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# The Foundation of Modern Spin-Crossover

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5 **The first explanation of spin-crossover in iron(II) complexes was published in *Chem. Comm.* in 1966. This has led to nearly 50 years of research in coordination chemistry, crystal engineering, solid state chemistry and physics, and nanoscience involving this class of molecular switch.**

10 In 1964, Baker and Bobonich reported the magnetic moments of the series of compounds *cis*-[FeX$_2$(phen)$_2$] (phen = 1,10-phenanthroline; Fig. 1).[1] When X$^-$ = Cl$^-$, Br$^-$, I$^-$ or N$_3^-$ the compounds obey the Curie law,[2] exhibiting effective magnetic moments (μ_{eff}) that are constant between 110 K and room

15 temperature at 5.0-5.3 BM †. However, different behaviour was observed when X$^-$ = NCS$^-$ or NCSe$^-$. The expected $\mu_{eff} \approx 5$ BM was observed at higher temperatures as before, but μ_{eff} then fell sharply to 1.4±0.1 BM on cooling, at around 180 K (X$^-$ = NCS$^-$) or 230 K (X$^-$ = NCSe$^-$). A similar drop in μ_{eff} was also shown by

20 the related complex *cis*-[Fe(NCS)$_2$(bipy)$_2$] (bipy = 2,2'-bipyridyl).[1] Such behaviour is anomalous according to the Curie law, which predicts that μ_{eff} should be invariant with temperature for samples composed of discrete paramagnetic molecules, like these.[2] Baker and Bobonich noted that the drop in μ_{eff} for the

25 thiocyanate and selenocyanate complexes is reminiscent of antiferromagnetic coupling between the paramagnetic iron centres, but were unable to explain the data in more detail.[1]

[Fe(NCX)$_2$(phen)$_2$]
X = S or Se
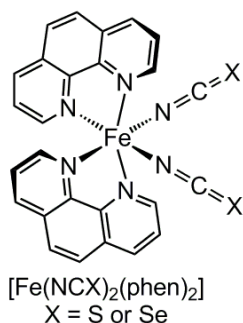
30 Two years later König and Madeja proposed the alternative explanation, that [Fe(NCS)$_2$(phen)$_2$] and [Fe(NCSe)$_2$(phen)$_2$] were undergoing a thermal transition between their diamagnetic low-spin ($S = 0$) and paramagnetic high-spin ($S = 2$) states. This

35 idea was communicated in *Chem. Comm.* in 1966,[3] then developed in a full paper the following year.[4] They simulated the magnetic susceptibility curves using a van Vleck equation for a system with an $S = 0$ magnetic ground state and a fixed $S = 2$ excited state.[2] Although it could not model the complete
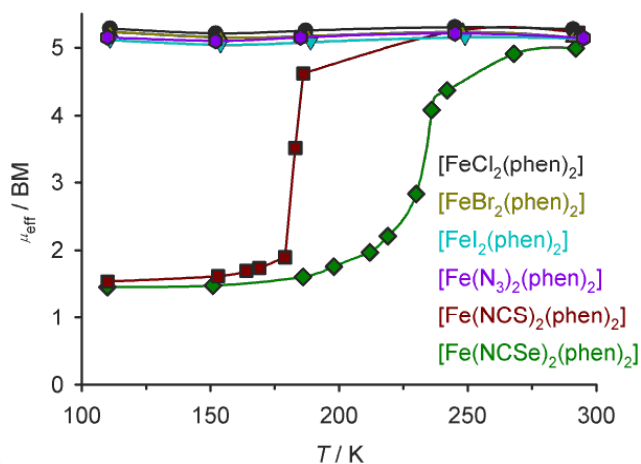
40 **Fig. 1.** Variable temperature magnetic moments of six compounds of type [FeX$_2$(phen)$_2$], replotted from Baker and Bobonich's original report †.[1] The data points for each compound are linked by spline curves for clarity.

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temperature range, this approach reproduced the magnetic moments reasonably well in the region of the transitions.[3] The validity of their idea was also supported by Mössbauer, IR and diffuse reflectance UV/vis spectroscopies at room temperature

50 and at liquid nitrogen temperatures, which all showed strong changes either side of the magnetic transition. That implies the transitions involve a significant change in electronic structure at the iron centres in the materials, that could not be simply explained by antiferromagnetic coupling between them.[4]

55 In fact, treating spin-crossover as a Boltzmann distribution between ground and excited states with fixed energies is an oversimplification, which explains why König and Madeja had only partial success with their equation. Rather, spin-crossover is a balance between the higher enthalpy of the low-spin state

60 (which has stronger metal–ligand bonds) *vs.* the greater electronic and vibrational entropy of the high-spin state. The high-spin state is stabilised relative to the low-spin as the temperature is raised, so that above the transition temperature the high-spin state becomes the thermodynamic ground state of the compound.

65 Equations that treat the magnetic transition as a thermodynamic equilibrium between starting materials (low-spin) and products (high-spin) are required to reproduce the behaviour in practise.[5]

König and Madeja's papers were not the first statement of the spin-crossover effect. While the idea had been discussed

70 previously,[6] the first rigorous treatment had come in 1964 from Ewald, Martin *et al.*[7] That study had used spin-crossover to

explain temperature-dependent magnetic moments in a series of iron(III) complexes dating from the 1930s. None-the-less, König and Madeja's extension of the rationale to iron(II) compounds is still significant, since iron(II) compounds have played the dominant role in spin-crossover research over the last 20 years.[8-11] Moreover, $[Fe(NCS)_2(phen)_2]$ and $[Fe(NCSe)_2(phen)_2]$ were the first examples of spin-crossover taking place abruptly at a specific temperature (Fig. 1). The iron(III) complexes studied by Ewald and Martin,[7] and cobalt(II) compounds that were also discovered in the 1960s,[6] all exhibit spin-crossover as a gradual thermal equilibrium spanning tens or hundreds of degrees.

Several metal ions in different coordination geometries can undergo spin-crossover.[8,9] However, the field is dominated by six-coordinate iron(II) complexes of N-donor ligands, hundreds of which exhibit the effect.[12] One reason that iron(II) compounds of this type have been most investigated, is because they tend to afford the most novel structural chemistry and physics. The structural difference between the spin states of a $[FeN_6]^{2+}$ centre is greater than for other metal/ligand combinations that commonly yield spin-crossover.[13] Thus, a spin transition in a solid $[FeN_6]^{2+}$ compound involves a particularly large change in its atomic structure, which propagates the transition through the material more efficiently. That can lead to abrupt switching, thermal hysteresis or more complicated transition properties. While there are isolated examples of cooperative, hysteretic spin-transitions in iron(III) and cobalt(II) chemistry,[14,15] they are far more common in iron(II) complexes.[16,17]

Another reason for the ubiquity of iron(II) spin-crossover complexes is because their spin-transitions are often accompanied by strong colour changes. The high-spin state of an iron(II) complex with heterocyclic N-donor ligands is usually pale in colour or even colourless, while the low-spin state is strongly coloured (Fig. 2). That reflects their metal-to-ligand charge transfer absorptions in the blue region of the spectrum, which are *ca.* 10x more intense in the low-spin state than in the high-spin. Such colour changes are less pronounced in iron(III) or cobalt(II) spin-crossover complexes, for example, where both spin states exhibit strong MLCT absorptions in the visible region.

A third factor, is that spin-crossover in six-coordinate iron(II) compounds switches the material between a diamagnetic and a paramagnetic state. Thus, spin-crossover in iron(II) complexes switches the paramagnetism of the material on and off (Fig. 2).
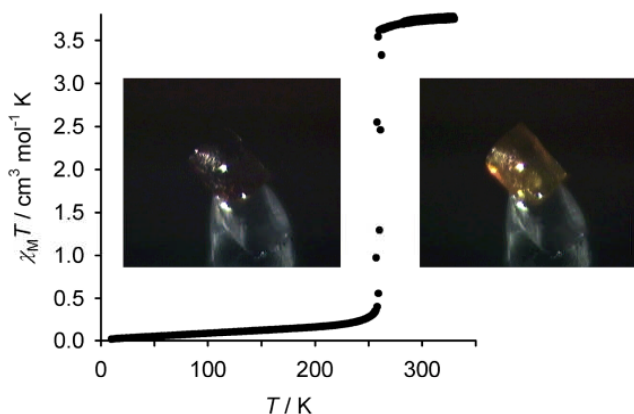
Fig. 2. Magnetic susceptibility data from an iron(II) spin-crossover complex †, and a single crystal of the same compound in its low-spin (dark brown) and high-spin (yellow) states. Data are taken from ref. 18.

Other metal ions and coordination geometries that commonly undergo spin-crossover have at least one residual unpaired electron in their low-spin states, and the change in their magnetic properties during the transition is therefore less pronounced.

A final contributor is that iron(II) complexes are the most favourable for spin-state trapping experiments, where a material is trapped in an excited spin-state at low temperatures. This spin-state trapping can be achieved in several ways, but the most common (and the first to be discovered) is by irradiation of a solid, low-spin iron(II) complex with a green laser below 10 K (Fig. 3).[19] The resultant high-spin sample is metastable under the conditions of the experiment, but relaxation back to its ground state may be kinetically inhibited at such low temperatures. In that case the material remains trapped in its high-spin excited state, for a period of hours if kept cold enough. The excited state will only decay significantly back to the low-spin ground state if the temperature is raised, to a level that overcomes the activation barrier to thermal relaxation. This critical relaxation temperature (T_{LIESST} in Fig. 3) is often below 50 K, but can be as high as 130 K in favourable cases.[20] This Light-Induced Spin-State Trapping (LIESST) effect is a type of bistability, that could be of interest for device applications if T_{LIESST} can be raised sufficiently high.[21]
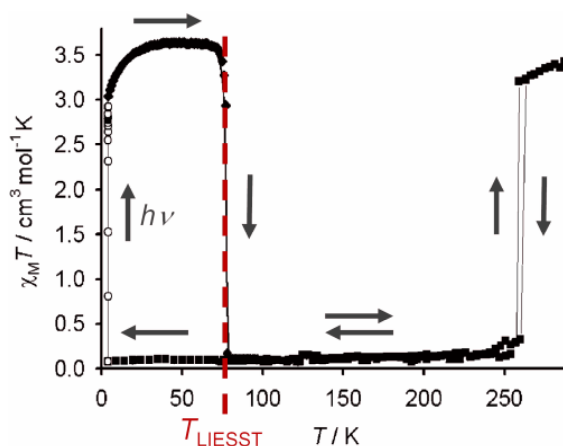
Fig. 3. The LIESST effect, as measured for the compound in Fig. 2 †. The compound was cooled, then irradiated at 5 K, then rewarmed. The critical temperature for relaxation of the trapped high-spin state (T_{LIESST}) is 81 K. Data are taken from ref. 18.

LIESST phenomena are common in iron(II) chemistry, rare in iron(III) complexes and are unknown for any other metal ion.[8,9,21] This again relates to the large structure change between the high- and low-spin states in six-coordinate $[FeN_6]^{2+}$ centres, mentioned previously. A large atomic rearrangement between the ground and excited states of the material implies the activation barrier for thermal relaxation following the excitation event should be high, as required. Moreover, it also inhibits relaxation of the material below T_{LIESST} by quantum mechanical tunnelling.[5]

Interest in the spin-crossover phenomenon greatly increased in the 1990s. This was inspired by Kahn *et al.*, who realised that spin-transition compounds with thermal hysteresis exhibit magnetic and colorimetric bistability, which could be harnessed in display or memory devices. That requires a hysteretic spin transition spanning room temperature, which had not been

achieved at the time. Kahn *et al.* produced the first such material in 1993, a formulation of an iron(II)/1,2,4-triazole coordination polymer (Fig. 4),[22] and then used it in a prototype display device.[23] Twenty years later only one more compound is known

[5] with similarly favourable spin-switching properties, namely the coordination network [Fe(μ-pyrazine)Pt(μ-CN)$_4$].[24] Most studies of spin-crossover applications use one of those iron(II) materials, or a derivative of them.[10]
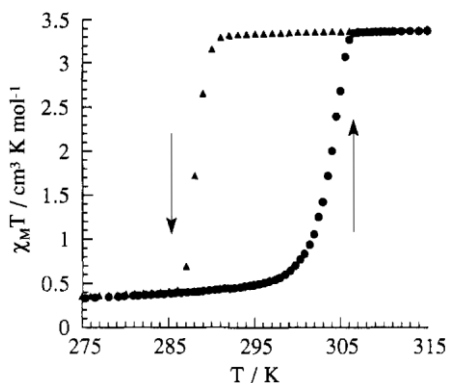
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Fig. 4. Spin-crossover switching in Kahn *et al.*'s iron(II)/1,2,4-triazole coordination polymer, which is bistable at room temperature †.[22] Copyright 1993, American Chemical Society.

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The state-of-the-art in spin-crossover research includes nanoscience. Nanoparticles, thin films, amphiphile structures and surface patterns of spin-crossover materials are all now

[20] available.[9,10] The switching performance of these nanostructures is often attenuated as their size decreases, but this is now quite well understood. The miniaturisation of spin-crossover has also recently extended down to the observation of spin-state switching in single molecules.[25] Another area is the incorporation of spin-

[25] crossover switches into multifunctional materials. Use of spin-crossover centres to modulate fluorescence has been particularly successful, in crystals, nanoparticles[26] and an electroluminescent device.[27] A third topic is the crystal engineering of spin-crossover materials, which is benefitting from a wider availability of

[30] structural data[16] and the development of new diffraction methods.[9,28] A last example is supramolecular chemistry, of spin-crossover hosts that respond to the binding of guest species. These include molecular receptors that function in solution,[29] and nanoporous crystals that are sensitive to guest inclusion.[30]

[35] All of these fields rely especially on iron(II) compounds because of their superior switching characteristics, their strong colour changes and their property of diamagnetic/paramagnetic switching. In that regard, König and Madeja's *Chem. Comm.* paper can be considered to be the foundation of modern spin-

[40] crossover research.[3]

Notes and references

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† Magnetic susceptibility data from molecular compounds are often quoted in the literature as the effective magnetic moment μ_{eff}, or as $\chi_M T$

where χ_M is the molar susceptibility of the compound. The two parameters are related by eq 1:

$$\mu_{eff} = \sqrt{\frac{3k}{N\beta^2}\chi_M T} = 2.828\sqrt{\chi_M T} \qquad (1)$$

[50]

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