

Thermal Spin Crossover in Binuclear Iron(II) Helicates: Negative Cooperativity and a Mixed Spin State in Solution

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The phenomenon of spin crossover continues to intrigue chemists,¹ as much for its theoretical aspects as for possible applications such as optical data storage devices. The most common and convenient system to be studied is the low spin iron(II) ($S = 0$) to high spin iron(II) ($S = 2$) transition, which is accompanied by a dramatic change in magnetic properties, Mössbauer spectra, and color. In solution or in diluted solid state samples, the spin transition curve may be described by a simple chemical equilibrium, in which the unfavorable enthalpy change associated with the low spin to high spin transition is compensated as the temperature rises by the greater entropy of the high spin state. In the solid state, however, the different iron centers are coupled by the intermolecular forces holding the crystal together, and cooperative effects may be observed. For positive cooperativity, the spin transition curve no longer shows Boltzmann behavior, but shows a very sharp transition in which the iron centers switch from essentially all low spin to all high spin over a very small temperature range.

Binuclear iron complexes are particularly interesting since the iron centers are coupled by intramolecular interactions. There are relatively few studies on such systems, all of which, to our knowledge, concern the solid state. In a series of studies on bipyrimidine bridged complexes,^{2–4} Real and co-workers have shown that the behavior depends strongly on the other ligands present. In some cases, only one of the two iron ions underwent a spin transition,^{2,4} whereas in others,^{3,4} both ions showed spin crossovers, albeit at different temperatures. Very recently a tetranuclear iron grid was shown to undergo spin crossover both in the solid state and in solution.⁵

In all these cases, study of the solid state samples implies the simultaneous presence of intra- and intermolecular forces. To study the effect of intramolecular interactions in the spin crossover process of binuclear compounds, it is necessary to isolate the binuclear species, for example, by working in solution. Recently we observed that the iron(II) triple helicate $[\text{Fe}_2(\mathbf{2})_3]^{4+}$ showed spin crossover behavior in solution⁶ which appeared to be significantly different from that of its mononuclear analogue $[\text{Fe}(\mathbf{1a})_3]^{2+}$, and this seemed an ideal system in which to study the

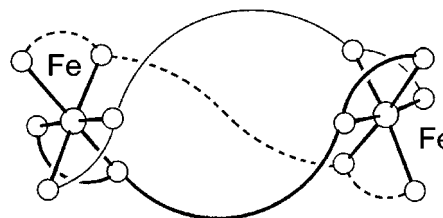
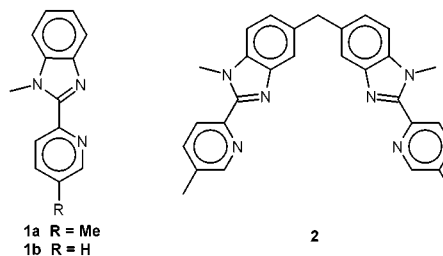


Figure 1. Schematic view of the structure of $[\text{Fe}_2(\mathbf{2})_3]^{4+}$.

Chart 1. Ligands Used in This Work.



intramolecular interactions between the two iron centers. Figure 1 shows a schematic representation of the structure of $[\text{Fe}_2(\mathbf{2})_3]^{4+}$ and shows how the centers are linked through the strands of the ligands.

Although we believe that this is the first example of binuclear thermal spin crossover to be studied in solution, allosteric effects associated with a high spin to low spin transition observed for iron(II) are of course well-known in hemoglobin, where the spin change is induced by binding of molecular oxygen rather than temperature change, and binding of oxygen at an A site enhances the affinity for oxygen at a B site.⁷

The ligands **1a**,⁶ **1b**,⁸ and **2**⁹ were obtained following literature procedures, and the complexes $[\text{Fe}(\mathbf{1a})_3]^{2+}$,⁶ $[\text{Fe}(\mathbf{1b})_3]^{2+}$,¹⁰ and $[\text{Fe}_2(\mathbf{2})_3]^{4+}$ ⁶ were prepared as their perchlorate salts, see Chart 1. (**WARNING!** Perchlorate salts of complexes with organic ligands are potentially explosive and should be treated with great care.¹¹ Only small amounts of complex were used in the course of these experiments).

The spin crossover was followed by observation of the intense MLCT transition of low spin iron(II) around 540 nm, which is an order of magnitude weaker in the high spin complexes. The initial investigation⁶ of $[\text{Fe}(\mathbf{1a})_3]^{2+}$ and $[\text{Fe}_2(\mathbf{2})_3]^{4+}$ in acetonitrile solution showed that the spin transition was far from complete at the boiling point, so a less volatile solvent had to be used.

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Table 1. Calculated Spin Crossover Thermodynamic Parameters

complex	$T_{1/2}$ (K)	ΔH (kJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)
[Fe(1a) ₃] ²⁺	302.3(1)	33.6(2)	111(1)
[Fe(1b) ₃] ²⁺	323.4(1)	30.8(2)	96(1)
Fe ₂ (2) ₃ ⁴⁺	341(4)	32(4)	94(14)
	402(3)	50(7)	124(18)

Propylene carbonate gave good results; control experiments with a slight excess of free ligand showed that decomplexation did not occur in this solvent (unlike in DMF and DMSO).¹² Solutions of the complexes (approximately 10⁻⁴ M) were placed in a variable temperature bath, and the absorbance was measured with an immersible optrode. The experiments were performed under N₂ although, due to the high potentials of these complexes,⁶ oxidation would not be expected. Measurements were made upon heating and cooling and showed no hysteresis.

The absorbance data were fitted, after correction for the slight change in density of propylene carbonate as a function of temperature,¹³ to the desired equilibrium model (see below) using a nonlinear least-squares algorithm with the critical spin transition temperature $T_{1/2}$, the crossover enthalpy change ΔH , and the absorbances of the fully high spin and the fully low spin species as parameters. The calculated thermodynamic parameters are presented in Table 1.

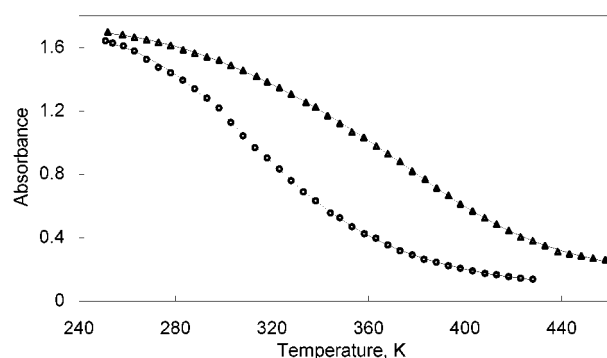
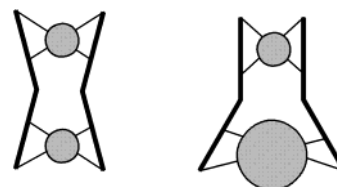
The mononuclear complexes [Fe(**1a**)₃]²⁺ and [Fe(**1b**)₃]²⁺ show a simple equilibrium between low spin and high spin forms, with parameters comparable to those reported for similar complexes in solution¹⁴ and in the solid state.¹⁰ The parameters calculated here for [Fe(**1a**)₃]²⁺ can be considered as an improvement over those previously reported from this laboratory⁶ given the wider temperature range covered in the present investigation.

The data for the binuclear complex [Fe₂(**2**)₃]⁴⁺ showed a gradual transition over a much greater temperature range (Figure 2). A model with a single equilibrium constant did not fit the data, showing systematic deviations between observed and calculated values, and giving a physically nonsensical negative absorption for the high spin form (Figure S1). A two step model (Equation 1) with two different equilibrium constants was therefore used:



The absorbance of the intermediate mixed spin species was assumed to be the average of the all high spin and all low spin values. The three spin forms are simultaneously present in solution over a wide temperature range, and consequently the parameters for the two steps are strongly correlated; this is the origin of the rather large standard deviations of the parameters. Nonetheless, it is certain that the system shows negative cooperativity, in that the transition at the first site stabilizes the low spin form at the second site, and a higher transition temperature for the spin change of the second site results.

The first spin transition of the dinuclear complex has a slightly larger $T_{1/2}$ compared to the analogous mononuclear complex, stemming from a marginally lower ΔS , which may be tentatively ascribed to a smaller increase in vibrational disorder in the more rigid helicate.¹⁵ The close ΔH values underscore the similarity in coordination sphere and geometry around the iron centers of the mono- and dinuclear species.^{6,15} Similar values were calculated

**Figure 2.** The absorbance change (540 nm) with temperature for [Fe(**1a**)₃]²⁺ (●) and [Fe₂(**2**)₃]⁴⁺ (▲) in propylene carbonate. The fitted curves are also shown.**Figure 3.** The coordination sphere of the upper, low spin iron(II) is distorted in the all low spin form (left), but this is released in the mixed spin form (right); the changes are exaggerated for clarity.

by Piguet and co-workers¹⁶ for mixed triple helical structures of the type [LnFeL₃]⁵⁺ in which the iron has an almost identical coordination sphere and where the parameters lie in the range $\Delta H^\circ = 28.3\text{--}30.5$ kJ mol⁻¹, $\Delta S^\circ = 82\text{--}92$ J mol⁻¹ K⁻¹, with transition temperatures in the range 331–353 K.

The second spin transition step is clearly disfavored, with a significant increase in the transition temperature. How may this increase arise? The crystal structure of [Fe₂(**2**)₃]⁴⁺ in the all low spin form shows that the iron coordination site is distorted from ideal octahedral geometry, where, in particular, the iron–benzimidazole bonds (average 1.96 Å) are shorter than the *exo*-iron–pyridine bonds (average 2.00 Å). One result of the transition at the first iron atom is an increase of its Fe–N bond distances by approximately 0.2 Å.¹ Examination of the crystal structure suggests that this enlargement at the high-spin iron site will lead to a more regular coordination geometry at the low spin site; the ligand strands will separate and the low-spin iron will act as a pivot, so that the *exo*-coordinating atoms (the pyridine nitrogens) will be brought closer to the low-spin iron atom. This is shown in an exaggerated way in Figure 3. Given that the ligand field strength is extremely sensitive to M–L bond distances,¹ the low spin site in [Fe_{hs}Fe_{ls}(**2**)₃]⁴⁺ would be stabilized, leading to the observed increase in $T_{1/2}$ for the second spin transition.

Further support for this hypothesis was obtained with experiments on solutions of the complexes [MFe(**2**)₃]⁴⁺ (M = Ni, Zn), which were obtained by mixing ligand **2** with solutions of M(ClO₄)₂ and Fe(ClO₄)₂ (9:1). The observed transition temperatures for these complexes were 393(3) K and 365(3) K, respectively (Figure S2).¹⁷ Nickel and zinc ions are intermediate in size between high and low spin iron(II);¹⁸ thus, one would predict transition temperatures higher than that found for the first transition of [Fe₂(**2**)₃]⁴⁺ but lower than the second, as observed.

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In summary, the study of the two-step spin crossover of $[\text{Fe}_2(\mathbf{2})_3]^{4+}$ in solution shows negative cooperativity via a ligand-mediated interaction between the two iron sites. Further work in this laboratory regarding the influence of the bridge between the two chelate units on the cooperativity of the transition is underway.

Supporting Information Available: Figure S1, showing the attempted fitting of the data for $[\text{Fe}_2(\mathbf{2})_3]^{4+}$ with a single equilibrium model, and Figure S2, showing the spin transition curves for $[\text{NiFe}(\mathbf{2})_3]^{4+}$ and $[\text{ZnFe}(\mathbf{2})_3]^{4+}$.

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