br_2]$ -A) of the two independent complexes present in the crystals of $[Fe(1)Br_2]$ (50% probability ellipsoids).



Fig. S2 The structure of one ($[Fe(1)Br_2]$ -B) of the two independent complexes present in the crystals of $[Fe(1)Br_2]$ (50% probability ellipsoids).



Fig. S3 The structure of the complex cation present in the crystals of $[Fe(1)(CH_3CN)_2](ClO_4)_2$ (50% probability ellipsoids).



Fig. S4 The structure of the C₂-symmetric complex cation present in the crystals of $[Fe(1)](OTf)_2$ (50% probability ellipsoids). Atoms labelled with an "A" after the number are related to their counterparts without the letter by the C₂ axis that passes through Fe(1), N(1) and C(4).

Additonal NMR spectra



Figure S5 : VT 1 H NMR spectra in the temperature range 233 to 343 K for [Fe(1)Br₂] in CD₃CN.



Figure S6: VT-¹⁹F-NMR spectra in the temperature range 233 to 343K for $[Fe(1)](OTf)_2$ in CD₃CN.



Figure S7: VT ¹H NMR spectra in the temperature range 203 to 303K for $[Fe(1)](OTf)_2$ in CD_2Cl_2 .



Figure S8: Fraction of the complexes $[Fe(1)]^{2+}$ (black) and $[Fe(1)(OTf)_2]$ (red) in % as a function of temperature for $[Fe(1)](OTf)_2$, determined by integration of the triflate signals in CD_2Cl_2 by ¹⁹F NMR (see Figure 5).



Figure S9: VT ¹H NMR spectra in the temperature range 243 to 343K for $[Fe(1)](OTf)_2$ in 1,2-C₂D₄Cl₂.



Figure S10: VT ¹H NMR spectra in the temperature range 233 to 343 K for $[Fe(1)(CH_3CN)_2](SbF_6)_2$ in CD₃CN.



Figure S11: VT 19 F NMR spectra in the temperature range 233 to 343K for [Fe(1)(CH₃CN)₂](SbF₆)₂ in CD₃CN.



Figure S12: VT ¹H NMR spectra in the temperature range 233 to 343K for $[Fe(1)(CH_3CN)_2](ClO_4)_2$ in CD₃CN.



Figure S13: VT-¹H-NMR spectra in the temperature range 233 to 343K for $[Fe(1)](ClO_4)_2$ in 1,2-C₂D₂Cl₄.



Figure S14: VT-UV/Vis spectra of [Fe(1)](OTf)₂ in acetonitrile (0.2 mM).



Figure S15: Effective magnetic moments measured for complexes $[Fe(1)Br_2]$ and $[Fe(1)](X)_2$, (X = OTf, SbF₆ and ClO₄) between 233 and 343 K in acetonitrile.



Figure S16: Van't Hoff plot of $\ln K$ versus 1/T for complex $[Fe(1)](SbF_6)_2$ to determine the thermodynamic values ΔH° and ΔS° for the 7-5 coordination equilibrium. Determined by ¹H NMR in CD₃CN.



Figure S17: Temperature dependence of the Gibbs energy in acetonitrile for the 7-5 coordination equilibrium (determined by NMR).

When the thermodynamic parameters were determined by using the VT-UV/Vis spectra measured in 1,2-dichloroethane, the concentration of each species is calculated from the extinction coefficients. The values of $\ln K$ (at 374 nm) have been plotted against 1/T and the enthalpy (ΔH°) and the entropy (ΔS°) terms were determined from the slope of the linear fit (Figure S18). The enthalpy value of 21.6 ± 2.5 kJ mol⁻¹ and entropy value of 53 ± 9 J K⁻¹ mol⁻¹ are in reasonble agreement with the data obtained previously from NMR experiments. The thermodynamic values were also calculated from UV/Vis spectra in acetonitrile (see Figure S19) and all thermodynamic values are summarised in Table S1 showing good agreement for the values obtained for ΔH° . The values determined by UV/Vis are comparable to those determined by NMR spectroscopy, although the entropy value was somewhat higher at $\Delta S^{\circ} = 91 \pm 4$ JK⁻¹mol⁻¹, possibly a consequence of the larger errors associated with determining entropy values from the intercept of the graph and due to the relatively small changes that are observed by UV/Vis spectroscopy.



Figure S18: Plot of $\ln K$ versus 1/T (left) and the temperature dependence of the Gibbs energy (right) in 1,2-dichloroethane for the 5-7 coordination equilibrium of complex [Fe(1)](OTf)₂.



Figure S19: Plot of $\ln K$ versus 1/T (left) and the temperature dependence of the Gibbs energy (right) in acetonitrile for the 5-7 coordination equilibrium of complex [Fe(1)](OTf)₂.

Table S1: Summary of calculated thermodynamic values for the 7-5 coordination equilibrium of $[Fe(1)]^{2^+}$.

solvent	concentration [mM]	ΔH° [kJ mol ⁻¹]	ΔS° [J K ⁻¹ mol ⁻ 1]	method
1,2-dichloroethane	3	21.6 ± 2.5	53 ± 9	UV/Vis
acetonitrile	2	21.6 ± 1.7	44 ± 6	UV/Vis
acetonitrile	15	25.1 ± 1.1	91 ± 4	NMR

Error analyses:

Table S2. Error analysis for thermodynamic parameters

Linear Regress Y = A + B * X	(130 in DCE)		
Parameter	Value	Error	
А	6.42838	1.10607	
В	-2596.10339	304.33916	
R	SD	N	Р
-0.96116	0.25898	8	1.42E-04

[09/08/2013 11:23 "/Folder1/Graph3" (2456513)] (130_2 in CH3CN) Linear Regression for Book4_C: Y = A + B * X

Parameter	Value	Error
A	5.34277	0.7306
D	- 2502 1/1287	205 20101
D 	2392.14207	

R		SD		Ν		Р
	-0.98469		0.13704		7	<0.0001

	(from
[09/08/2013 11:19 "/Folder1/Graph1" (2456513)]	NMR)
Linear Regression for Book1_G:	
Y = A + B * X	

Parameter	Value	Error		
 A	10.88491	0.4615		
В	- 3016.41554	134.74576		
R	SD	N	Ρ	
 -0.99702	0.04987	5		1.95E-04

DFT calculations

DFT calculations have been carried out at the wB97X-D level using 6-31G(d) basis sets for all atoms, except Fe, which was 6-31G(2df) for a quintet spin state, and including a continuum solvation correction for acetonitrile. Full details for the calculations can be found in the following DOI's:

DOI:10.6084/m9.figshare.96072 contains the calculations for the seven-coordinate complex $[Fe(1)(CH_3CN)_2](OTf)_2$ (Figure S20). One of the acetonitrile ligands coordinates on an angle, which is also seen in the X-ray structure (Figure S3), though to lesser degree.

DOI:10.6084/m9.figshare.791639 is the same structure, but with a wavefunction suitable for performing QTAIM calculations.

DOI:10042/to-9389 is the calculation of the 7-coordinate complex $[Fe(1)(OTf)_2]$ (Figure S21). While this is a 7-coordinate complex, the iron-oxygen distances are somewhat different for the two triflate ligands. Attempts to remove one of the triflate anions to generate a 6-coordinate complex and free triflate anion failed and resulted in the 7-coordinate complex. Similarly, attempts to remove both triflate anions to calculate the 5-coordinate complex failed and resulted again in the same 7-coordinate complex.

DOI:10042/to-9383 is acetonitrile, which coupled with the other two allows the energy difference between $[Fe(1)(CH_3CN)_2](OTf)_2$ and $[Fe(1)(OTf)_2]$ (and two CH₃CN) to be computed.



Figure S20. Optimised geometry for complex [Fe(1)(CH₃CN)₂](OTf)₂.



Figure S21. Optimised geometry for complex [Fe(1)(OTf)₂].

Cyclic Voltammetry:



Figure S22. Cyclic voltammogram for complex $[Fe(1)](OTf)_2$ in acetonitrile (5 mM) and (NBu₄)PF₆ (0.1 M) measured at different scan rates (0.1-0.5 V/s) *vs.* Ag/AgNO₃ (1 mM).

Table S3. Redox and half-potentials of iron bistriflate complex in acetonitrile (5 mM) vs. $Ag/AgNO_3$ (1 mM).

Complex	E_{ox}/V	E _{red} (V)	<i>E</i> _{1/2} (V)	ΔE_p (V)	i _{rev} /i _{for}	Properties
$[Fe(1)](OTf)_2$	0.89	0.60	0.75	0.29	0.48	irrev.

The half potential $E_{1/2} = 0.75$ V vs. Ag/AgNO₃ can be converted to the half potential $E_{1/2} = 0.99$ V vs. SCE, by adding 0.24 V. For conversions see: http://www.consultrsr.com/resources/ref/refpotls.htm

References:

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