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# Anion-Dependent Spin Crossover in Solution for an Iron(II) Complex of a 1*H*-Pyrazolyl Ligand†

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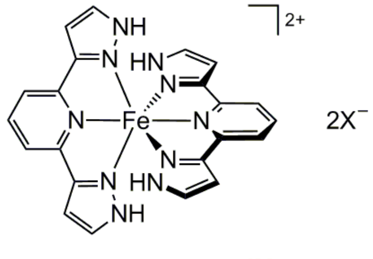
**The spin-crossover equilibrium midpoint temperature ($T_{½}$) in $[Fe(3\text{-bpp})_2]X_2$ (3-bpp = 2,6-di{pyrazol-3-yl}pyridine) varies from 259 K when $X^− = BPh_4^−$ to 277 K when $X^− = Br^−$, at 10 mM concentrations in an acetone:water solvent mixture.**

Metal-organic spin-crossover (SCO) materials continue to be heavily studied in the solid state,[1] with particular current interest in their applications in nanoscience.[2] However, while ultrafast spectroscopy in solution has elucidated the atomistic mechanism of the spin-transition event,[3] interest in solution-phase SCO has otherwise developed more slowly.[4,5] Individual examples of cooperative SCO switching in micelles,[6] a spin-state dependent MRI response from an iron complex,[7] an SCO complex that binds barbiturate in solution[8] and designs of anion-responsive SCO centre,[9,10] have all been demonstrated. These results imply the UV/vis and paramagnetic NMR changes induced by SCO could be of use for sensor applications, for example.[5]

The anion-dependent complexes $[Fe(H_2bip)_2L]^{2+}$ ($H_2bip$ = 2,2′-bi{1,4,5,6-tetrahydropyrimidine}; L = $H_2bip$, bipy etc) are the best characterised system where SCO is triggered by supramolecular host:guest binding.[9] The low-spin state of these complexes is favoured in the presence of strongly associating halide anions, which interact with the chelating N–H groups at the periphery of the $H_2bip$ ligands. Earlier investigations of anion-dependent SCO in other compounds had shown negative results,[11,12] possibly because those studies were performed in aqueous solution or water-containing solvent mixtures. Water tends to disrupt host:guest interactions to anions, all other things being equal, because of its polarity and strong hydrogen-bonding character.[13] A contributing factor to the successful observation of anion binding by $[Fe(H_2bip)_2L]^{2+}$ may be that those studies were performed in the less competitive solvent dichloromethane.[9]

The complex $[Fe(3\text{-bpp})_2]^{2+}$ (**$1^{2+}$**; 3-bpp = 2,6-di{pyrazol-3-yl}pyridine) has been important to the development of several aspects of SCO research.[14] Its chemistry was originally developed by Goodwin *et al.,*[12,15-17] but it has since been employed by others in a variety of supramolecular and multi-functional spin-crossover materials.[18,19] These studies have been facilitated by the unusual stability of **$1^{2+}$** in water,[20] which has allowed a large number of salts of this complex to be precipitated and crystallsed. Twenty years ago Goodwin *et al.* reported solution-phase SCO data for the $I^−$, $BF_4^−$ and $PF_6^−$ salts of **$1^{2+}$** in an unspecified acetone:water mixture, concluding that "…all three salts show essentially the same behaviour".[12] However, reexamination of their data implies that the SCO midpoint temperature ($T_{½}$) for $[Fe(3\text{-bpp})_2]I_2$ (**$1I_2$**) lies 10 K higher than for the other two salts (ESI†). That follows the trend expected from the $[Fe(H_2bip)_2L]^{2+}$ system,[9] and would be another rare observation of anion-dependent spin-crossover. This result required clarification, however, since SCO in **$1^{2+}$** in acetone:water is sensitive to the composition of the solvent mixture.[20] We report here a re-examination of this system which confirms that guest-responsive SCO can be observed in **$1^{2+}$**, even in a competitive solvent.



$[Fe(3\text{-bpp})_2]X_2$ (**$1X_2$**)
$X^−$ = $BPh_4^−$, $BF_4^−$, $CF_3SO_3^−$, $NCS^−$, $NO_3^−$ or $Br^−$

The salts **$1X_2$** ($X^−$ = $BPh_4^−$, $BF_4^−$, $CF_3SO_3^−$, $NO_3^−$ and $Br^−$) were prepared by the literature procedures‡.[12,15,19] The $BPh_4^−$, $BF_4^−$ and $CF_3SO_3^−$ salts were recrystallised from $MeNO_2/Et_2O$, while the other less soluble salts were recrystallised from MeOH/Et$_2$O. While **1[BF$_4$]$_2$** was isolated as a solvent-free powder after drying *in vacuo*, all the other salts contained water or methanol of crystallisation in their purified forms by microanalysis (ESI†; hydrate formation is a common feature of the chemistry of **1X$_2$** salts[14]). Preliminary screening by $^1$H NMR in CD$_3$CN, (CD$_3$)$_2$CO and a 9:1 v/v (CD$_3$)$_2$CO:D$_2$O mixture at 293 K established a small, but consistent dependence of the paramagnetic isotropic shifts from **1X$_2$** on the anion X$^-$ (ESI†). In both solvents, the contact shifts (and hence the magnetic moment[21]) of the sample followed the order in X$^-$: $BPh_4^- \approx BF_4^- > CF_3SO_3^- > NO_3^- \approx Br^-$ (**1[NO$_3$]$_2$** and **1Br$_2$** were only soluble in the mixed solvent system). This is the trend expected if the high:low-spin state population of the complex in solution is perturbed by more coordinating anions.[22] Consistent with that suggestion, all five salts gave identical isotropic shifts within experimental error in the more polar solvent CD$_3$OD, where hydrogen bonding between **1**$^{2+}$ and X$^-$ should be weaker.

These initial observations were quantified by variable temperature Evans method measurements (Fig. 1, Table 1). These were performed in the 9:1 v/v (CD$_3$)$_2$CO:D$_2$O solvent mixture, corresponding to 31.2 mol % D$_2$O. Addition of water to the solvent was necessary to afford a medium in which all five salts were sufficiently soluble. The data for **1[BF$_4$]$_2$** under these conditions are consistent with those we have reported for that salt in other (CD$_3$)$_2$CO:D$_2$O solvent compositions.[20]

All five salts exhibit an SCO equilibrium under these conditions, centred just below room temperature (Fig. 1). The $T_{½}$ values obtained show the clear trend in X$^-$:

$$BPh_4^- \approx BF_4^- > CF_3SO_3^- > NO_3^- > Br^-$$

This correlates perfectly with the hydrogen-bonding capability of those anions, as expressed by Lungwitz and Spange's $\beta^N$ parameter (Fig. 2).[22] Importantly, Goodwin's original data for **1[PF$_6$]$_2$** and **1I$_2$** in an unspecified (CD$_3$)$_2$CO:D$_2$O solvent composition also agree well with these new results (Table 1, Fig. 2).[12] The enthalpy and entropy of SCO for four of the salts in Table 1 (from van'T Hoff isochore plots) are similar, and are consistent with previously reported values for **1[BF$_4$]$_2$** in (CD$_3$)$_2$CO:D$_2$O mixtures.[20] The exception is **1Br$_2$**, whose $\Delta H$ and $\Delta S$ values are unexpectedly lower, and closer to those shown by salts of **1**$^{2+}$ in pure organic solvents including (CD$_3$)$_2$CO (Table 1). A reduction in $\Delta H$ and $\Delta S$ was also observed when Br$^-$ was titrated into **1[BPh$_4$]$_2$** (see below, Table 1). We suggest that it may reflect a weaker solvation shell about the **1**$^{2+}$ cations induced by the strongly associated Br$^-$ anions, which would reduce the rearrangement of the solvent accompanying SCO. That remains to be confirmed, however. Notably nucleophilic displacement of 3-bpp from the iron centre by Br$^-$, which is a potential side-reaction in the high-spin form of the complex, would have the opposite effect of raising $\Delta H$ and $\Delta S$.[4]

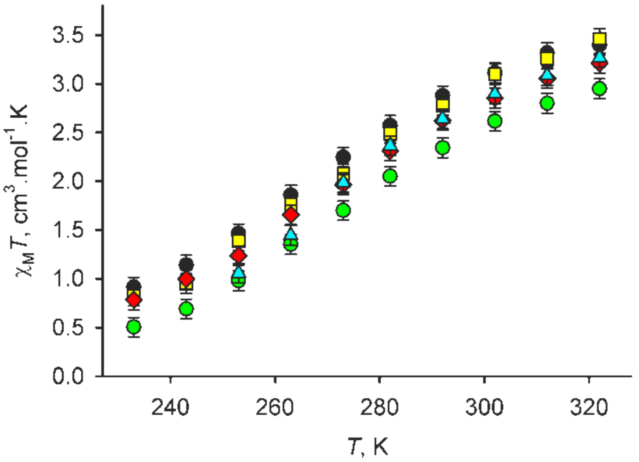


**Fig. 1** Variable temperature magnetic susceptibility data for **1X$_2$** in 9:1 v/v (CD$_3$)$_2$CO:D$_2$O, with X$^-$ = BPh$_4^-$ (black circles), BF$_4^-$ (yellow squares), CF$_3$SO$_3^-$ (red diamonds), NO$_3^-$ (cyan triangles) and Br$^-$ (green circles) §.

**Table 1** Spin-crossover parameters for the salts [Fe(3-bpp)$_2$]X$_2$ (**1X$_2$**) in 9:1 v/v (CD$_3$)$_2$CO:D$_2$O and pure (CD$_3$)$_2$CO, measured by Evans method (Figs. 1 and 2) §. See ref. 22 for the definition of $\beta^N$.

| X$^-$ | $\beta^N$ | $T_{½}$, K[a] | $\Delta H$, kJ mol$^{-1}$ | $\Delta S$, J mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|---|
| **1X$_2$**, 9:1 v/v (CD$_3$)$_2$CO:D$_2$O | | | | |
| BPh$_4^-$ | 0 | 259(1) | 31.5(4) | 121(2) |
| PF$_6^-$ [a] | 0.64 | 258 | – | – |
| BF$_4^-$ | 0.69 | 261(1) | 30.6(4) | 117(2) |
| CF$_3$SO$_3^-$ | 0.74 | 264(1) | 29.9(4) | 113(2) |
| NO$_3^-$ | 0.86 | 268(1) | 33.2(4) | 124(2) |
| I$^-$ [a] | 0.88 | 268 | – | – |
| Br$^-$ | 0.93 | 274(1) | 25.9(4) | 95(2) |
| **1X$_2$**, (CD$_3$)$_2$CO | | | | |
| BPh$_4^-$ | 0 | 243(1) | 20.3(2) | 83(1) |
| BF$_4^-$ [b] | 0.69 | 247(1) | 24.8(2) | 100(1) |
| CF$_3$SO$_3^-$ | 0.74 | 252(1) | 22.0(2) | 87(1) |
| **1[BPh$_4$]$_2$** + $y$[NBu$_4$]Br, 9:1 v/v (CD$_3$)$_2$CO:D$_2$O | | | | |
| $y = 0$ | – | 259(1) | 31.5(4) | 121(2) |
| $y = 0.78$ | – | 264(1) | 29.7(4) | 111(2) |
| $y = 1.71$ | – | 269(1) | 25.0(4) | 93(2) |

[a] From ref. 12. The stoichiometry of the (CD$_3$)$_2$CO:D$_2$O solvent mixture used in ref. 12 was not specified, but is probably similar to that in this work.[20]
[b] From ref. 20.

For comparison, the three **1X$_2$** salts that are soluble in pure (CD$_3$)$_2$CO were also measured in that solvent (Table 1, Fig. 2 and ESI†). The results are consistent with those above in showing a 9 K increase in $T_{½}$ for **1[CF$_3$SO$_3$]$_2$** compared to **1[BPh$_4$]$_2$**, a slightly larger difference than in the more polar solvent mixture. Lastly, titration of [NBu$_4$]Br into **1[BPh$_4$]$_2$** in 9:1 (CD$_3$)$_2$CO:D$_2$O yielded an increase in $T_{½}$ with increasing bromide concentration, that is consistent with the behaviour of the pure **1[BPh$_4$]$_2$** and **1Br$_2$** salts (Table 1 and ESI†).

The salts **1[BPh$_4$]$_2$**, **1[BF$_4$]$_2$**, **1[CF$_3$SO$_3$]$_2$**, **1[NO$_3$]$_2$** and **1Br$_2$** all show the same UV/vis metal-to-ligand charge-transfer (MLCT) maximum, at $\lambda_{max}$ = 456 nm ($\varepsilon_{max}$ = 3.6±0.1 x10$^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$) in 9:1 v/v (CH$_3$)$_2$CO:H$_2$O at 293 K (ESI†). The invariance of these spectra with the anion present is inconsistent with the Evans method data, since $\varepsilon_{max}$ of this MLCT band should increase with $T_{½}$ which raises the low-spin fraction of the complex at room temperature.[20] That might reflect the sample concentrations in the UV/vis measurements (0.2 mM), which were *ca.* 50x lower than for the Evans method experiments (10 mM). Low concentrations promote host:guest dissociation in solution, which would explain the discrepancy between the techniques.

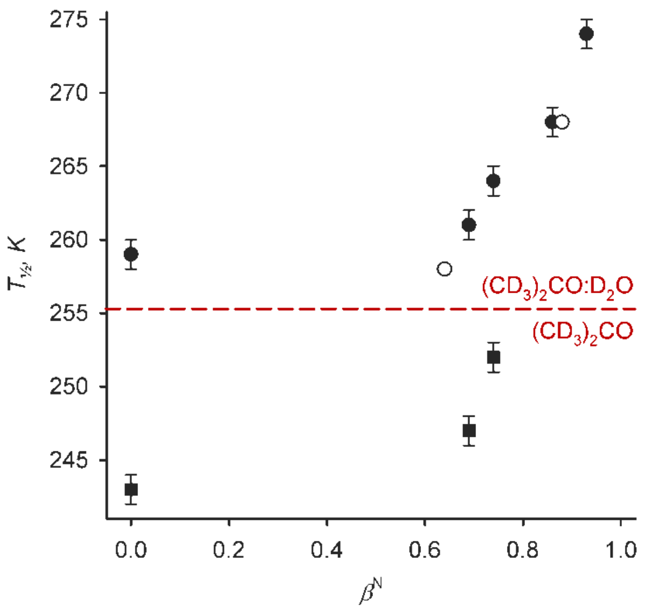


**Fig. 2** Plot of the spin-crossover mid-point temperature $T_{\frac{1}{2}}$ of the salts **$1X_2$** *vs.* the hydrogen-bonding power of the $X^-$ anion ($\beta^{N}$ [21]) in 9:1 v/v $(CD_3)_2CO:D_2O$ (circles) and pure $(CD_3)_2CO$ (squares) §. The black data points are from this work, while the white circles are the $I^-$ and $PF_6^-$ salts measured by Goodwin *et al.*[12] The solvent dependence of these data is discussed in ref. 20.

In conclusion, we have demonstrated a dependence between spin-crossover in $[Fe(3\text{-bpp})_2]^{2+}$ (**$1^{2+}$**) and the presence of hydrogen bonding anions, in a polar solvent mixture at NMR concentrations (*ca.* 10 mM). As with the $[Fe(H_2bip)_2L]^{2+}$ system,[9] more strongly associating anions favour the low-spin state of the complex and increase $T_{\frac{1}{2}}$. That is noteworthy, because evidence for the influence of hydrogen-bonding anions on $T_{\frac{1}{2}}$ in solid SCO materials has been contradictory up to now.[23] The sensitivity of **$1^{2+}$** to hydrogen bonding to anions (and to solvent[20]) arises because the hydrogen bond-donor N−H groups in 3-bpp are directly covalently bonded to the metal-donor N atoms. Hence small perturbations in the electronic character of the ligand, caused by changes in hydrogen bonding, are transmitted effectively to the coordinated iron atom.

Although the response of $T_{\frac{1}{2}}$ to different anions in **$1^{2+}$** is smaller than in $[Fe(H_2bip)_2L]^{2+}$ derivatives, this work was performed in more competitive solvents (including an acetone:water mixture) where hydrogen bonding between **$1^{2+}$** and $X^-$ is expected to be weaker.[13] The fact that any correlation between $T_{\frac{1}{2}}$ and $X^-$ is observed under our conditions is noteworthy for a monodentate hydrogen bond-donor like **$1^{2+}$**, and confirms that SCO in **$1^{2+}$** is sensitive to host:guest interactions. Therefore, the $[Fe(3\text{-bpp})_2]^{2+}$ motif is a promising platform for the development of SCO-based sensor applications. Our current work aims to modify the 3-bpp ligand design, to maximise its host:guest binding capabilities.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental details, elemental microanalysis, NMR, Evans method and UV/vis data. For ESI see DOI: 10.1039/####.

‡ The salt **$1[NCS]_2$**[16] was also investigated in this work. However, solutions of this compound substantial amounts of uncoordinated 3-bpp by $^1H$ NMR (ESI†), which probably reflects competitive displacement of 3-bpp from the metal centre by the nucleophilic $NCS^-$ ion.[24] For this reason, **$1[NCS]_2$** was not investigated further during this study. Smaller amounts (<10 %) of free 3-bpp are also present in solutions of **$1[NO_3]_2$** and **$1Br_2$** by NMR, and ligand displacement equilibria may make a small contribution to $\Delta H$ and $\Delta S$ of SCO in those salts.[4,20]

§ The differing values of $\chi_M T$ at the high- and low-temperature ends of these plots reflect the temperature window of the measurements, which was limited by the liquid range of the solvent. Hence the data do not cover the full the spin-state equilibria, which will span a temperature range of *ca.* 150 K from start to finish.[4,5] The $T_{\frac{1}{2}}$ values in Table 1 and Fig. 2, and the van'T Hoff plots, were calculated assuming that the fully high-spin complex exhibits $\chi_M T$ = 3.5±0.1 $cm^3$ $mol^{-1}$ K under all the conditions used. That approximation is supported by our earlier work.[20]

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