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Influence of Ligand Substituent Conformation on the Spin State of an Iron(II)/Di(pyrazol-1-yl)pyridine Complex†‡

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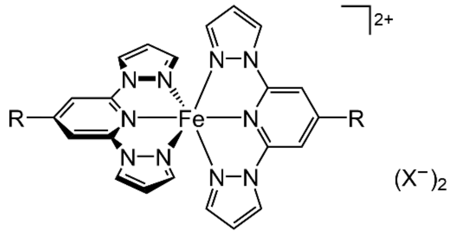
The temperature of the solution-phase spin-crossover equilibrium in iron(II) complexes of 4-alkylsulfanyl-2,6-di{pyrazol-1-yl}pyridine (bpp^{SR}) complexes depends strongly on the alkylsulfanyl substituent. DFT calculations imply this reflects the conformation of the alkylsulfanyl groups, which lie perpendicular to the heterocyclic ligand donors in [Fe(bpp^{StBu})$_2$]$^{2+}$ but are oriented co-planar with the ligand core for smaller SR substituents.

The utility of base metal complexes as catalysts,[1,2] light-harvesting dyes[3] or in functional molecular materials[4] often depends on their spin state. That is particularly true of iron compounds, which are of special interest for these applications. High-, low- and intermediate-spin states of iron are all accessible with the right combination of ligands, but have very different physical properties and chemical reactivity.[5] This can lead to unexpectedly subtle catalytic pathways through two-state reactivity, when a low-spin catalyst generates high-spin intermediates during a catalytic cycle (or *vice versa*).[1,6]

Modulation of metal spin state is often done *via* the steric environment generated by a protecting ligand. Bulky substituents adjacent to metal–ligand bonds usually favour a high-spin state, other things being equal.[7,8] In contrast the electronic influence of ligand substituents on metal spin state has been less clear-cut, with different trends being reported for different groups of compounds.[8-12] We addressed this with a library of compounds derived from [Fe(bpp)$_2$]$^{2+}$ (bpp = 2,6-di{pyrazol-1-yl}pyridine), which often undergo thermal spin-crossover (SCO) equilibria near room temperature.[13] As part of that work, we used linear free energy plots[14] to show electron-withdrawing 4-pyridyl substituents ('R', Scheme 1) stabilise the low-spin state of the complex in solution, and *vice versa*.[15] This was explained computationally by R (which is *para* to the Fe−N{pyridyl} bond) being positioned to conjugate to the Fe−N bond, giving it a strong influence on π-back bonding in the complex.[15,16] We now report a new observation from the same family of compounds, which adds extra detail to these insights by quantifying how the conformation of an 'R' substituent perturbs the ligand field of the iron centre.



[Fe(bpp^R)$_2$]X$_2$

1X$_2$, R = SMe
2X$_2$, R = S*i*Pr
3X$_2$, R = S*t*Bu

Scheme 1 The structure of [Fe(bpp^R)$_2$]$^{2+}$ complex salts, and the compounds referred to in this study (X$^−$ = a monovalent anion). The parent compound [Fe(bpp)$_2$]$^{2+}$ has R = H.

A CD$_3$CN solution of **3[BF$_4$]$_2$** (R = S*t*Bu)[17] undergoes a thermal SCO equilibrium, with $T_{½}$ = 241±2 K, ΔH = 23.5±0.5 kJmol^{-1} and ΔS = 98±2 Jmol^{-1}K^{-1}. These are typical thermodynamic values for SCO-active [Fe(bpp^R)$_2$]$^{2+}$ derivatives.[15] Interestingly, the solution $T_{½}$ for iron(II)/4-alkylsulfanyl-2,6-di(pyrazol-1-yl)pyridine (bpp^R; R = SR', R' = alkyl) complexes depends significantly on the thioether substituent, with $T_{½}$ = 194±2 K for **1[BF$_4$]$_2$** (R = SMe)[18] and 215±4 K for **2[BF$_4$]$_2$** (R = S*i*Pr; Figure 1).[19] This contrasts with [Fe(bpp^R)$_2$]$^{2+}$ salts bearing carboxy substituents (R = CO$_2$R', R' = H, alkyl or aryl), where a larger number of published compounds span a narrower range of 273 ≤ $T_{½}$ ≤ 292 K.[15,20] That is consistent with the Hammett parameters of carboxy substituents, which are almost invariant for different R' groups.[14] It is unclear how **1[BF$_4$]$_2$**-**3[BF$_4$]$_2$** map onto that trend, however, since the relevant σ_P and σ_P^+ Hammett parameters are not available for S*i*Pr and S*t*Bu substituents.

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‡ Data associated with this study are available from the University of Leeds library at http://doi.org/10.5518/###

† Electronic Supplementary Information (ESI) available: experimental procedures and atomic coordinates, metric parameters and orbital plots for the energy-minimised molecules. See DOI: 10.1039/x0xx00000x

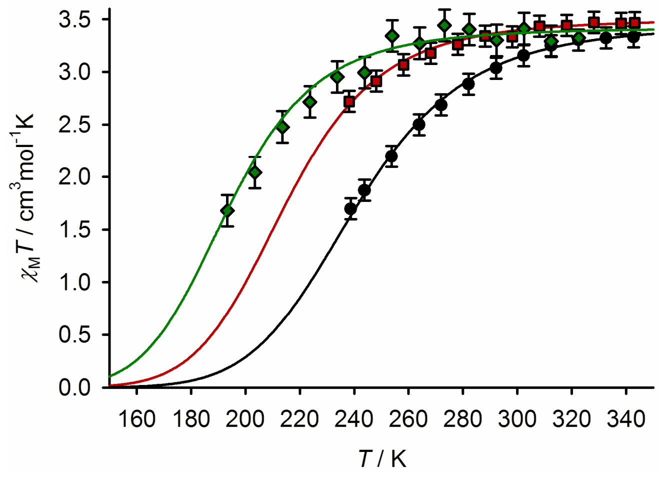

Figure 1 Magnetic susceptibility data from **1[BF$_4$]$_2$** in (CD$_3$)$_2$CO solution (green ◆),[16] **2[BF$_4$]$_2$** in CD$_3$CN (red ■)[17] and **3[BF$_4$]$_2$** in CD$_3$CN (black ●).[21] The curves show the fits of these data to a thermodynamic SCO equilibrium (ESI†).

This observation was investigated by gas phase DFT calculations, at the B86PW91/def-SVP2 level. This and closely related methods perform well in comparative spin state energy calculations of [Fe(bpp^R)$_2$]$^{2+}$ and other iron(II) complexes.[15,22,23] The high-spin and low-spin forms of [Fe(bpp^R)$_2$]$^{2+}$ (R = SMe, **1**$^{2+}$; *S**i*Pr, **2**$^{2+}$; and *St*Bu, **3**$^{2+}$) were freely minimised, which placed their alkylsulfanyl substituents co-parallel with the pyridyl rings. More minimisations were then performed with the C{pyridyl}–C{pyridyl}–S–C{alkyl} torsions fixed at ±90° so the SR groups are perpendicular to the pyridyl rings (Figures 2 and S2†).[24]

The parallel alkylsulfanyl conformations are lower in energy than the perpendicular conformations (Table 1), by the following amounts for the high-spin/low-spin molecules:

1^{2+} (16.2/14.8) > **2**$^{2+}$ (14.0/13.1) >> **3**$^{2+}$ (8.9/7.7 kcal mol^{-1})

These are up to 6x larger than expected from the equivalent energy differences for the free organic ligands, computed by the same method (Table S1†):[27]

bpp^{SMe} (4.5) > bpp^{SiPr} (3.3) >> bpp^{StBu} (0.7 kcal mol^{-1})

Hence, metal coordination evidently affects the rotational freedom of the sulfanyl substituents. That must be an electronic influence, since the sulfanyl substituents are too remote from the metal centre to be in steric contact with other parts of the molecule (Figure 2).

Consistent with these data, only the parallel conformation occurs crystallographically in **1X$_2$** and **2X$_2$** salts.[18,25,26] However, different **3X$_2$** crystals adopt parallel or perpendicular ligand conformations, which sometimes interconvert during SCO.[17] Hence, the perpendicular geometry is experimentally accessible for the bulkier *St*Bu substituent in **3**$^{2+}$, despite being computed at 8-9 kcal mol^{-1} higher in energy by our protocol.[27]

The absolute spin state energies in Table 1 are inaccurate, since pure density functionals like B86PW91 overstabilise the low-spin state.[28] However the energy difference between the spin states, relative to the unsubstituted parent complex [Fe(bpp)$_2$]$^{2+}$ (ΔE_{rel}{HS-LS}), is a reliable gauge of their behaviour (Table 1).[15,23] A plot of ΔE_{rel}{HS-LS} *vs* the measured solution $T_{½}$ values in the parallel ligand conformation showed good agreement between theory and experiment for **1**$^{2+}$ and **2**$^{2+}$, but

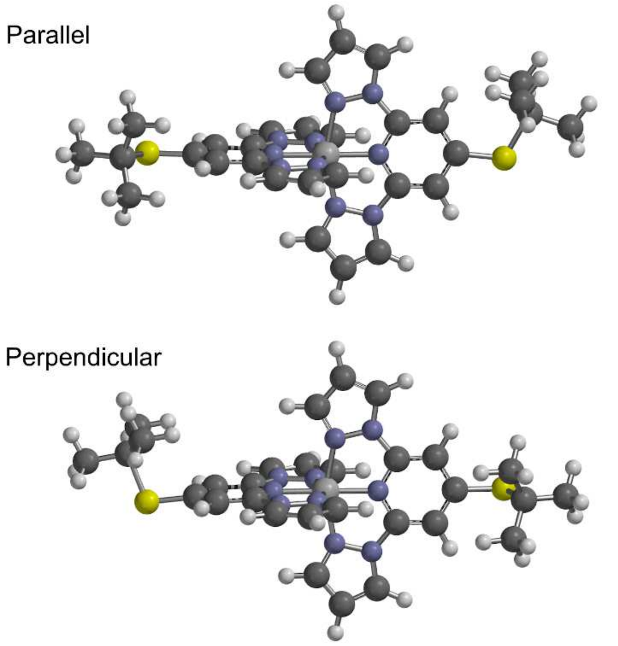

Figure 2 Energy-minimised structures of low-spin **3**$^{2+}$ in the gas phase, with parallel and perpendicular *St*Bu substituent conformations.

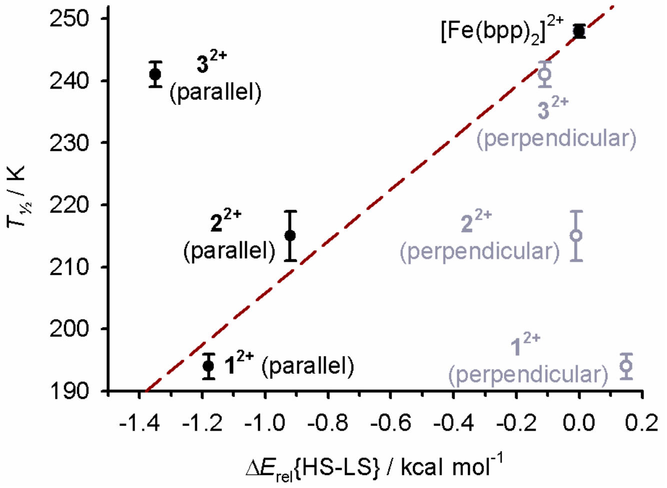

Figure 3 Plot of measured solution $T_{½}$ *vs* the computed spin state energies in the parallel (black ●) and perpendicular (grey ○) ligand conformations of **1**$^{2+}$-**3**$^{2+}$ and [Fe(bpp)$_2$]$^{2+}$ (Table 1). The red line shows the linear regression best fit for [Fe(bpp)$_2$]$^{2+}$ and the parallel conformations of **1**$^{2+}$ and **2**$^{2+}$.

not for **3**$^{2+}$ whose ΔE_{rel}{HS-LS} value is –1.2 kcal mol^{-1} more negative than predicted experimentally (Figure 3). However the perpendicular ligand conformation stabilises the low-spin state of the complexes by a similar amount, so the computed ΔE_{rel}{HS-LS} for **3**$^{2+}$ in that geometry maps onto the trend of the other compounds in the parallel conformation (Figure 3). Hence, the higher $T_{½}$ for **3**$^{2+}$ can be explained, if its bulky *St*Bu groups adopt the perpendicular conformation in solution.[27]

The stabilisation of the low-spin state in the perpendicular conformation reflects that the sulfur lone pairs cannot conjugate with the pyridyl π-system in that geometry (Figures 4 and S3-S7†). That reduces the electron-richness of the pyridyl rings, which are then more available for π-back-donation from

Table 1 Minimized energies of the high-spin (HS) and low-spin (LS) $[Fe(bpp^R)_2]^{2+}$ complexes in this work. $\mathbf{1}^{2+}$-$\mathbf{3}^{2+}$ are the dications from the $\mathbf{1X_2}$-$\mathbf{3X_2}$ salts in Scheme 1. The parallel and perpendicular alkyl sulfanyl group conformations are shown in Figures 2 and S1. Data for $[Fe(bpp)_2]^{2+}$ are taken from ref. 23.

	R (Scheme 1)	Conformation	*E*{HS} / Ha	*E*{LS} / Ha	Δ*E*{HS-LS} / Ha	Δ*E*{HS-LS} / kcal mol^{-1} [a]	Δ*E*$_{rel}${HS-LS} / kcal mol^{-1} [b]
$[Fe(bpp)_2]^{2+}$	H	–	−2659.474752	−2659.500527	0.025775	16.17	0
$\mathbf{1}^{2+}$	SMe	parallel	−3534.310211	−3534.334105	0.023894	14.99	−1.18
$\mathbf{2}^{2+}$	S*i*Pr	parallel	−3691.507623	−3691.531936	0.024313	15.26	−0.92
$\mathbf{3}^{2+}$	S*t*Bu	parallel	−3770.097248	−3770.120872	0.023624	14.82	−1.35
$\mathbf{1}^{2+}$	SMe	perpendicular	−3534.284440	−3534.310457	0.026017	16.33	0.15
$\mathbf{2}^{2+}$	S*i*Pr	perpendicular	−3691.485311	−3691.511060	0.025749	16.16	−0.01
$\mathbf{3}^{2+}$	S*t*Bu	perpendicular	−3770.083019	−3770.108618	0.025599	16.06	−0.11

[a] Δ*E*{HS-LS} = *E*{HS}−*E*{LS}. [b] Δ*E*$_{rel}${HS-LS} = Δ*E*{HS-LS}−[Δ*E*{HS-LS, $[Fe(bpp)_2]^{2+}$}]. A negative Δ*E*$_{rel}${HS-LS} value means the high-spin state is more stable than for $[Fe(bpp)_2]^{2+}$, and *vice versa*.[15,23]

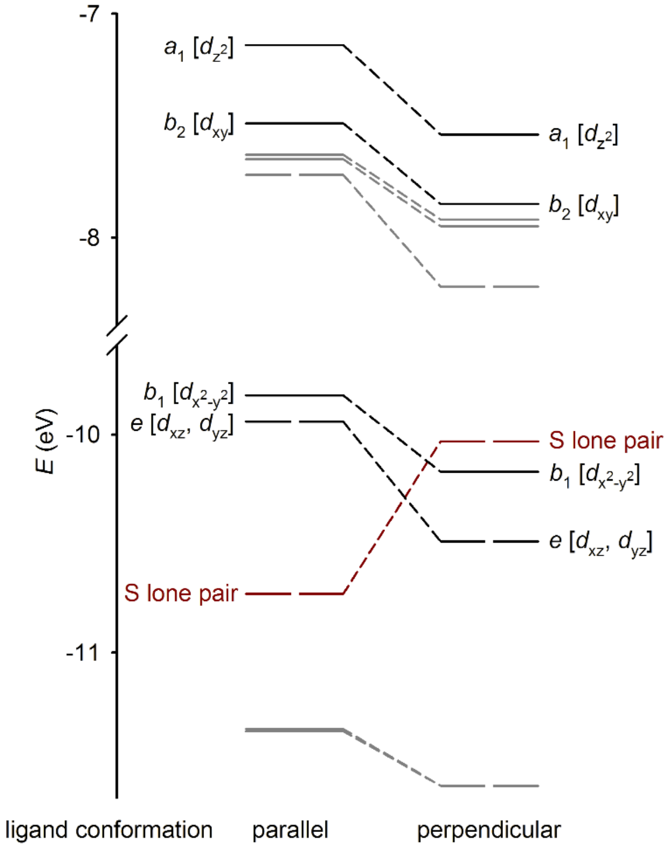

Figure 4 Computed frontier orbital energies for the parallel and perpendicular conformations of low-spin $\mathbf{3}^{2+}$. Energy levels are colour coded as: metal-based *d*-orbitals (black); sulfur atom lone pair orbitals (red); and ligand-based π or π* MOs (grey). The *d*-orbitals have D_{2d} symmetry labels, which is the point group of an idealised $[Fe(bpp)_2]^{2+}$ cation.

the iron t_{2g} *d*-subshell. While all the *d*-orbital energies are lowered in the perpendicular conformation, the difference is *ca* twice as large for the *e* [d_{xz}, d_{yz}] orbitals which are responsible for that back-bonding. Calculated from the average t_{2g} and e_g *d*-orbital energies, Δ_{oct} in the perpendicular conformation is 2.3-2.4 kcal mol^{-1} larger than for the parallel conformation in each complex. That stronger ligand field thus favours the low-spin form, and increases $T_{½}$ as observed.[15,16]

In conclusion, $T_{½}$ for SCO in solution for $\mathbf{3[BF_4]_2}$ is *ca* 40 K higher than expected when compared with its analogues $\mathbf{1[BF_4]_2}$ and $\mathbf{2[BF_4]_2}$. DFT calculations imply this reflects the conformational preferences of their alkylsulfanyl substituents which lie coparallel with their pyridyl rings in $\mathbf{1}^{2+}$ (Scheme 1, R = SMe) and $\mathbf{2}^{2+}$ (R = S*i*Pr), but adopt a perpendicular orientation in $\mathbf{3}^{2+}$ (R = S*t*Bu; Figure 2). These results quantify the contribution of metal/ligand π-bonding to the spin state of $[Fe(bpp^R)_2]^{2+}$ derivatives,[15] and other complexes of aromatic ligands.[8-12] They also highlight that the conformation of a ligand substituent should be considered when rationalising or designing the spin state of a complex, for catalysis or functional materials applications.[1-5]

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Conflicts of interest

There are no conflicts to declare.

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