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

Simon A. Barrett and Malcolm A. Halcrow*

The spin-crossover equilibrium midpoint temperature ($T_{1/2}$) in [Fe(3-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, with particular current interest in their applications in nanoscience. However, while ultrafast spectroscopy in solution has elucidated the atomistic mechanism of the spin-transition event, interest in solution-phase SCO has otherwise developed more slowly. Individual examples of cooperative SCO switching in micelles, a spin-state dependent MRI response from an iron complex, an SCO complex that binds barbiturate in solution and designs of anion-responsive SCO centre, all three salts show essentially the same behaviour. However, reexamination of their data implies that the SCO midpoint temperature ($T_{1/2}$) for [Fe(3-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$_2$bip)$_2$L]$^{2+}$ system, 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. 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.

The anion-dependent complexes [Fe(H$_2$bip)$_2$L]$^{2+}$ (H$_2$bip = 2,2′-bi{1,4,5,6-tetrahydropyrimidine}; L = H$_2$bip, bipy etc) are the best characterised system where SCO is triggered by supramolecular host:guest binding. 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$_2$bip ligands. Earlier investigations of anion-dependent SCO in other compounds had shown negative results, 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. A contributing factor to the successful observation of anion binding by [Fe(H$_2$bip)$_2$L]$^{2+}$ may be that those studies were performed in the less competitive solvent dichloromethane.

The complex [Fe(3-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. Its chemistry was originally developed by Goodwin et al., but it has since been employed by others in a variety of supramolecular and multi-functional spin-crossover materials. These studies have been facilitated by the unusual stability of 1$^{2+}$ in water, which has allowed a large number of salts of this complex to be precipitated and crystallised. 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”. However, reexamination of their data implies that the SCO midpoint temperature ($T_{1/2}$) for [Fe(3-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$_2$bip)$_2$L]$^{2+}$ system, 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. 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.

The salts 1X$_2$ (X$^-$ = BPh$_4^-$, BF$_4^-$, CF$_3$SO$_3^-$, NCS$^-$, NO$_3^-$ or Br$^-$) were prepared by the literature procedures. The BPh$_4^-$, BF$_4^-$ and CF$_3$SO$_3^-$ salts were recrystallised from MeNO$_2$/Et$_2$O.
while the other less soluble salts were recrystallised from MeOH/Et₂O. While 1[BF₄]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 1X₂ salts)¹⁴. Preliminary screening by ¹H NMR in CD₂CN, (CD₃)₂CO and a 9:1 v/v (CD₃)₂CO:D₂O mixture at 293 K established a small, but consistent dependence of the paramagnetic isotropic shifts from 1X₂ on the anion X⁻ (ESI†). In both solvents, the contact shifts (and hence the magnetic moment) of the sample followed the order in X⁻: BF₄⁻ > CF₃SO₃⁻ > NO₃⁻ ≈ Br⁻ (1[NO₃]₂ and 1Br₂ 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.²⁰ Consistent with that suggestion, all five salts gave identical isotropic shifts within experimental error in the more polar solvent CD₃OD, where hydrogen bonding between 1⁺ 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 (CD₃)₂CO:D₂O solvent mixture, corresponding to 31.2 mol % D₂O. Addition of water to the solvent was necessary to afford a medium in which all five salts were sufficiently soluble. The data for 1[BF₄]₂ under these conditions are consistent with those we have reported for that salt in other (CD₃)₂CO:D₂O solvent compositions.²⁰

All five salts exhibit an SCO equilibrium under these conditions, centred just below room temperature (Fig. 1). The Tₛ values obtained show the clear trend in X⁻: BPh₄⁻ > BF₄⁻ > CF₃SO₃⁻ > NO₃⁻ > Br⁻ This correlates perfectly with the hydrogen-bonding capability of those anions, as expressed by Lungwitz and Spange’s βN parameter (Fig. 2).²³ Importantly, Goodwin’s original data for 1[PF₆]₂ and 1I₂ in an unspecified (CD₃)₂CO:D₂O 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[BF₄]₂ in (CD₃)₂CO:D₂O mixtures.²⁰ The exception is 1Br₂, whose ∆H and ∆S values are unexpectedly lower, and closer to those shown by salts of 1⁺ in pure organic solvents including (CD₃)₂CO (Table 1). A reduction in ∆H and ∆S was also observed when Br⁻ was titrated into 1[BPh₄]₂ (see below, Table 1). We suggest that it may reflect a weaker solvation shell about the 1⁺ 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 ∆H and ∆S.⁴

For comparison, the three 1X₂ salts that are soluble in pure (CD₃)₂CO 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 Tₛ for 1[CF₃SO₃]₂ compared to 1[BPh₄]₂, a slightly larger difference than in the more polar solvent mixture. Lastly, titration of [NBu₄]Br into 1[BPh₄]₂ in 9:1 (CD₃)₂CO:D₂O yielded an increase in Tₛ with increasing bromide concentration, that is consistent with the behaviour of the pure 1[BPh₄]₂ and 1Br₂ salts (Table 1 and ESI†).

The salts 1[BPh₄]₂, 1[BF₄]₂, 1[CF₃SO₃]₂, 1[NO₃]₂ and 1Br₂ all show the same UV/vis metal-to-ligand charge-transfer (MLCT) maximum, at λmax = 456 nm (εmax = 3.6±0.1 x10⁵ dm³ mol⁻¹ cm⁻¹) in 9:1 v/v (CH₃)₂CO:H₂O at 293 K (ESI†). The invariance of these spectra with the anion present is inconsistent with the Evans method data, since εmax of this MLCT band should increase with Tₛ 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.

Table 1 Spin-crossover parameters for the salts [Fe(3-bpp)₃]X₂ (1X₂) in 9:1 v/v (CD₃)₂CO:D₂O and pure (CD₃)₂CO, measured by Evans method (Figs. 1 and 2) ⁶. See ref. 22 for the definition of βN.

<table>
<thead>
<tr>
<th>X⁻</th>
<th>βN</th>
<th>Tₛ, K</th>
<th>∆H, kJ mol⁻¹</th>
<th>∆S, J mol⁻¹ K⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPh₄⁻</td>
<td>0</td>
<td>259(1)</td>
<td>31.5(4)</td>
<td>121(2)</td>
</tr>
<tr>
<td>PFB⁺</td>
<td>0.64</td>
<td>258</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>BF₄⁻</td>
<td>0.69</td>
<td>261(1)</td>
<td>30.6(4)</td>
<td>117(2)</td>
</tr>
<tr>
<td>CF₃SO₃⁻</td>
<td>0.74</td>
<td>264(1)</td>
<td>29.9(4)</td>
<td>113(2)</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.86</td>
<td>268(1)</td>
<td>33.2(4)</td>
<td>124(2)</td>
</tr>
<tr>
<td>I⁻</td>
<td>0.88</td>
<td>268</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Br⁻</td>
<td>0.93</td>
<td>274(1)</td>
<td>25.9(4)</td>
<td>95(2)</td>
</tr>
<tr>
<td>BF₄⁻</td>
<td>0.69</td>
<td>247(1)</td>
<td>24.8(2)</td>
<td>100(1)</td>
</tr>
<tr>
<td>CF₃SO₃⁻</td>
<td>0.74</td>
<td>252(1)</td>
<td>22.0(2)</td>
<td>87(1)</td>
</tr>
</tbody>
</table>

| 1[X₂, (CD₃)₂CO] ± ν[NBu₄]Br, 9:1 v/v (CD₃)₂CO:D₂O |
|----|-----|--------|--------------|-----------------|
| y = 0 | 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)           |

From ref. 12. The stoichiometry of the (CD₃)₂CO:D₂O solvent mixture used in ref. 12 was not specified, but is probably similar to that in this work.⁶

From ref. 20.
In conclusion, we have demonstrated a dependence between spin-crossover in [Fe(3-bpp)]^{3+} (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_{2}bip)]^{2+} system,^{9} more strongly associating anions favour the low-spin state of the complex and increase T_{1/2}. That is noteworthy, because evidence for the influence of hydrogen-bonding anions on T_{1/2} in solid SCO materials has been contradictory up to now.^{23} The sensitivity of T_{1/2} to hydrogen bonding to anions (and to solvent) 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_{1/2} to different anions in 1^{2+} is smaller than in [Fe(H_{2}bip)]^{2+} derivatives, this work was performed in more competitive solvents (including an acetonewater mixture) where hydrogen bonding between 1^{2+} and X− is expected to be weaker.^{13} The fact that any correlation between T_{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-bpp)]^{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


