Anion-Dependent Spin Crossover in Solution for an Iron(II) Complex of a 1H-pyrazolyl Ligand

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Electronic Supplementary Information

Experimental details

Figure S1 Variable temperature magnetic susceptibility data for three salts [Fe(3-bpp)$_2$]X$_2$ ($X^-$ = I$^-$, BF$_4^-$ and PF$_6^-$) as reported by Goodwin et al.

Figure S2 $^1$H NMR spectra of five [Fe(3-bpp)$_2$]X$_2$ ($1X_2$) salts in 9:1 v/v (CD$_3$)$_2$CO:D$_2$O at 298 K, showing the variation in the isotropic shifts with the anion present.

Table S1 Experimental details for the single crystal structure determinations of solvates of [Fe(3-bpp)$_2$][BF$_4$].

Figure S3 Comparison of the solvent dependence of the $^1$H isotropic shifts of [Fe(3-bpp)$_2$]X$_2$ ($1X_2$) on the anion X$^-$, in four different solvents (Table S1).

Figure S4 Variable temperature magnetic susceptibility data for $1X_2$ in neat (CD$_3$)$_2$CO.

Figure S5 Variable temperature magnetic susceptibility data for $1$[BPh$_4$]$_2$ in 9:1 v/v (CD$_3$)$_2$CO:D$_2$O, in the presence of [NBu$_4$]Br.

Figure S6 Dependence of $T_1/2$ on bromide ion concentration for $1$[BPh$_4$]$_2$ in the presence of y equivalents of [NBu$_4$]Br.

Figure S7 UV/vis spectra of five of the compounds in this work.

References
Experimental

Reaction of Fe[BF$_4$]$_2$·6H$_2$O (0.20 g, 0.59 mmol) by 3-bpp$_2$ (0.25 g, 1.18 mmol) in nitromethane (25 cm$^3$) at room temperature rapidly afforded a yellow-brown solution. This was filtered, concentrated to 5 cm$^3$. Slow diffusion of diethyl ether vapour into the filtered solution yielded large brown blocks, that decompose to yellow solvent-free 1[BF$_4$]$_2$ when dried in vacuo.

A similar complexation of FeBr$_2$·4H$_2$O (0.17 g, 0.59 mmol) and 3-bpp (0.25 g, 1.18 mmol) in methanol (25 cm$^3$) gave an orange solution, that yielded the methanol solvate of 1Br$_2$ as an orange-brown powder following the work-up as above.

The other salts of [Fe(3-bpp)$_2$]$_{2+}$ (2$x$) were prepared by warming a mixture of FeCl$_2$·4H$_2$O (0.12 g, 0.59 mmol) and 3-bpp (0.25 g, 1.18 mmol) in water (50 cm$^3$), until all the ligand had dissolved. Adding excess NaBPh$_4$·H$_2$O, NaCF$_3$SO$_3$, KNCS or NaNO$_3$ to the filtered brown solutions immediately yielded an orange or brown precipitate, which was collected, washed with water and dried in vacuo. Recrystallisation by slow diffusion of diethyl ether vapour into a solution of the compounds in nitromethane (X$^-$ = BPh$_4^-$ or CF$_3$SO$_3^-$), or methanol (X$^-$ = NCS$^-$, NO$_3^-$) gave the pure complexes as brown solids.

For 1[BPh$_4$]$_2$·½H$_2$O:[3] found C, 74.9; H, 5.15; N, 12.6 %. Calcd. for C$_{70}$H$_{58}$B$_2$FeN$_{10}$·½H$_2$O C, 75.7; H, 5.28; N, 12.4 %.

For 1[BF$_4$]$_2$:[4,5] found C, 40.5; H, 3.05; N, 21.4 %. Calcd. for C$_{22}$H$_{18}$B$_2$FeN$_{10}$ C, 40.5; H, 2.78; N, 21.5 %.

For 1[CF$_3$SO$_3$]$_2$·H$_2$O:[6] found C, 36.1; H, 2.50; N, 17.3 %. Calcd. for C$_{24}$H$_{18}$FeN$_{10}$O$_6$S$_2$·H$_2$O C, 36.3; H, 2.54; N, 17.6 %.

For 1[NCS]$_2$·H$_2$O:[7] found C, 46.4; H, 3.15; N, 27.2 %. Calcd. for C$_{24}$H$_{18}$FeN$_{12}$S$_2$·H$_2$O C, 47.1; H, 3.29; N, 27.4 %.

For 1[NO$_3$]$_2$·2H$_2$O:[8] found C, 41.4; H, 3.35; N, 26.4 %. Calcd. for C$_{22}$H$_{18}$FeN$_{10}$O$_6$·2H$_2$O C, 41.4; H, 3.47; N, 26.3 %.

For 1Br$_2$·CH$_3$OH: found C, 41.2; H, 3.05; N, 20.7 %. Calcd. for C$_{22}$H$_{18}$Br$_2$FeN$_{10}$·CH$_3$OH C, 41.2; H, 3.31; N, 20.9 %. This salt has been previously reported as its pentahydrate and anhydrous solid forms.[9]

Other measurements

UV/visible spectra were obtained with a Perkin-Elmer Lambda 900 spectrophotometer operating between 200–1,500 nm, in 1 cm quartz cells. Paramagnetic $^1$H NMR spectra were measured with a Bruker DPX300 spectrometer operating at 300.2 MHz. Magnetic susceptibility measurements in solution were obtained by Evans method using Bruker DRX500 or Bruker Avance500 spectrometers operating at 500.13 MHz. Duplicate measurements on both spectrometers were performed to confirm their temperature calibration was consistent. Tetramethylsilane was added to all the solutions as an internal standard. A diamagnetic correction for the sample, and a correction for the variation of the density of the solvent with temperature, were applied to these data. All magnetochemical data manipulation and graph plotting was carried out using SIGMAPLOT.

Each Evans method measurement was performed at a concentration of 10±1 mM. The UV/vis spectra required lower concentrations, of 0.16-0.20 mM.
Fig. S1 Variable temperature magnetic susceptibility data for [Fe(3-bpp)$_2$]X$_2$ (1X$_2$; X$^-$ = I$^-$, BF$_4^-$ and PF$_6^-$), as reported by Goodwin et al.[8] The data have been converted from $\mu_{\text{eff}}$ to $\chi_M T$, and replotted.

These measurements were performed in “acetone containing a few drops of water”, and in the presence of excess 3-bpp ligand. The excess ligand has no apparent influence on the results, based on the similarity between the data for 1[BF$_4$]$_2$ in the Figure, and in this study.
\[ X^- \]

\[ \text{BPh}_4^- \]

\[ \text{BF}_4^- \]

\[ \text{CF}_3\text{SO}_3^- \]

\[ \text{NO}_3^- \]

\[ \text{Br}^- \]

**Fig. S2** $^1$H NMR spectra of five [Fe(3-bpp)$_2$]X$_2$ (1X$_2$) salts in 9:1 v/v (CD$_3$)$_2$CO:D$_2$O at 298 K, showing the variation in the isotropic shifts with the anion present. See Table S1 for the assignment of these resonances.

Reduced isotropic shifts imply the sample contains a smaller high-spin population at room temperature,\[^{13}\] which would be consistent with an increased spin-crossover $T_{1/2}$ value. These isotropic shifts do not depend on concentration, all other things being equal.\[^{13}\]
Table S1: \(^1\)H NMR data for [Fe(3-bpp)\(_2\)]X\(_2\) (1X\(_2\)) in different solvents at 298 K, at a concentration of 15 mmol dm\(^{-3}\). These data are plotted in Fig. S1.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>X</th>
<th>(\beta^N[14])</th>
<th>Py H(^\delta)</th>
<th>NH H(^\delta)</th>
<th>Py H(^\delta)</th>
<th>Pz H(^\delta) &amp; Pz H(^\delta)</th>
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<tr>
<td>CD(_3)CN</td>
<td>BPh(_4^-)</td>
<td>0</td>
<td>18.6</td>
<td>32.7</td>
<td>45.5</td>
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<td></td>
<td>BF(_4^-)</td>
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<td>18.5</td>
<td>32.8</td>
<td>45.5</td>
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<tr>
<td></td>
<td>CF(_3)SO(_3^-)</td>
<td>0.74</td>
<td>18.2</td>
<td>32.6</td>
<td>44.6</td>
<td>52.0, 52.8</td>
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<tr>
<td>(CD(_3))(_2)CO</td>
<td>BPh(_4^-)</td>
<td>0</td>
<td>18.6</td>
<td>33.4</td>
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<td>18.1</td>
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<td>32.7</td>
<td>42.4</td>
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<td>CD(_3)OD</td>
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<td>–</td>
<td>42.2</td>
<td>49.4, 49.8</td>
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<tr>
<td></td>
<td>NCS(^-)(^a)</td>
<td>0.78</td>
<td>18.2</td>
<td>–</td>
<td>42.0</td>
<td>49.2, 49.6</td>
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<tr>
<td></td>
<td>NO(_3^-)(^b)</td>
<td>0.86</td>
<td>18.2</td>
<td>–</td>
<td>42.0</td>
<td>49.2, 49.6</td>
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<tr>
<td></td>
<td>Br(^-)(^b)</td>
<td>0.93</td>
<td>18.3</td>
<td>–</td>
<td>42.2</td>
<td>49.5, 49.8</td>
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<tr>
<td>9:1 v/v (CD(_3))(_2)CO:D(_2)O</td>
<td>BPh(_4^-)</td>
<td>0</td>
<td>16.9</td>
<td>–</td>
<td>38.7</td>
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<td>0.74</td>
<td>16.6</td>
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<td>16.3</td>
<td>–</td>
<td>37.0</td>
<td>43.2, 44.0</td>
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</table>

\(^a\)Spectrum also contains broad peaks assignable to free 3-bpp at 6.9, 7.6, 7.7 and 7.8 ppm with a 2:2:2:1 integral ratio. This species has a 40 % integral ratio compared to the main, paramagnetic complex. This is evidence for substantial dissociation of the complex in this solvent, probably from displacement of 3-bpp by the nucleophilic NCS\(^-\) ion.

\(^b\)Spectrum contains free 3-bpp (see above), with a 6-10 % integral ratio compared to the main, paramagnetic complex. This is evidence for a small degree of dissociation of the complex in this solvent (the integral of the diamagnetic free ligand will be overestimated compared to the paramagnetic complex, because of line-broadening in the contact-shifted peaks).

The \(\beta^N\) parameter is a measure of the hydrogen-bond acceptor character of an anion, derived from a \(^1\)H NMR measurement of its association with the 1-butyl-3-methylimidazolium ([Bmim]\(^+\)) cation in CD\(_2\)Cl\(_2\).[14]

The relationship between \(\delta\) and the different solvents used, for a given anion X\(^-\), has been reported in ref. [5].
Fig. S3 Comparison of the solvent dependence of the $^1$H isotropic shifts of [Fe(3-bpp)$_2$]X$_2$ (1X$_2$) on the anion X$^-$, in three different solvents (Table S1). Colour code: X$^-$ = BPh$_4^-$ (black), BF$_4^-$ (yellow), CF$_3$SO$_3^-$ (red), NCS$^-$ (white), NO$_3^-$ (cyan), Br$^-$ (green).

There is a small but consistent decrease in the isotropic shifts ($\delta$) in CD$_3$CN and (CD$_3$)$_2$CO when X$^-$ = CF$_3$SO$_3^-$, compared to BPh$_4^-$ and BF$_4^-$. A comparable trend was also seen for all the salts in the acetone/water mixed solvent. That implies that salts of the complex with more associating anions have a slightly greater low-spin population at room temperature. This was subsequently confirmed by the Evans method study described in the main article.

No comparable relationship between $\delta$ and X$^-$ was observed in CD$_3$OD, implying that hydrogen bonding between 1$^{2+}$ and X$^-$ is weaker in that solvent, as expected.
Fig. S4 Variable temperature magnetic susceptibility data for $\mathbf{1X_2}$ in neat $(\text{CD}_3)_2\text{CO}$, with $X^- = \text{BPh}_4^-$ (black circles), $\text{BF}_4^-$ (yellow squares) and $\text{CF}_3\text{SO}_3^-$ (red diamonds).
**Fig. S5** Variable temperature magnetic susceptibility data for 1[BPh$_4$]$_2$ in 9:1 v/v (CD$_3$)$_2$CO:D$_2$O, in the presence of $y$ equivalents of [NBu$_4$]Br: $y = 0$ (black circles), $y = 0.78$ (green squares) and $y = 1.71$ (pink triangles).

**Fig. S6** Dependence of $T_{1/2}$ on bromide ion concentration for 1[BPh$_4$]$_2$ in the presence of $y$ equivalents of [NBu$_4$]Br. The open circle is for pure 1Br$_2$ (putatively, $y = 2$).
**Fig. S5** UV/vis spectra of five of the compounds in this work, in 9:1 v/v (CH$_3$)$_2$CO:H$_2$O at 293 K: 1[BPh$_4$]$_2$ (black), 1[BF$_4$]$_2$ (yellow), 1[CF$_3$SO$_3$]$_2$ (red), 1[NO$_3$]$_2$ (cyan) and 1Br$_2$ (green).

The differing depth of the trough against the solvent shoulder, near 360 nm, reflects small differences in the concentrations of the samples, which were between 1.6–2.0 x10$^{-4}$ mol dm$^{-3}$. Otherwise, these spectra are identical within experimental error, and are consistent with those reported previously for 1[BF$_4$]$_2$ in (CH$_3$)$_2$CO:H$_2$O solvent mixtures.$^{[5]}$

The invariance of these spectra with the anion present may reflect the sample concentrations used in the UV/vis measurements, which were ca. 50x lower than for the NMR and Evans method experiments. This lower concentration will promote dissociation of any supramolecular anion complexes of 1$^{2+}$. 
References


