Invited Review

Spin Equilibrium in Solutions

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Summary. The newer literature on spin equilibria of Fe(II) complexes in solution is reviewed. The thermodynamics as well as the kinetics in different solvents are discussed.

Keywords. Spin crossover; Equilibrium; Kinetics; Liquid state.

Introduction

The spin crossover phenomenon has been studied very intensely during the last decade. The main focus has been on the solid-state behaviour [1], but some important investigations on spin change in solution have also been performed. Since most of the older work in this field has been covered in a review in 1989 [2], the present paper will mainly describe recent accomplishments.

Octahedral iron(II) complexes showing equilibrium between $^1A_{1g}$ and $^5T_{2g}$ are by far the most intensively studied examples of the spin crossover phenomenon. There are many reasons for that; some of them will be explained below. With this in mind it is surprising that the oldest known compounds showing the crossover phenomenon are actually a series of iron(III)dithiocarbamate complexes. This type of complexes was discovered by the French chemist *Marcel Delépine* in 1908 [3], but their anomalous magnetic properties were not described until 1931 [4]. The first example of an iron(II) spin crossover system is usually assumed to be [Fe(*phen*)$_2$(NCS)$_2$], which was investigated by *Madeja* and *König* [5] in 1963. The phenomenon was, however, predicted by *Orgel* [6] seven years before the first system was actually characterized. A more careful examination of the older literature shows that Fe(II) compounds nowadays known to be spin crossover compounds have been prepared as early as 1938. *Paul Pfeiffer*, the well-known student and collaborator of *Alfred Werner*, reported on *tris*-(2-methyl-1,10-phenanthroline)-iron(II) and pointed out that the absorption spectrum of this complex is much weaker than that of its unsubstituted 1,10-phenanthroline iron(II) analogue [7]. He even noticed the solvatochromism of this system: whereas a methanolic solution of the perchlorate salt is orange, a solution in nitromethane is

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a Dedicated to the memory of Prof. *Christian K. Joergensen*

yellow. Later, *R. J. P. Williams* noticed the unusual high magnetic moment of these complexes, and he actually suggested spin crossover as a possible explanation for this phenomenon [8]. These early observations have since been confirmed to be due to spin crossover [9].

Thermodynamics

The requirement for the observation of the spin equilibrium phenomenon is that the potential minima of the low-spin (LS) and high-spin (HS) surfaces are so close in energy that both can be thermally populated. In the case of Fe(II), the two relevant states are $^1A_{1g}$ and $^5T_{2g}$. Due to the large difference in the number of available electronic and vibrational levels in these two states, the thermal transformation from $^1A_{1g}$ to $^5T_{2g}$ is to a large extend entropy driven, and the equilibrium is most clearly observed if the singlet state is the real ground state. The strategy usually used in creating new crossover systems is to fine-tune the ligand field strength of a ligand system known to be close to the crossover point by chemical modifications. Considering the large number of Fe(II) spin crossover systems known today it is clear, from pure statistical reasons, that many equilibrium systems with the quintet state as the true ground state must also exist. Because of the experimental difficulties in detecting such a system, practically no compounds of this type are described in the literature. One simple way to test if a given system belongs to this category is to change the relative energy of the two states by pressure. A short metal-ligand distance favours the LS state; pressure will therefore stabilize the LS state, resulting in a pressure induced HS-to-LS transformation if the energies of the two states are sufficiently close to each other at ambient pressure.

The thermodynamic parameters for a series of iron(II) complexes for which the $^1A_{1g} \rightleftharpoons {}^5T_{2g}$ equilibrium has been studied in solution are listed in Table 1. The data are typically obtained from UV/Vis, magnetic susceptibility, or NMR data. In contrast to the solid-state behaviour, solvent and counter ion effects are rather modest in dilute solutions. Since no cooperativity is present in solutions, all reported transition curves are gradual. *Linert et al.* have analyzed the possible effects of non-ideality on the shape of the transition curve. Effects from the internal pressure are predicted to result in non-gradual spin crossover for concentrated solutions [33]. In a few cases, dramatic solvent effects have been reported even for dilute solutions. Typically, one of the solvents is very polar, and substitution reactions where some of the ligands are replaced by solvent molecules cannot be ruled out. *Linert et al.* have investigated [Fe(*pyben*H)$_3$]$^{2+}$ [20] and [Fe(*bispybim*)]$^{2+}$ [28] in a number of different solvents (for abbreviations, see Appendix).

In these cases, interactions between the benzimidazole NH function and the different solvents seem to modify the ligand field strength and thereby change the ratio between HS and LS in different solutions. A set of data on [Fe(*pyben*H)$_3$]$^{2+}$ in *DMF* from an other group [21] shows unreasonably large ΔH^0 and ΔS^0 values; in this case ligand, dissociation is likely to have occurred. Obviously, data of this latter type should not be considered as true spin crossover interconversions. Ligand dissociation and replacement reactions are more likely to occur for complexes of

Table 1. Thermodynamic parameters for some Fe(II) spin crossover systems in solution

Complex	Solvent	$\Delta H^0/\text{kJ} \cdot \text{mol}^{-1}$	$\Delta S^0/\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	Ref.
$[\text{Fe}(pyim\text{H})_3]^{2+}$	$(\text{CH}_3)_2\text{CO}$	15.9	48.3	[19]
$[\text{Fe}(pyben\text{H})_3]^{2+}$	$(\text{CH}_3)_2\text{CO}$	19.7	78.0	[19]
$[\text{Fe}(pyben\text{H})_3]^{2+}$	*DMF*	42.7	140.9	[21]
$[\text{Fe}(bispybim)]^{2+}$	$(\text{CH}_3)_2\text{CO}$	22.5	68.1	[33]
$[\text{Fe}(\text{HB}(pz)_3)_2]$	$(\text{CH}_3)_2\text{CO}$	16.1	47.7	[22]
$[\text{Fe}(\text{HC}(pz)_3)_2]^{2+}$	MeCN	18	53	[14]
$[\text{Fe}(\text{HC}(3,5\text{-Me}_2pz)_3)_2]^{2+}$	*DMF*	20	58	[13]
$[\text{Fe}(tacn)_2]^{2+}$	D_2O	23	67	[23]
$[\text{Fe}(tp[10]ane\text{N}_3)]^{2+}$	EtCN	23.6	84	[24]
$[\text{Fe}(lpp[9]ane\text{N}_3)]^{2+}$	MeOH	17.1	59	[25]
$[\text{Fe}(tpt\text{Me}tame)]^{2+}$	EtCN	19.4	85	[11]
$[\text{Fe}(btpa)]^{2+}$	MeOH	27.6	89	[26]
$[\text{Fe}((\text{NH}_2)_2sar)]^{2+}$		12	30	[27]
$[\text{Fe Fe}(L)_3]^{4+\text{a}}$	MeCN	24	72.9	[36]
$[\text{Fe Fe}(L)_3]^{4+\text{b}}$	MeCN	41	104.6	[36]

[a] First step; [b] Second step

uni- and bidentate ligands, but even for multidentate ligands, replacement of a single chelate arm has been observed [10].

It is obvious that the accessible temperature range is limited by the boiling and freezing points of the solvents; therefore, certain selections of systems with optimal parameters have been performed. The spin transition in solution is so gradual that it will extend over more than hundred degrees in the accessible temperature range. Even if the critical temperature T_c (the temperature where the HS and LS concentrations are equal) is situated in the middle of the chosen temperature range it is often difficult to cover the complete spin transition. This usually results in a loss of accuracy in the determinations of the equilibrium constants. Nevertheless, quite good and straight *van't Hoff* plots are obtained in most cases. The quality of the data ought to be reflected in good linear isokinetic plots (ΔH^0 *vs.* ΔS^0). Such a plot based on the data of Table 1 shows quite a large scatter. However, if the systems are arranged according to the nature of ligands, much better correlations are obtained. Systems with bidentate and tridentate ligands show large reaction enthalpy values and define a line with a slope of 385 K. Systems based on hexadentate ligands generally show small reaction enthalpies, and the slope of this plot is 223 K. Within this type of systems some still deviate from the rest. An extreme case is $[\text{Fe}(tpt\text{Me}tame)]^{2+}$, which combines an unusual low reaction enthalpy with high reaction entropy. It is believed that this anomaly reflects the stiffness of the system [11]. It is remarkable that the cage system $[\text{Fe}((\text{NH}_2)_2sar)]^{2+}$ fits into the plot even though both the enthalpy and the entropy changes are small [27]. In this system, all donor atoms are secondary nitrogen functions, whereas in the *tpt*Me*tame* system they are all tertiary nitrogen functions.

There are not enough thermodynamic studies of other spin crossover systems. Iron(III) and cobalt(II) crossover complexes have rarely been studied in solution. Recent systematic deuterium NMR studies on *bis*-(cyclopentadienide)-manganese(II) complexes [12] reveal common features, which are reflected in a very well

defined isokinetic plot with a slope 328 K. In this case, both HS and LS signals were observed at low temperature. It is very unusual that spin crossover phenomena are studied in this straightforward manner. Previous investigations using ^{1}H NMR also turned out to have been misinterpreted. A very recent study on *bis*-[*tris*-(pyrazolyl)-methane]iron(II) in *DMF* where it is claimed that HS and LS signals are observed at temperatures below 283 K [13] is clearly in contradiction with previous laser flash studies where the relaxation time for this system in MeCN is found to be about 25 ns at room temperature [14]. Obviously, what has been assigned to signals of an LS iron(II) complex are just signals from the free ligand obtained as a result of dissociation. On the other hand, with higher magnetic fields and therefore increased NMR time scales at hand, maybe some of the classical systems considered be too fast for the technique ought to be reinvestigated.

Interpretations of minor differences between solid-state and solution data are probably not meaningful. There seems to be a tendency towards stabilization of LS in the solid phase compared to solution, but there are exceptions to this rule. Dramatic differences might be related to changes in the molecular structures in the different phases. [Fe(*tacn*)$_2$]Br$_2 \cdot 4H_2O$ is LS in the solid phase but becomes paramagnetic when the crystallization water is removed under vacuum [29]. In aqueous solution this compound is a spin equilibrium system [23]. Apparently, hydrogen bonding to the NH functions is important in controlling the ligand field strength in this case. The corresponding N-methylated ligand Me$_3$*tacn* forms a HS *bis*-complex with Fe(II), but recently *Hagen et al.* have shown that the combination of three acetonitrile molecules and one Me$_3$*tacn* moiety in the coordination sphere of Fe(II) gives a crossover complex [30]. In this case, the T_c of the acetonitrile solution is about 100 K lower than that of the neat solid. A detailed NMR study, however, indicates that rapid exchange with the triflate counter ions might be responsible for the change in behaviour. 1,4,7-Triazacyclononane functionalized with 2-pyridylmethyl and 6-methyl-2-pyridylmethyl groups provides an environment around Fe(II) which is in the crossover region. [Fe(*lpp*[9]*ane*N$_3$)] shows a decrease in T_c of 90° for the methanol solution compared to the solid perchlorate [25]. A comparison with similar systems suggests that the bulky 6-methyl-2-pyridylmethyl group might be replaced by a methanol molecule upon dissolution of the complex salt.

In recent years a couple of oligomeric spin crossover systems have been investigated in solution. *Williams et al.* have prepared an interesting series of homo- and heterodimetallic podates with helicate structures [34, 35]. A comparison of thermal spin crossover transitions of a solution of a Fe(II) dinuclear triple helicate with an analogous mononuclear complex shows the helicate transition to occur at higher temperature in a two-step process, implying a negative cooperativity [36].

Lehn et al. have reported an even more complex supramolecular structure [37]. The introduction of sterically demanding substituents in certain dinucleating pyridyl ligands enabled them to assemble [Fe(II)$_4L_4$]$^{8+}$ grid structures which show the crossover phenomenon both in solid state and in solution. ^{1}H NMR spectra at variable temperature in an acetone/acetonitrile mixture show a rather complicated behaviour with both HS and LS signals, suggesting an apparent slow HS $\rightleftharpoons$ LS interconversion.

Dynamics of Spin Crossover Reactions

The interchange between HS and LS states of a metal ion can be considered as simple intramolecular electron transfer processes, and an understanding of the detailed mechanism of these fundamental reactions is therefore highly desirable. Since 1989 the kinetics of many new systems have been investigated. The laser flash technique is now established as the most commonly used for this type of study in solution at temperatures down to 180 K. Activation parameters for some recently reported systems are collected in Table 2.

Variable pressure studies of spin crossover complexes [15] have provided molar activation volumes that in general imply the volume of the transition state to be placed about midway between the HS and LS relaxed states, so contraction of the solvated complex occurs on going from HS to the transition state. The solution activation parameters for most of the systems in Table 2 fall in the usual range for iron(II) spin crossover compounds. In view of the large change in coordination distances (approximately 0.2 Å) it is frequently assumed that the reaction coordinate is primarily of radial nature [16]. However, the importance of other conformational changes and twisting modes has also been stressed [2, 16].

It has been suggested that the variation of the activation energy, as *e.g.* represented by $\Delta H^{\ddagger}$ can be linked to the ligand structure [2]. In this pictures ligands that more readily accommodate twisting modes should reach their transition state more easily, and consequently have lower activation barriers than complexes with ligands which prevent easy twisting, thereby necessitating a more radially expanded transition state with a higher barrier. In Table 2, especially the low values of $\Delta H^{\ddagger}$ for [Fe(*dpa*)$_2$]$^{2+}$ as compared to the hexadentate ligand systems have been suggested as evidence that the activation process consists largely of a twist mode [16]. The facial coordinating tridentate *dpa* ligand poses no restraints on a trigonal twist motion. The relatively large value obtained for the new complex [Fe(*lpp*[9]*ane*N$_3$)]$^{2+}$ might be in favour of this model. The increased barrier could be considered to result from the fact that a twisting mode is less favourable for this complex due to steric interactions between the methyl group in position six of one of the pyridine groups and the two other pyridine moieties.

Table 2. Activation parameters for the HS to LS process for some spin crossover complexes in solution

Complex	Solvent	$\Delta H^{\ddagger}/\text{kJ} \cdot \text{mol}^{-1}$	$\Delta S^{\ddagger}/\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	Ref.
[Fe(*dpa*)$_2$]$^{2+}$	MeOH	2.14		[26]
[Fe(*tp*[10]*ane*N$_3$)]$^{2+a}$	EtCN	28.49	−18.3	[24]
[Fe(*lpp*[9]*ane*N$_3$)]$^{2+}$	MeOH	9.4	−63.5	[25]
[Fe(*tpt*Me*tame*)]$^{2+}$	MeOH	5.6	−75	[11]
[Fe(*btpa*)]$^{2+}$	MeCN/PrCN	15.5[b]		[17]
[Fe(*btpa*)]$^{2+a}$	MeCN/PrCN	27.5[b]		[17]
[Fe(*tpchxn*)]$^{2+}$	MeOH	9.72	−68.1	[31]
[Fe(*tpchxn*)]$^{2+a}$	MeOH	26.39	−8.3	[31]
[Fe(*tpen*)]$^{2+}$	MeOH	7.23	−76.5	[16]

[a] Slow process; [b] E_a from an *Arrhenius* plot

It is of interest to investigate whether special structural features of the ligands can be used to design systems which can be trapped in a certain conformation and thereby slow the relaxation rate considerably. *Toftlund et al.* have pursued such a strategy. Some of the highest barriers observed up to now have been obtained following this strategy. However, a common feature of these new systems is the occurrence of biphasic relaxation kinetics. The fast decay processes show barriers typical for other crossover systems, whereas the slow decay processes have activation barriers that are almost twice as large as those of the fast systems. Such high values indicate that bigger geometrical rearrangements of the coordination sphere take place than simple lengthening of the metal-ligand bonds. In the case of $[Fe(btpa)]^{2+}$ the crystal structure analysis of the PF_6^- salt might provide a clue [18]. The Fe(II) complexes occupy two crystallographic non-equivalent lattice sites. One site has an almost octahedral $[FeN_6]$ coordination sphere with mean Fe-N lengths of 2.00 Å. The other site consists of a highly distorted $[FeN_6]$ unit with mean Fe-N bond lengths of 2.23 Å and a twisting of the bipyridyl backbone along the 2,2′-C,C bond. One of the two non-coordinating pyridyl arms points towards the Fe centre with a Fe-N distance of only 3.16 Å. No HS $\rightleftharpoons$ LS interconversion is observed in the solid state, probably because the lattice packing does not allow large conformational changes to occur.

In order to explain the biphasic kinetics in solution it has been concluded that two metastable HS states with distinctly different equilibrium geometries and lifetimes exist side by side [11]. One denoted HS_A differs from the LS state
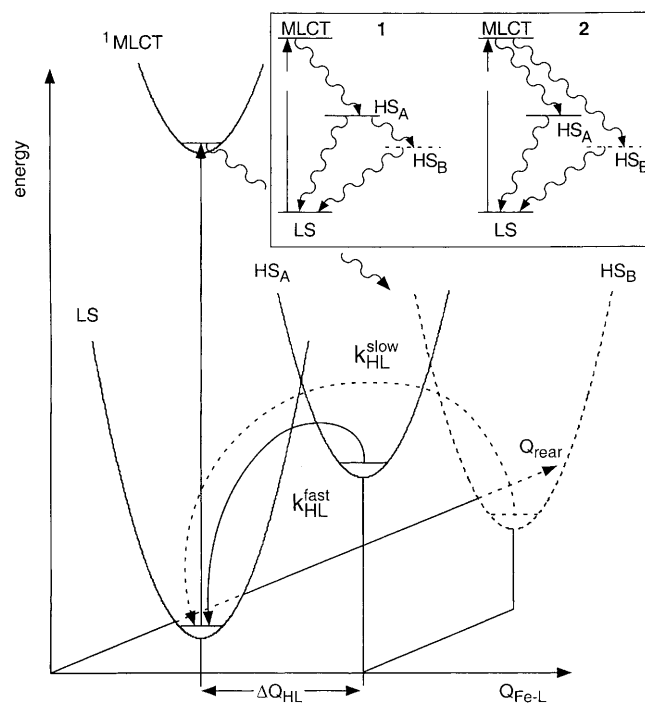

Fig. 1. Configurational coordinate diagram with the LS, MLCT, HS_A, and HS_B potential wells schematically illustrating the biphasic HS $\rightleftharpoons$ LS relaxation process following pulsed laser excitation of $[Fe(btpa)]^{2+}$ [17]

basically by substantially longer Fe-L bonds. For the other one, denoted HS_B, an additional rearrangement of the pyridyl arms is involved. From kinetics, HS_B is inferred to be at lower energy than HS_A. This is summarized in the two-dimensional configurational coordinate diagram of Fig. 1. The two different pathways resulting in transient populations of the two HS states after pulsed laser excitation into the $^1A_1$ to ^{1}MLCT transition is sketched in the insert of Fig. 1. They cannot be distinguished on the basis of the laser flash photolysis experiments alone; however, combination with the finding by *McCusker* [32] that HS states generally are populated a few picoseconds after the ^{1}MLCT transition it seems that the consecutive decay pathway (mechanism 1) is the most likely in this case.

Conclusions

The development of advanced materials and devices for nanotechnology requires systems that form switchable molecules or supermolecular systems which enable highly efficient information storage. The light-induced excited spin state trapping of crossover compounds provides promising examples of materials for this application. Most studies in this area have been performed on crystalline solids [1], but recent studies on polymeric films doped with [Fe(*btpa*)]$^{2+}$ have shown that room temperature trapping of a metastable HS form is possible [38]. This is an encouraging result as it demonstrates that constructing ligands with very specific and restrictive demands on the molecular structural dynamics may substantially increase the intersystem crossing barrier.

Acknowledgments

Appendix

Abbreviations:

bispybim:	2,6-*bis*-(benzimidazol-2-yl)-pyridine
btpa:	N,N,N′,N′-*tetrakis*-(2-pyridyl)-6,6′-*bis*-(aminomethyl)-2,2′-bipyridine
(NH$_2$)$_2$*sar*:	dimethylsarcofagine
dpa:	*bis*-(2-pyridylmethyl)-amine
HB(*pz*)$_3^-$:	hydro-*tris*-(1-pyrazolyl)-borate
HC(*pz*)$_3$:	*tris*-(1-pyrazolyl)-methane
HC(3,5-Me$_2$*pz*)$_3$:	*tris*-(3,5-dimethyl-1-pyrazolyl)-methane
L:	*bis*-(5-(1-methyl-2-(6′-methyl-2′-pyridyl)-benzimidazol-2-yl)-methane
*pyim*H:	2-(2′-pyridyl)-imidazole
*pyben*H:	2-(2′-pyridyl)-benzimidazole
lpp[9]*ane*N$_3$:	1-(6-methyl-2-pyridylmethyl)-4,7-*bis*-(2-pyridylmethyl)-1,4,7-triazacyclononane
tp[10]*ane*N$_3$:	1,4,7-*tris*-(2-pyridylmethyl)-1,4,7-triazacyclodecane
tacn:	1,4,7-triazacyclononane

Me$_3$*tacn*:	1,4,7-trimethyl-1,4,7-triazacyclononane
*tpt*Me*tame*:	1,1,1-*tris*-((N-(2-pyridylmethyl)-N-methylamino)-methyl)-ethane
tpen:	N,N,N′,N′-*tetrakis*-(2-pyridylmethyl)-1,2-ethanediamine
tpchxn:	N,N,N′,N′-*tetrakis*-(2-pyridylmethyl)-1R,2R-cyclohexanediamine

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