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Magnetic Observation of Anion Binding in Iron Coordination Complexes: Toward Spin-Switching Chemosensors

Zhaoping Ni and Matthew P. Shores*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523-1872

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An emerging goal in preparing functional materials from spin-crossover (SC) complexes[1] is to harness secondary noncovalent interactions to affect spin-state changes in a controlled manner. This has been investigated most recently in liquid crystalline materials containing spin labile ions.[2] The spectroscopic, magnetic, and physical changes associated with spin state switching may serve as a multichannel reporter for host−guest interactions. Although anion-, solvent-, or guest-induced SC changes in the solid state are known,[3] such guest-dependent spin switching has not been observed for molecular species in solution. Herein, we present initial findings on a prototype spin-switching anion receptor, $[Fe(H_2bip)_3](BPh_4)_2$ (**1**) (Figure 1, H_2bip = 2,2′-bi-1,4,5,6-tetrahydropyrimidine), which exhibits dramatic spin state changes in dichloromethane solution when interrogated by anions capable of hydrogen bonding interactions.

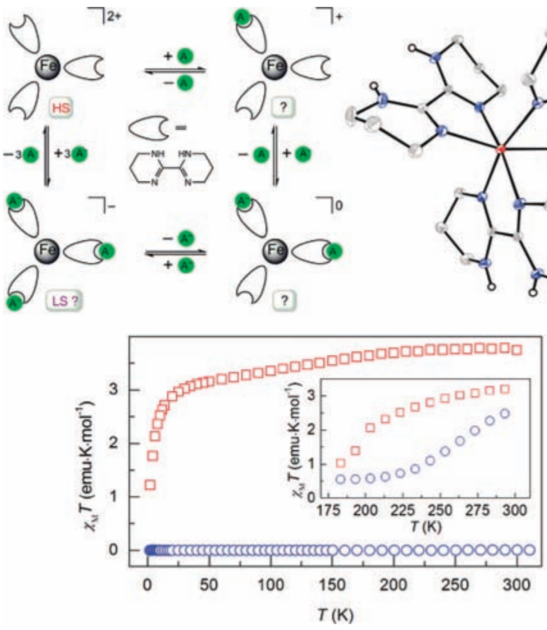

Figure 1. Top left: Schematic representation of a prototypical spin-switching anion sensor based on **1**. Top right: Crystal structure of the $[Fe(H_2bip)_3]^{2+}$ cation in **1**, rendered at 40% ellipsoids. Red, blue, and gray ellipsoids represent Fe, N, and C atoms; H atoms bound to C atoms are removed for clarity. Bottom: Temperature dependence of the solid-state magnetic susceptibility for **1** (red) and **2** (blue), measured at 1000 G. Inset: Solution (CD_2Cl_2) magnetic susceptibility data for **1** and **2**.

Anion recognition has received increasing attention because of its important roles in biological and environmental systems.[4] The incorporation of diamagnetic transition metal and organometallic species into receptor assemblies has led to the development of several new strategies for reporting anion binding.[5] A recently reported Fe(II)-containing species uses the metal ion to poise the receptor moieties for efficient anion-binding but does not display distinctive changes in magnetism.[6] Nevertheless, switching between the high- and low-spin (HS and LS) states in suitably designed Fe(II) complexes offers the potential to use magnetometry to report anion binding.

The observation of anion dependence in the SC properties of $[Fe(H_2bip)_3]X_2$ complexes ($X = BPh_4^-$, ClO_4^-) intrigued us, because simple changes of the charge balancing anion were shown to produce substantial differences in solid state spin-transition temperatures.[7] To elucidate key magnetostructural correlations, we sought heretofore missing solution and solid state structural data for these complexes. The BPh_4^- salt **1** was prepared according to the literature,[7,8] and modification of these methods allowed for the preparation of the Br^- salt **2** and mixed anion salt $[Fe(H_2bip)_3](BPh_4)Br$ **3**. Details can be found in the Supporting Information. The low temperature (100 K) X-ray structure of the complex cation in **1** shows a distorted octahedral FeN_6 geometry and Fe−N distances (avg $d_{Fe-N} = 2.172(1)$ Å) characteristic of HS Fe(II) ions[1] (Figure 1). The closest contact between the complex cation and charge-balancing anion ($N(H_2bip)\cdots C(BPh_4^-)$) is 3.273(2) Å and does not follow any obvious hydrogen-bonding pathway (Figure S1). Although **2** forms microcrystals only, X-ray analysis of **3** shows an LS Fe(II) ion (avg $d_{Fe-N} = 1.978(3)$ Å) and close $N-H\cdots Br^-$ contacts (shortest $d_{N-Br} = 3.301(3)$ Å) consistent with hydrogen bonding interactions (Figure S4).

The temperature dependence of the solid state magnetic susceptibilities of **1** and **2** were investigated down to 2 K (Figure 1, bottom). For **1**, $\chi_M T$ values gradually decrease from 3.74 emu·mol^{-1}·K at 300 K to 2.87 emu·mol^{-1}·K at 20 K then suddenly decrease below 20 K, indicative of a magnetically anisotropic HS Fe(II) ion.[3b,7] In contrast, the negligible magnetic susceptibility of **2** at all temperatures measured signifies an LS Fe(II) species.[1]

The ^1H NMR spectra of **1** and **2** collected at 293 K in CD_2Cl_2 (Figure S6) are consistent with D_3-symmetric structures on the NMR time scale.[8] The N−H signal from the cation shifts greatly from 86.0 ppm for **1** to 67.4 ppm for the Br^- complex **2**, suggesting significant $N-H\cdots Br^-$ interactions in solution. The temperature dependencies of the magnetic susceptibilities (Evans method,[9] CD_2Cl_2) show that both **1** and **2** possess spin-crossover properties in solution,[10] albeit with considerable anion dependence (Figure 1, bottom inset). The $\chi_M T$ values for **1** gradually decrease from 3.21 emu·mol^{-1}·K at 293 K to 2.52 at 223 K and then drop off more steeply to 1.03 emu·mol^{-1}·K at 183 K. Meanwhile, the $\chi_M T$ values for **2** decrease steadily from 2.49 emu·mol^{-1}·K at 293 K to 0.73 at 223 K and then change very little down to 183 K (0.55 emu·mol^{-1}·K). The largest $\chi_M T$ difference (1.82 emu·mol^{-1}·K) occurs at 233 K. At this temperature, **1** and **2** are essentially in the HS and LS states, respectively.

Although spin switching at room temperature is very weak, dichloromethane solutions of **1** do exhibit a slight color change

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from dark red to violet upon addition of anions. An absorption at 497 nm, assignable to charge-transfer bands in **1**,[7,8] shifts by 32 nm when combined with excess Bu_4NBr; at the same time, a new shoulder at 580 nm continuously increases in intensity (Figures S7 and S8). The Job plot of **1** with Br^- at 529 nm shows a 1:3 stoichiometry (Figure S9), which is consistent with three binding ligands.[11] Titrations with other anions do not significantly change the spectral progression but do show different concentration dependencies. Association constants for the $[Fe(H_2bip)_3]^{2+}$ receptor determined from these titrations are summarized in Table 1. The affinities track in the order $Br^- > Cl^- > I^- > NO_3^- > ClO_4^-$.

Table 1. Overall Anion Binding Constants (log β)[a] for Interaction of **1** with Bu_4NX in Dichloromethane at 296 K[b]

X	log β_{11}	log β_{12}	log β_{13}
Cl^-	5.7	10.7	14.1
Br^-	6.4	11.0	14.3
I^-	5.5	9.6	13.4
NO_3^-	4.5	8.6	12.5
ClO_4^-	4.5	8.0	11.3

[a] $\beta_{mn} = [H_mG_n]/[H]^m[G]^n$, where [H] and [G] denote the concentration of free host and guest, respectively. [b] Values were determined by UV−visible spectroscopic titrations. All anions were used in the form of their respective tetrabutylammonium salts.

While it can be challenging to separate anion binding effects from solvent and steric influences,[12] literature precedent suggests that hydrogen bonding and anion-ligand interactions primarily increase the σ-donating ability of ligands bound to Fe(II) ions in the solid state.[13] Reminiscent of the "magnetochemical" series proposed by Reed,[14] a weakly HS Fe(II) complex subjected to a moderately strong interaction between an anion and the ligand should aid in stabilization of the LS state. To ascertain if binding affinity correlates with spin switching, we investigated the anion recognition abilities of **1** toward Br^-, I^-, and ClO_4^- via ^1H NMR titration experiments (CD_2Cl_2, Figure 2a). At both 293 and 233 K, the N−H signal in **1** displays significant upfield shifts upon addition of 3 equiv of Bu_4NBr.[4] Slightly less dramatic movement occurs for iodide, whereas only gradual shifting is found in the perchlorate titration. These results are consistent with the room temperature UV−visible spectrophotometric titrations. Furthermore, there is no evidence of free ligand appearing even after addition of excess salt, indicating that the $[Fe(H_2bip)_3]^{2+}$ species is stable in this environment.

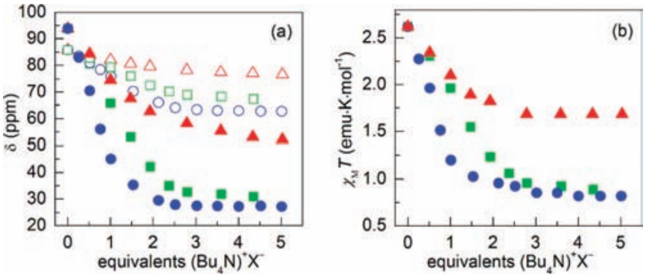

Figure 2. Change in (a) N−H chemical shifts at 293 K (open data) and 233 K (closed data); and (b) magnetic susceptibility data at 233 K upon the addition of Bu_4NX ($X = Br^-$ (blue), I^- (green), ClO_4^- (red)) to **1** in CD_2Cl_2.

Most significantly, the magnetic susceptibility measured at 233 K (Figure 2b) shows a nearly monotonic correlation between anion-binding strength and Fe(II) spin state population. Whereas perchlorate titration does not achieve a complete switch from an HS to LS state, the more strongly interacting iodide and bromide species cause spin state changes after addition of *ca.* 3 and 2 equiv, respectively.

Although the susceptibility of spin-crossover compounds to small external perturbations is often considered problematic,[15] this particular characteristic has the potential to be exploited in chemical sensing applications, where sensitivity and rapid response to subtle environmental stimuli are desirable qualities. The foregoing results demonstrate that significant changes in spin state can be achieved in solution via secondary host−guest interactions. Experiments are underway in our laboratory to further elucidate the factors that affect this spin-transition, so as to more robustly link analyte binding to spin switching, with the goal to shift the sensing phenomenon to higher working temperatures and more environmentally relevant solvents.

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Supporting Information Available: X-ray structural data (cif, CCDC reference numbers 708760−708764); details of experimental procedures and fitting of guest binding curves (pdf). These materials are available free of charge via the Internet at http://pubs.acs.org.

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