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# Advances in Polynuclear Iron(II), Iron(III) and Cobalt(II) Spin-Crossover Compounds

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*Dedicated to Professor Bruce West on the occasion of his 80th birthday*

**Keywords:** Iron(II) / Iron(III) / Cobalt(II) / Spin-crossover / Polynuclear compounds / Magnetism / Photomagnetism

This review describes the recent advances made in the syntheses, structures (including the use of synchrotron sources and variable-temperature crystal structures and PXRD determinations of unit cell axes), magnetism, and photomagnetism of dinuclear and 1-D chain spin-crossover compounds of (primarily) iron(II), iron(III) and cobalt(II). It focuses on the work of the author's group and also includes a discussion of related work by other groups. In particular, the early and ongoing work by Kahn, Real, Gütlich and co-workers on bipyrimidine-bridged $Fe^{II}$ dinuclear materials has been extended by us and others to include many other new bridging and capping ligands. This had led to a fuller understanding of the spin transitions that involve HS-HS, HS-LS and LS-LS pair states. The same is being achieved for new 1-D chain materials, and notable advances include structural observation of ordered and disordered metal centres and corresponding spin states.

## 1. Introduction

While the study of spin crossover (SCO) in $d^4$–$d^7$ metal complexes goes back some 77 years,[1] it is only in recent years that research has begun to focus on polynuclear compounds in which more than one metal centre capable of undergoing a spin transition exists.[2] One reason for this interest relates to the bistability and cooperativity in crystalline SCO materials, these key features being possibly enhanced in covalently bridged clusters or in extended 1D, 2D or 3D frameworks compared to mononuclear complexes where weak intermolecular (supramolecular) interactions are known to mediate cooperativity and often enhance thermal hysteresis in these bistable species. The other key reason is that these "memory" features, in combination with the color change that these materials undergo (e.g. pale yellow $Fe^{II}$ $d^6$ HS; violet $Fe^{II}$ $d^6$ LS), has led to more applied chemical/materials investigations of their possible use in devices such as electronic data storage, displays, sensing and binary switching.[3]

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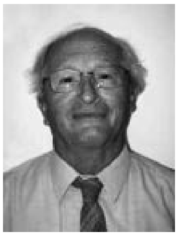


*Keith Murray was born at Setmurthy, near Bassenthwaite, in the Lake District area of England in 1942, educated at Workington Grammar School, Cumbria, and at Manchester University (PhD 1966; supervisor Dr. David Machin). His academic career has been spent entirely at the School of Chemistry, Monash University, Melbourne, firstly as a Postdoctoral Teaching Fellow, with Professor Bruce O. West, then rising through the ranks to be awarded a Personal Chair in Chemistry in 1997. He has had a long association with Professors Hans Toftlund and Christine McKenzie of the Institute of Physics and Chemistry at the University of Southern Denmark, Odense, where he is an Adjunct Professor. His research interests are broadly in the area of d-block metal chemistry, magnetochemistry, bioinorganic chemistry and molecular materials chemistry. More specifically, of relevance to this Microreview, he has strong interests in molecule-based magnetic materials of the extended framework, high-spin cluster (Single Molecule Magnets) and polynuclear spin-crossover types. He has published 340 papers and reviews, his recent work on molecular magnetism leading to awards and invited lectures and articles, including the inorganic chemistry Burrows Award of the Royal Australian Chemical Institute (RACI), 2003. He is a regular speaker and contributor to the biannual International Conference on Molecule-based Magnetism (ICMM), and he has active collaborative projects underway with colleagues in European universities and research institutes. Following recent "Murraystock" festivities to mark his 65th birthday, Keith now has a fractional position at Monash University, where he concentrates fully on the research work of his Post-doctoral fellows, PhD and BSc. Honours students, ably assisted by his colleagues Dr. Stuart Batten and Dr. Boujemaa Moubaraki, the work being supported by Discovery grants from the Australian Research Council (ARC) and by a French-Australia (FAST-DEST) award, in collaboration with Professors Cameron Kepert (University of Sydney) and Jean-Francois Létard (CNRS, Bordeaux).*

Our interests in mononuclear SCO compounds started in the 1980s[4] and in di- and polynuclear species in the late 1990s/early 2000s.[5] In the latter area, a number of fundamental questions continue to intrigue us as they also intrigued the groups of Kahn and Real et al.,[6] Reedijk et al.[7] and Lehn et al.,[8] that first studied di- and polynuclear $Fe^{II}$ SCO species. These questions include:

(i) In covalently bridged species such as dinuclear $Fe^{II}$, $Fe^{III}$ or $Co^{II}$ does synergy occur between exchange coupling effects and SCO involving spin states HS-HS, HS-LS or LS-LS? The same for not covalently bridged (supramolecular) polynuclear systems.

(ii) Can the HS-LS states be fully characterised in two-step spin transitions displayed by dinuclear systems and is their long-range structural ordering of the HS-LS species at the intermediate plateau temperature; likewise in 1-D species is there ordering in individual chains of the HS-LS-HS-LS species or does random disorder occur?

(iii) Is cooperativity (e.g. thermal hysteresis/memory) enhanced in crystalline, cluster SCO materials compared to mononuclear complexes, and can intracluster interactions be distinguished from intercluster effects?

(iv) As well as posing the above questions for molecular framework (coordination polymers; 1-D, 2-D, 3-D) SCO materials, can such frameworks also display nanoporosity and host–guest features that can trigger or remove spin transitions. This aspect of our work is led by C. J. Kepert, University of Sydney, and will not be described here.

(v) Can "hybrid" SCO/paramagnetic or SCO/exchange cluster (e.g. SMM) mixed-metal compounds be made and, if so, how do their respective electronic substates interact?

(vi) How does the photomagnetic LIESST effect (light-induced excited spin state trapping) for polynuclear SCO species compare with that for mononuclear species? This aspect is led by J-F. Létard, University of Bordeaux, CNRS.

This short review will focus on our work and will make reference to related SCO studies, carried out elsewhere, where appropriate. Inevitably, it will not be exhaustive and apologies are extended to authors whose work we do not include. Two short reviews have appeared recently on a related topic to the present one, by Real et al.,[9] and by Bousseksou et al.[10] Overlap of topics will be kept to a minimum herein. Emphasis will be placed on dinuclear and 1-D chain species.

## 2. Design and Synthesis

As in most chemical projects, the syntheses and structural characterisation of the desired compounds are paramount to the success of the project. The design strategies used here to prepare dinuclear SCO compounds have been summarised in graphical form in two articles.[11a,11b] In essence, one needs a bridging ligand that can be either rigid and directing and likely to mediate spin-spin exchange [say between $Fe^{II}\cdots Fe^{II}$; $S = 2$ (HS), $S = 2$ centres] or a long linking moiety, probably flexible, that binds the two SCO metal centres together and not likely to mediate magnetic exchange but more likely to allow exploration of mechanical or elastic effects upon SCO at the metal centres within the dinuclear milieu. In the case of $Fe^{II}$, $Fe^{III}$ or $Co^{II}$ as constituent ions, with preferred six-coordinate geometries (sometimes five-coordinate for $Co^{II}$), the bridge(s) usually provide(s) two, or one, of the donor sites to each metal atom and thus four, or five, terminal ("end group") ligand donor atoms are required to complete the octahedral geometry. These terminal ligands can be part of the bridging ligand or can be added separately. Until recently, the coordination set around $Fe^{II}$ that yields the crossover ligand field is generally of type $N_6$, made up of pyridine or related heterocyclic rings;[2] however, $N_4O_2$- or $N_5O$-donor–donor sets, within Schiff bases or from separate O- and N-donor chelates, are now known to provide the required ligand field.[12,13] On the other hand, mixed N,O-donors have long been known to provide the crossover criterion in $Fe^{III}$ and $Co^{II}$ complexes.[4,14]

In $Fe^{II}$ or $Co^{II}$ SCO systems, N-donor terminal ligands, when added separately to the bridging ligand, are often made up of the monoanionic N-donors $NCX^-$ (X = S, Se, $BH_3$) or $N(CN)_2^-$ in combination with chelating N-donors of the 2,2′-bipy or tpa (tripyridylmethylamine) types. Because of the multiligand additions involved, and possible deposition of side products such as $Fe(L)_3^{2+}$, prior to, or as well as, the desired dinuclear complex e.g. of type $[(L)_2(NCX)_2Fe^{II}(\mu\text{-}L')Fe^{II}(NCX)_2(L)_2]^{x+}$, where L is a bidentate N,N′-donor that might be the same as L′ (for example in the μ-bpym series of Real et al.[9,15]) great care has to be exercised in controlling molar ratios of ligands, order of ligand addition, not to mention use of anaerobic conditions or addition of ascorbic acid to prevent the formation of an $Fe^{III}$ product. Indeed, we found when using pypzH as both bridging and terminal ligand in making crossover materials $[(py)(NCX)(pypzH)_2Fe^{II}(\mu\text{-}pypz)_2Fe^{II}(pypzH)_2(NCX)(py)]$,[5a,16] that a different pseudodimeric water-bridged complex,[17] of similar colour, could be isolated unless the effective pH of the solution was carefully monitored and, even then, the ability to isolate good yields of crystals of the μ-pypz family depended upon the X group, with X = S still being problematic. In contrast, the formation of the related μ-pyrazolato compounds, $[(py)(NCX)Fe^{II}(\mu\text{-}bpypz)_2Fe^{II}(NCX)(py)]$, in which the bis(bidentate) $bpypz^-$ ligand also provides both bridging and terminal N-donors, is much more straightforward and single-product-yielding.[18,19] However, surprises were forthcoming in the X = S example of this family such that the powder sample first isolated by Kaizaki et al.[18b] displayed SCO whereas the crystalline sample of it that we isolated, when making comparisons to μ-triazolato analogues, showed HS behaviour at all temperatures. Such a dependence of SCO magnetic behaviour upon crystallite size, grinding of crystallites, etc., has long been known in mononuclear materials,[20] and is probably also influenced in this specific case by a mol-equiv. of $H_2O$ being present in the rapidly precipitated powder sample perhaps with polymorphism also playing a part.[18b,19]

Even when all the design criteria and donor-type selection (with appropriate ligand field, as judged by mononuclear analogues) are in place for making a "one-shot certainty" dinuclear (or polynuclear) SCO material, it is common to produce a compound that remains HS-HS at all temperatures.[11] Thus, systematic preparative studies are generally found to be necessary with variations being made in all ligand components. The effects of outer-sphere anions and solvate molecules are less easy to predict and control, as is the contribution to the single-ion ligand-fields provided by bridging ligand(s); it does not always appear possible to "cut the ligand-field in half" when using, say, a 2-connecting bipyridine or a bis(bidentate) {N,N···N,N} bridge.

Growing crystals of dinuclear or polynuclear SCO compounds can pose challenges, the first such reported dinuclear family of bipyrimidine-bridged $Fe^{II}$ has only recently yielded detailed, variable-temperature data, some 16 years after their first reported synthesis.[21] In our hands, we were not able to obtain crystals of $[(1,10\text{-phen})(NCS)_2Fe^{II}(\mu\text{-bpym})Fe^{II}(NCS)_2(1,10\text{-phen})]$, for example,[11b] whereas Real and co-workers obtained crystals of the bt/NCS and bpym/NCS derivatives by allowing the final preparative solution to slowly concentrate.[6,9,15,21] The pyrazolate- and triazolate-bridged species such as $[(py)(NCX)Fe^{II}(\mu\text{-bpypz})_2Fe^{II}(NCX)(py)]$ yielded crystals more readily[18,19] by means of slow diffusion techniques in which a methanolic solution of $NH_4SCN$ and $Fe(ClO_4)_2{\cdot}6H_2O$, and a trace of ascorbic acid, is contained in one arm of an H-shaped tube while $(n\mathrm{Bu}_4N)$(bpypz) [or $(n\mathrm{Bu}_4N)$(bpytz)] in pyridine is held in the other arm. Layering with methanol/pyridine to fill the H-tube allowed crystals to form after a period of 2 weeks. This is the same slow diffusion method used by Kepert and co-workers to obtain many SCO coordination polymers of the extended framework type containing a range of two-connecting di-pyridyl and related linkers.[5b,22] We have also used the H-tube approach, or achieved slow diffusion by layering the reagent solutions in a small test tube, to obtain dipyridylamine (dpa)-linked 1-D and dinuclear $Fe^{II}$ SCO compounds.[23]

## 3. Dinuclear Iron(II) $d^6$–$d^6$ Spin-Crossover Compounds

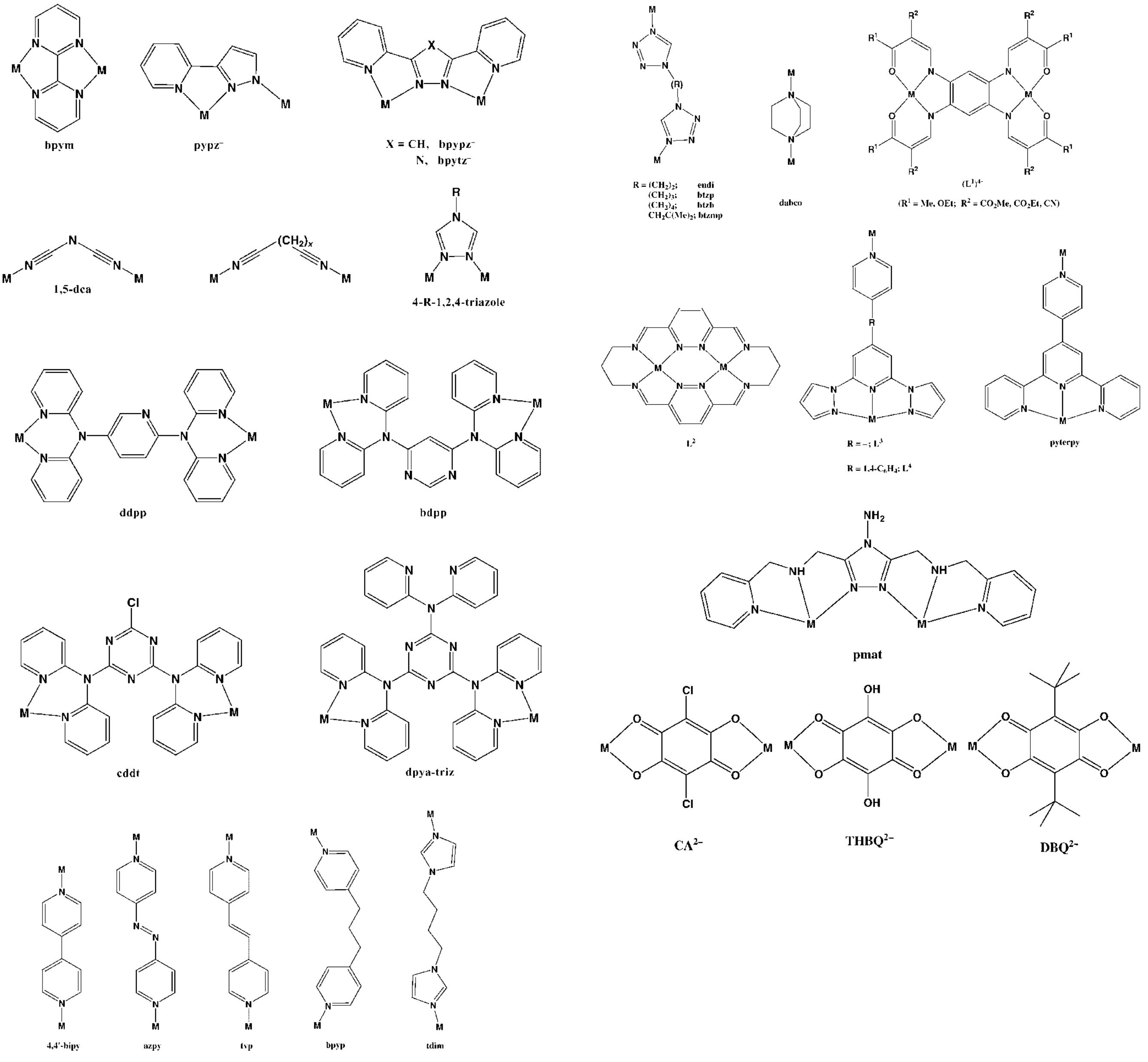
As indicated above, the first reported dinuclear SCO compounds contained bipyrimidine *trans*-$(N,N)_2$-bridging and *cis*-$\{(NCX)_2(N,N)\}$ end groups and their properties have been reviewed extensively and recently.[9,10,15,21] Other bridging ligand systems have received some attention,[9,10] and we focus on these materials here, with emphasis on our own work.

### 3.1. $N_6$-Donor Sets Around $Fe^{II}$

Six N-donors made up from combinations of pyridyl-type, amine and $NCX^-$ nitrogen atoms provide the most common SCO ligand-field in both mononuclear and dinuclear species. In dinuclear examples, the N-donors from the bridging ligands can be neutral, as in pyrazoles, triazoles and dinitriles (NC–R–CN) or anionic as in pyrazolates, triazolates and $CN^-$. The bridging ligands used to date, some of which also provide end-group N-donors, are shown in Scheme 1.

As well as trying to answer the fundamental points given in the Introduction, we aimed, at the outset of the project (around 1998), to expand the chemical range of dinuclear SCO iron(II) compounds because the only known group of compounds at that time contained the μ-bpym bridge.[6,15] We wanted to test some of the predictions that had emerged from that work, one, for example, being that dinuclear $Fe^{II}$ compounds would always display "half"-crossover (HS-HS → HS-LS or HS-HS → 0.5(HS-HS + LS-LS) or two-step crossover transitions (HS-HS → HS-LS → LS-LS). Many of our first attempts, building, for example, upon the known propensity of bis[tris(pyrazolyl)methane]$Fe^{II}$ monomers to display SCO with $T_{1/2}$ close to 300 K,[5c] led to compounds such as the dicyanamide (dca)-dibridged compound, $[(N(CN)_2)(pz_3CH)Fe(\mu\text{-}1,5\text{-}N(CN)_2)_2Fe(pz_3CH)(N(CN)_2)]$, remaining HS-HS at all temperatures.[11b] In this case the three $dca^-$ nitrile donors, plus the three pyrazole N-donors from the *facially* tridentate $pz_3CH$, provided too weak a ligand-field around each $Fe^{II}$ atom to achieve SCO. Subsequently, Real et al.[24] observed a two-step spin transition in a singly 1,5-dca-bridged compound, $[(bztpen)Fe(\mu\text{-}N(CN)_2)Fe(bztpen)](PF_6)_3$, that had a pentadentate pyridylamino $N_5$-donor set (bztpen)[25] as end group, with the crossover ligand-field now achieved. Crystal structures of the two-step material were obtained at temperatures where the HS-HS, HS-LS and LS-LS forms existed ("HS-LS" form discussed further below). Interestingly, a structural isomer of their compound remained HS-HS at all temperatures, thus showing how very sensitive the crossover point is to small changes.[24]

Toftlund and co-workers found that other neutral dinitrile bridges of the type NC–R–CN formed "weakly linked" dinuclear $Fe^{II}$ crossover compounds such as $[(TpyA)Fe(\mu_{1,8}\text{-}NC(CH_2)CN)_2Fe(TpyA)](ClO_4)_2$ when the tetradentate TpyA end blocker was employed.[11b] The LS-LS → HS-HS spin transition was gradual and started above 300 K. We are presently reinvestigating an early report[26] that dinitriles can yield 3-D SCO networks of the type $[Fe^{II}(NC\text{–}R\text{–}CN)_3](M^{III}Cl_4)_2$ (M = In, Fe), and the structures of such nets have recently been elucidated for the first time.[27] There are also early reports of tetranuclear (phosphane)$Fe^{II}$ clusters showing some evidence for SCO; these incorporate dinitrile bridging, including $dca^-$, and they deserve further scrutiny from the perspective of making medium to large SCO clusters.[28] The simplest nitrile-bridging ligand is, of course, cyanide ($CN^-$), a strong-field C-donor and weak-field N-donor. Vahrenkamp et al.[29] and Oshio et al.[30] have utilised this feature in square, tetranuclear species built up from *cis*-$(2,2'\text{-bipy})_2Fe^{II}(CN)_2$ and $[Fe^{II}(TpyA)]^{2+}$ synthons. The product, $[(2,2'\text{-bipy})_4(TpyA)_2Fe_4(\mu\text{-}CN)_4](PF_6)_4$, behaved like a dinuclear SCO cluster because the N-bonded cyanide donors yielded a two-step



Scheme 1. Bridging ligands and modes of bridging in the dinuclear and 1-D spin crossover compounds.

spin transition at the two [(TpyA)Fe$^{II}$(NC)$_2$ centres, while the *cis*-(2,2′-bipy)$_2$Fe$^{II}$(CN)$_2$ centres remained LS. Toftlund and co-workers had, independently, been developing such CN-bridged crossover cluster species for some time.[31]

Importantly, we subsequently showed,[5a] as did Kaizaki et al.[18] in related, contemporaneous studies, that di-μ-pyrazolato bridging in combination with pyridyl and NCX⁻ end donors yielded full one-step HS-HS → LS-LS spin transitions. This negated the prediction of a universal two-step transition that had emanated from the μ-bipyrimidine work at that time, the latter work also then yielding a one-step example, [(dpa)(NCS)$_2$Fe(μ-bpym)Fe(NCS)$_2$(dpa)], with a somewhat broader spin transition than those observed in the pyrazolato-bridged compounds.[32] However, not all of the di-μ-pyrazolato compounds displayed full one-step transitions, some such as [(4-Phpy)(NCBH$_3$)-Fe$^{II}$(μ-bpypz)$_2$Fe$^{II}$(NCBH$_3$)(4-Phpy)] displayed a two-step crossover, HS-HS → 0.5(HS-HS + LS-LS) → LS-LS, the latter spin states being proven by observing, at the plateau temperature between the steps, the two molecular structures in one crystal, with typical HS Fe–N distances of 2.1 Å in the HS-HS form and 1.9 Å bond length in the LS-LS form.[18c] In collaborative work with Brooker et al.,[33a,33b] a di-μ-4-R-1,2,4-triazole compound, [Fe$_2$(pmat)$_2$](BF$_4$)$_4$·DMF, containing the bis(terdentate) ligand pmat, also showed magnetic data typical of a half crossover, but in this case the crystallography showed, for the first time, the dinuclear molecules to exist in a trapped (ordered) HS-LS form at temperatures below the spin transition, with HS Fe–N bond lengths observed on one Fe atom and LS lengths on the other LS Fe$^{II}$ atom. Brooker and co-workers[33c] are extending this work by making wide variations in the triazole 4-R "head group" substituent and in other features of dinucleating ligands of the pmat type, but achieving spin crossover is proving rather elusive. When 2-pyridyl rings were attached to the 3,5-positions of a 4-R-1,2,4-triazole, the resulting bis(bidentate) ligands tended to form monomeric, tris[mono(bidentate)] $FeL_3^{2+}$ complexes together with, in some cases, dinuclear $Fe_2L_2$ materials that remained HS-HS. With coligand $NCS^–$ they tended to form mononuclear $FeL_2(NCS)_2$.[33c] These bis(bidentate) ligands lack the control that the bis(terdentate) ligands provided. In contrast, we observed the ready formation of dinuclear (mainly) SCO compounds when using analogous bis(bidentate) triazolate ligands of the $bpytz^–$ type, described below.

Before describing the triazolates, our di-μ-pyrazolato systems involving the $pypz^–$ ligand, $[(py)(NCX)(pypzH)_2Fe^{II}(μ\text{-}pypz)_2Fe^{II}(pypzH)_2(NCX)(py)]·2H_2O$, shown in Figure 1 for X = Se, were explored with variations made in the $NCX^–$ ligand. This led to magnetic moment vs. temperature plots as shown in Figure 2. As expected, $T_{1/2}$ moved to higher values as X changed from Se to $BH_3$ in the stronger-field ligand $NCBH_3^–$. Frustratingly, we have been unable to obtain sufficient sample of the $NCS^–$ product, other than the crystals used for structural characterisation, to obtain magnetic data and, hence, the $T_{1/2}$ temperature. In such (small-yield) cases, use of variable-temperature X-ray crystallography, aided by a synchrotron source, would have pinned down the transition temperature through changes in the Fe–N bond-length values. The μ-bpypz (pyrazolato) and μ-bpytz (triazolato) families $[(py)(NCX)Fe^{II}(μ\text{-}bpyp(t)z)_2Fe^{II}(NCX)(py)]$ were more amenable to obtaining higher and more reproducible yields.[18,19] A typical structure is shown in Figure 3, and other members have the same structure. As in the μ-pypz family, the $T_{1/2}$ values increase in the order of the increasing ligand-field strength of the *trans*-disposed, unidentate anions: $NCS^– < NCSe^– < NCBH_3^–$. As indicated earlier, and shown in Figure 4, the $NCS^–$-ligated compound remained HS-HS at all temperatures providing a sample of lightly crushed single crystals, rather than of rapidly precipitated powder (probably a hydrate or a polymorph) was measured.[19] Variation of the bridging ligands, from $(bpypz^–)_2$ to $(bpytz^–)_2$, for constant py and $NCX^–$, led to HS-HS behaviour, with no SCO but rather very weak HS-HS antiferromagnetic coupling ($J <$ –1 $cm^{–1}$), for crystalline samples of the X = S pair of complexes. The X = Se pair showed a sharp, one-step transition for the bpypz-bridged compound ($T_{1/2}$ = 109 K) in the hands of both Kaizaki et al.[34] and ourselves,[19] while the bpytz-bridged analogue remained HS-HS, with $J$ = –0.83 $cm^{–1}$. The $[(py)(NCBH_3)Fe^{II}(μ\text{-}bpyp(t)z)_2Fe^{II}(NCBH_3)(py)]$ pair displayed a full one-step HS-HS → LS-LS transition at $T_{1/2}$ = 205 K for the bpypz compound,[18b] supported by crystal structures at 296 K and 100 K, and by Mössbauer spectroscopy determined at 275, 200 and 77 K. In contrast, we found a two-step transition [$T_{1/2(1)}$ = 194 K; $T_{1/2(2)}$ = 151 K] for the bpytz compound but were not able to obtain crystal-structure support.[19] In the Mössbauer spectrum, shown in Figure 5, the HS-HS and LS-LS isomer shift and quadrupole splitting values were typical of these $Fe^{II}$ spin states, but at an intermediate temperature (123 K) we found an unusual, broad lineshape, that was quite different to the HS plus LS resolved doublets observed for the $bpypz/NCBH_3$ complex.[18b] Nevertheless, the results show that the bpytz equatorial ligands produce a slightly weaker ligand field than do the bpypz bridges when all other coligands are kept constant. From a crystal packing perspective, the $[(py)(NCX)Fe^{II}(μ\text{-}bpyp(t)z)_2Fe^{II}(NCX)(py)]$ families all show interdinuclear π–π contacts, to varying degrees, forming layer-like motifs.

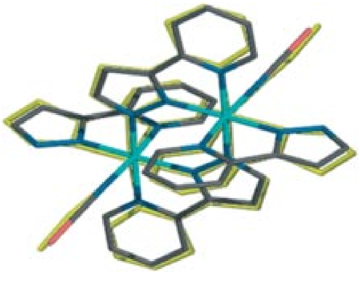


Figure 1. Structural comparison of $[(py)(NCSe)(pypzH)Fe(μ\text{-}pypz)_2Fe(pypzH)(NCSe)(py)]·2H_2O$ at 123 K (LS, coloured) and 298 K (HS, yellow).[5a]

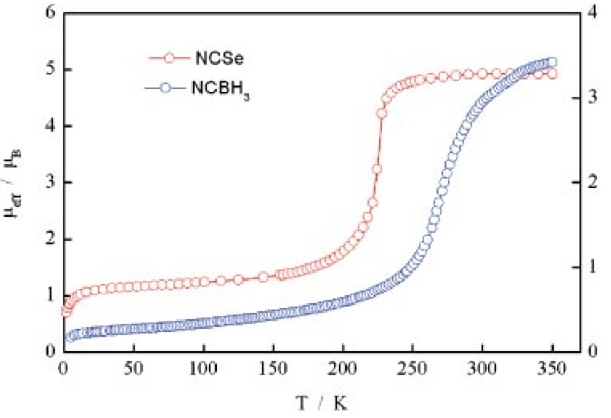


Figure 2. Magnetic moment, $\mu_{\mathrm{eff}}$ (per $Fe^{II}$), of $[(py)(NCSe)(pypzH)Fe(μ\text{-}pypz)_2Fe(pypzH)(NCSe)(py)]·2H_2O$ [where X = Se (red), $BH_3$(blue)].[16]

Kaizaki et al. also made changes to the *trans*-disposed, monodentate pyridine ligands in the bpypz-bridged compounds and this led, as mentioned earlier, to the two-step transition in the $4\text{-}Phpy/NCBH_3$ compound,[18c] with the 0.5(HS-HS + LS-LS) spin state situation at the plateau temperature. Other substituted pyridines led to the full one-step spin change.[18d] Changing the $NCX^–$ ligand to $NCS^–$, while keeping the axial base as 4-Phpy, also gave a full one-step change ($T_{1/2}$ = 150 K) in the $[(4\text{-}Phpy)(NCS)Fe^{II}(μ\text{-}bpypz)_2Fe^{II}(NCS)(4\text{-}Phpy)]$ derivative, its isostructural $Co^{II}Co^{II}$ analogue remaining HS-HS at all temperatures.[18d] Sorting out the precise differences in intermolecular packing that leads to a one-step vs. a two-step transition, in going from HS-HS to LS-LS states, is not trivial.

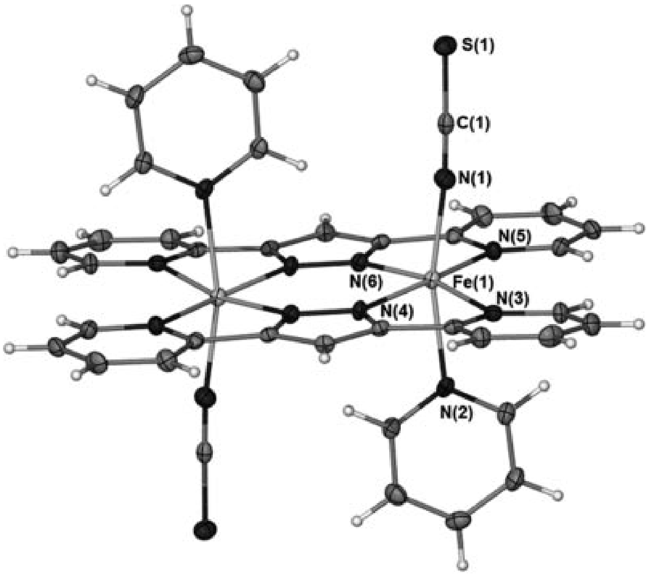


Figure 3. Structure of the pyrazolato-bridged complex [(py)(NCS)-$Fe^{II}$(μ-bpypz)$_2$$Fe^{II}$(NCS)(py)] at 123 K; that of the triazolato-bridged bpytz analogue is isostructural.[19] The other derivatives with different pyridine bases and $NCX^-$ ligands, investigated earlier by Kaizaki et al.,[18] have similar structures, the one with 4,4-bipy forming a chain of dinuclear compounds.[18d] Reproduced with permission from ref.[19]

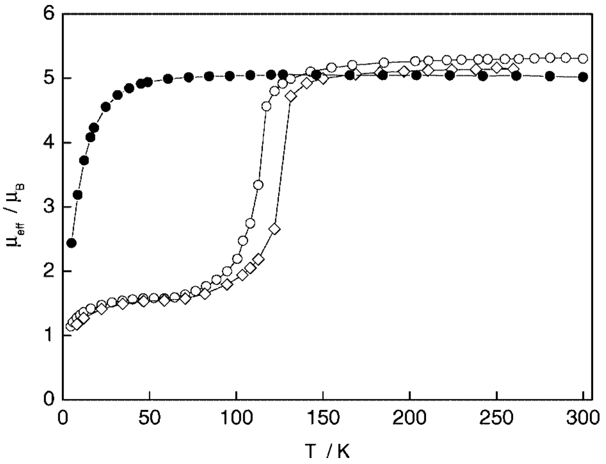


Figure 4. Plots of $\mu_{eff}$, per $Fe^{II}$, vs. temperature for the pyrazolato-bridged complex [(py)(NCS)$Fe^{II}$(μ-bpypz)$_2$$Fe^{II}$(NCS)(py)] in single crystal form (solid circles), precipitated powder form (open circles), and for [(py)(NCSe)$Fe^{II}$(μ-bpypz)$_2$$Fe^{II}$(NCSe)(py)] (diamonds). Reproduced with permission from ref.[19]

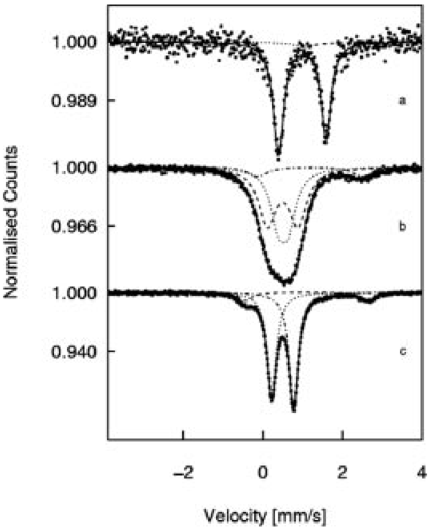


Figure 5. Mössbauer spectra, in zero applied field, of the triazolato-bridged complex [(py)($NCBH_3$)$Fe^{II}$(μ-bpytz)$_2$$Fe^{II}$($NCBH_3$)-(py)] at (a) 295 K, (b) 123 K and (c) 82 K. Reproduced with permission from ref.[19]

We are investigating other bridging ligands, particularly of the kind that have dipyridylamine (dpa) or dipyridylmethyl (dpm) N···N chelators symmetrically linked by central pyrimidine or pyridazine rings, attached either directly to the ring or through methylene groups. In some cases it appeared to be possible that the $Fe^{II}$ ions could coordinate to the N-donors in the central ring as well as to the terminal N···N chelator, thus making cross-ring exchange coupling, as well as SCO a possibility, despite the long Fe···Fe distances. Some of these ligands are shown in Scheme 1, and they, and close relatives, had been made by Steel and Sumby[35] as part of their wide study of small clusters and extended polymers of the helical and supramolecular types chelated mainly to $Cu^{II}$, $Ni^{II}$ and $Ag^{I}$. Indeed, a few dinuclear $Fe^{II}{}_2L_2$ metallo-helical compounds exhibiting SCO are known,[36] and these show scope, in future designs, for the reversible binding of guest molecules or anions that could, depending on the effect that guest binding/unbinding has on the spin transition, lead to applications in sensing.[37]

One of the pyridine-linked dinucleating dpa ligands, ddpp, (Scheme 1) that was initially used by Kepert and Amoore in attempts to make extended framework SCO materials, in fact yielded dinuclear species that exhibited some fascinating and hitherto unique properties.[38] The parent compound, [$Fe_2(ddpp)_2(NCS)_4$]·4$CH_2Cl_2$, has the dinuclear structure shown in Figure 6 with a packing diagram (Figure 7) indicative of a structurally ordered, not covalently bridged array that involves extensive ring-ring π–π interactions (intra- and interdinuclear) and various interactions involving the NCS sulfur atom.[38] Most striking is the way that three molecules of $CH_2Cl_2$ can be reversibly removed with little change occurring in the packing diagram, apart from a reduced, but very significant, number of interactions of the kind above. The parent ·4$CH_2Cl_2$ solvate displayed a two-step spin transition, with $T_{1/2(1)}$ at 180 K and $T_{1/2(2)}$ at 80 K (Figure 8), the structure in the plateau region between steps showing, for the first time in an HS-HS → HS-LS → LS-LS case, that each dinuclear molecule was trapped (ordered) in the HS-LS form with appropriate Fe–N distances and octahedral distortions, $\Sigma$, on the $Fe^{II}$ ions. Indeed, the $Fe^{II}$ centres in the HS-HS and LS-LS forms, while having typical HS and LS geometries, were also slightly inequivalent structurally. The trapped HS-LS structure contrasts with the averaged (disordered) structure found at the plateau temperature in the dca-bridged compound [(bztpen)Fe(μ-N(CN)$_2$)Fe(bztpen)](PF$_6$)$_3$ (vide supra),[24] such that the dinuclear molecules displayed crystallographically equivalent Fe atoms. The ·CH$_2$Cl$_2$ solvate of the ddpp complex showed only a one-step transition, with $T_{1/2}$ of 200 K. The fully desolvated compound remained HS-HS at all temperatures, thus indicating that the degree of solvation clearly plays a key role in the magnetism. The ability to reversibly desorb and resorb dichloromethane molecules allowed other solvents, such as CH$_2$Br$_2$ to be isolated and studied, and a wide range of such solvates, with their SCO properties, have been investigated.[39]

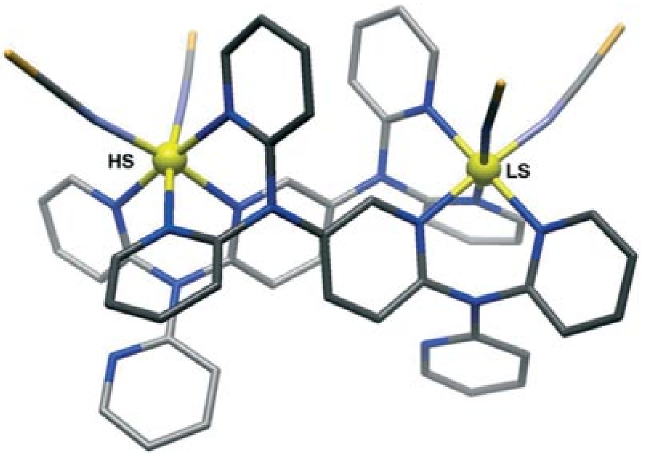


Figure 6. Structure of the dinuclear molecules of [Fe$_2$(ddpp)$_2$(NCS)$_4$]·4CH$_2$Cl$_2$ in the ordered HS-LS form at the intermediate plateau temperature range (IP). Reproduced with permission from ref.[38]

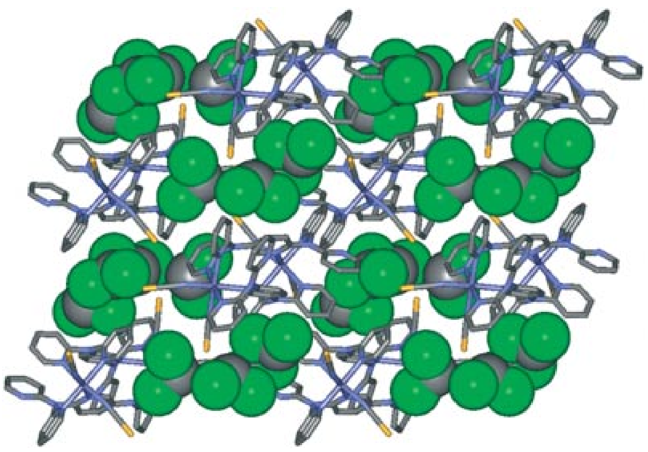


Figure 7. Packing diagram for [Fe$_2$(ddpp)$_2$(NCS)$_4$]·4CH$_2$Cl$_2$ with space filling for the CH$_2$Cl$_2$ molecules. The positions of the dinuclear molecules remains the same in the ·1CH$_2$Cl$_2$ form. Reproduced with permission from ref.[38]

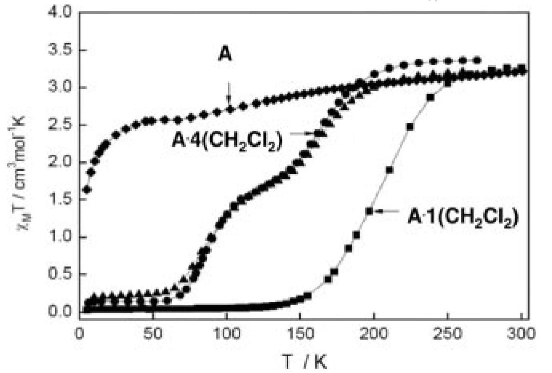


Figure 8. $\chi_M T$ values vs. temperature for the various solvates of [Fe$_2$(ddpp)$_2$(NCS)$_4$]·$x$CH$_2$Cl$_2$, **A**·$x$CH$_2$Cl$_2$, and of the non-solvated form, **A**. The solid circles and triangles are for the as-prepared ·4CH$_2$Cl$_2$ form and the resolvated form, respectively. Reproduced with permission from ref.[38]

Rosa et al.[40] have just reported a new dinuclear SCO compound, [(3-bpp)(NCS)$_2$Fe(μ-4,4′-bipy)Fe(NCS)$_2$(3-bpp)]·2MeOH, that displays a partial (≈ 50%) crossover at ca. 100 K and contains the simplest pyridine-linked bridging ligand, 4,4′-bipy, much used in extended framework crystalline species. The end groups assembled on the Fe$^{II}$(μ-4,4′-bipy)Fe$^{II}$ bridge were, perhaps surprisingly if one considers the other products that might have crystallised, two NCS$^-$ and one tridentate 2,6-bis(3-pyrazolyl)pyridine chelate (bpp), making up the N$_6$-donor sets around each Fe atom.[40] The synthesis was a sequential one in which the mononuclear [Fe(NCS)$_2$(3-bpp)(MeOH)] was prepared in situ, in methanol, and then a CH$_2$Cl$_2$ solution of 4,4′-bipy was cannulated into it. Three crystal phases were observed as a function of temperature, two of them being above and below $T_{1/2}$.[40b] Intradinuclear H-bonding occurs between the MeOH and the free pyrazole NH group in a similar way to that observed in "pseudodimeric" Fe$^{II}$(pypz) compounds.[17] Crystal packing revealed a dense network of intermolecular contacts that form sheets involving π–π and C–H···π(NCS) interactions, with the sheets connected through hydrogen bonds such as pyrazole –NH···S(CN). The $\chi_M T$ data showed a gradual spin crossover with no cooperativity, and this was supported by variable-temperature diffuse absorption spectra of the surface of the solid. The LIESST data are mentioned later. We see another 4,4′-bipy-bridged dinuclear example in section 4, this time of Fe$^{III}$, containing two pentadentate Schiff base end caps.

All of these dinuclear Fe$^{II}$ compounds, with Fe(N)$_6$-donor sets, including the bipyrimidine family,[9,10,15] show little or no thermal hysteresis in the spin transition, which, together with the observed gradual nature of the spin transition, indicate very weak cooperativity is occurring between the spin centres within, or between, the dinuclear molecules. This is despite the interdinuclear contacts commonly noted in the packing diagrams. An estimate of the cooperativity in the μ-bpypz compounds, for example, was obtained by Kaizaki et al.[18b] by use of the regular solution model[41] and the cooperativity factor, $C$ (= $\Gamma/2RT_{1/2}$). $\Gamma$ is an interaction parameter. Values of the enthalpy ($\Delta H_{HL}$) and entropy ($\Delta S_{HL}$) changes associated with the spin transitions (H = HS-HS; L = LS-LS) can be influenced by changes in both the X group of NCX$^-$, the py axial ligand, the in-plane dinucleating ligand and even in non-bonded solvate molecules. For example, [(4-Phpy)(NCS)Fe$^{II}$(μ-bpypz)$_2$Fe$^{II}$(NCS)(4-Phpy)]; $\Delta H_{HL}$ = 7.18 kJ mol$^{-1}$, $\Delta S_{HL}$ = 47.9 J K$^{-1}$,

$\Gamma$ = 1.08 kJ mol$^{-1}$, $C$ = 0.433 ($T_{1/2}$ = 150 K);[18c] [(py)(NCS)-Fe$^{II}$(μ-bpypz)$_2$Fe$^{II}$(NCS)(py)] rapidly precipitated powder (hydrate);[18b] $\Delta H_{HL}$ = 5.96 kJ mol$^{-1}$, $\Delta S_{HL}$ = 46.6 J K$^{-1}$, $\Gamma$ = 1.84 kJ mol$^{-1}$, $C$ = 0.87 ($T_{1/2}$ = 127 K); [(py)(NCBH$_3$)-Fe$^{II}$(μ-bpypz)$_2$Fe$^{II}$(NCBH$_3$)(py)]; $\Delta H_{HL}$ = 13.3 kJ mol$^{-1}$, $\Delta S_{HL}$ = 64.7 J K$^{-1}$, $\Gamma$ = 1.34 kJ mol$^{-1}$, $C$ = 0.39 ($T_{1/2}$ = 205 K).[18b] The smaller $C$ is, the more gradual is the SCO curve. Enthalpy differences were suggested to explain the differences in $C$ and $T_{1/2}$ found for the NCS/4-Phpy and py compounds. However, caution has to be exercised because the crystals of the NCS/py complex (non-crossover)[19] are not isomorphous to those of NCS/4-Phpy, and interdinuclear interactions such as π–π effects can also affect the cooperativity and nature (one-step vs. two-step) of the spin transition. Furthermore, the errors in these parameters are usually large (ca. ±30%).

### 3.2. $N_4O_2$- and $N_5O$-Donor Sets Around Fe$^{II}$

While the vast majority of Fe$^{II}$ SCO materials, both mono- and polynuclear in structure, contain octahedrally coordinated $N_6$-donor sets from pyridyl-like, amine and NCX$^-$ ligands, of the types described above, there are now a few recent examples known of nitrogen- and oxygen-containing chelating ligands, the syntheses being carried out under anaerobic Schlenk conditions. Presumably a precise combination of the N- and O-donor types in the ligands is required to create the crossover ligand-field. For example, in the chloranilato (CA$^{2-}$)/TPyA iron(II) systems described below (Scheme 1), Miller et al.[13] and, earlier, ourselves[42] had observed ferromagnetic coupling between HS Fe$^{II}$ centres, without any SCO evident, in dinuclear, [(TpyA)-Fe(μ-CA)Fe(TpyA)](BF$_4$)$_2$·2MeOH (2$J$ = +1.4 cm$^{-1}$) and 1-D chain, [Fe(H$_2$O)$_2$(μ-CA)]·H$_2$O (2$J$ = +0.94 cm$^{-1}$) compounds, respectively. The former has $N_4O_2$ coordination, the latter $O_6$ and, hence, weak field. A small change in the bridge, from CA$^{2-}$ to DBQ$^{2-}$, yielded a dinuclear complex [(TpyA)Fe(μ-DBQ)Fe(TpyA)](BF$_4$)$_2$, also with $N_4O_2$ coordination around each Fe$^{II}$, but now displaying SCO above 300 K, and not quite in the HS-HS state at 380 K.[13b] Interestingly, a further change of bridge to THBQ$^{2-}$, in [(TpyA)-Fe(μ-THBQ)Fe(TpyA)](BF$_4$)$_2$, led to a "half" SCO, with hysteresis ($T_{1/2}$ = 260 K; $\Delta T$ = 10 K), the structure at a temperature below $T_{1/2}$ showing 50% HS-HS and 50% LS-LS molecules,[13c] rather like the 4-Phpy/NCBH$_3$ bpyz-bridged system of Kaizaki et al. described earlier.[18c] The hysteresis was ascribed to interdinuclear hydrogen bonding involving the OH groups on TBHQ$^{2-}$. Most interestingly, ferromagnetic coupling was simultaneously observed as an increase in the $\mu_{eff}$ values below ca. 50 K, due presumably to HS($S$ = 2)-HS($S$ = 2) spin-spin coupling, in a related way to that observed by Brooker et al. in a pyridazine-bridged Co$^{II}$Co$^{II}$ SCO compound (vide infra).[43]

The other family of Fe$^{II}N_4O_2$ compounds displaying SCO is that first developed by Jäger and co-workers[44] and employing planar, tetradentate $N_2O_2$ Schiff base chelators (Scheme 1, ligand L$^1$) that look like the well-known salicylaldiminato ligand, salophen$^{2-}$, but with significantly different ligand-field strength, particularly when combined with *trans*-ligated pyridine-type N-donor ligands. Weber et al. have developed these systems and have observed SCO with high cooperativity (viz. abrupt transitions and thermal hysteresis) in mononuclear ($\Delta T$ = 9 K)[12b] and 1-D chain[12f] species ($\Delta T$ = 18 K; see also the 1-D section 6), the hysteresis being due to elastic and elastic-plus-covalent interactions, respectively.

A dinuclear Jäger-type design involved a ligand with two such $N_2O_2$ chromophores fused on the opposite side of an aromatic ring that yielded four examples of [Fe$_2$L$^1$(py)$_4$]·(py)$_x$ compounds having different combinations of substituent groups on the amino ketone part of the Schiff base moieties;[12a] (Scheme 1). Incomplete SCO transitions were noted in some cases ($T_{1/2}$ ≈ 150 K) and in one such the crystal structure, measured below $T_{1/2}$, showed the presence of equal numbers of independent dinuclear molecules having HS-HS and LS-LS geometries, as judged by Fe–N lengths and O–Fe–O angles. Above $T_{1/2}$, the Fe–N distances and O–Fe–O angles for both molecules were consistent with their Fe$^{II}$ centres being in HS-HS spin states. This situation mirrors that found in the TpyA/THBQ dinuclear system, above.[13c] Control of the degree of pyridine solvation, $x$, in the phenylene-linked Jäger-type complexes was difficult, and this influenced the ability to reproducibly observe SCO transitions, but their existence was not in doubt.[12a] Weber and Walker have recently used solution $^1$H NMR isotropic shifts of ligand methyl and methylene protons in the HS ($S$ = 2) fraction, as a function of temperature (350 to 200 K), to probe SCO in the dinuclear Fe$^{II}$ compounds,[12e] in a related way to that we used to probe exchange coupling in dinuclear (μ-oxido)Fe$^{III}$ Schiff base complexes.[45] Crystal packing effects were thus eliminated, and they found a good agreement of the $\gamma_{HS}$ vs. $T$ plots with those determined using the Evans NMR method. The gradual spin transition had moved to much higher temperature ($T_{1/2}$ ≈ 210 K) compared to where it was in the incomplete transition of the solid. There was some evidence from the deviations from Curie behaviour of the isotropic shifts for weak, cross-ring exchange coupling ($J$ ≈ –0.5 cm$^{-1}$). Other than this, it was concluded that the dinuclear molecules, in solution, behaved as two independent SCO centres, the NMR shifts and magnetic moments behaving, as a function of temperature, very much like the mononuclear analogues.

Conversion of the ($N_2O_2$)$^{2-}$ ligands into ($N_4$)$^{2-}$ macrocycles allowed Jäger and Weber and co-workers to make intermediate spin, $S$ = 1, [Fe$^{II}$(N$_4$)] complexes including weakly linked, dinuclear five-coordinate species of the type [(N$_4$)Fe(μ-dabco)Fe(N$_4$)].[12d] While there was some evidence for $S = 1 \rightarrow S = 0$ crossover in one of the monomeric compounds, the dabco-bridged species showed $S$ = 1 moments of ca. 3 $\mu_B$, with a rapid decrease below 20 K due to zero-field splitting in one example, and a more gradual decrease, perhaps due to weak interdinuclear antiferromagnetic coupling (4.21 Å separation, cf. Fe···Fe 7.27 Å), in another.

Gamez and co-workers[46] reported a dinuclear $Fe^{II}$ SCO complex, $[Fe_2(dpya\text{-}triz)_2(H_2O)_2(MeCN)_2](ClO_4)_4$, using a triazine-linked tris(dipyridylamine) ligand, shown in Scheme 1, in which only two of the dpya arms were bonded to each Fe atom, the remaining positions around Fe being occupied by water and MeCN, thus giving $Fe(N_5O)$ coordination. Magnetic and Mössbauer measurements showed a gradual, incomplete one-step spin transition ($T_{1/2}$ = 265 K) in which 65% of the HS-HS centres change spin. The room-temperature structure showed HS Fe–N distances; the intradinuclear Fe···Fe separation was 9.232(2) Å, and the closest interdinuclear Fe···Fe was 8.992 Å. Only weak electrostatic and van der Waals interactions were detected in the crystal packing. Structural details at the plateau temperatures, below 265 K, would have been useful. Changing MeCN to MeOH around each $Fe^{II}$ atom was enough to lower the ligand field and yield HS-HS magnetism at all temperatures.[46]

## 3.3. Spin-Crossover and Spin-Spin Exchange Coupling

The following comments refer to point (i) in the Introduction, i.e. possible synergy between exchange coupling and SCO, a key point of interest to Kahn at the outset of dinuclear SCO chemistry.[6] Qualitatively, it is known from the magnetochemistry of dinuclear and higher nuclearity clusters (commonly of $Cu^{II}$ or $Ni^{II}$, less commonly of $Fe^{II}$), and the best-fit $J$ values (using spin Hamiltonian $-2JS_1\cdot S_2$), that bridges between $Fe^{II}$ centres should yield antiferromagnetic coupling in the cases of bipyrimidine ($\approx -2$ cm$^{-1}$),[9,10,15] pyrazolate and triazolate ($\approx -1$ cm$^{-1}$, but much higher for $Cu^{II}$),[47] tetramminobenzene linker ($\approx -0.5$ cm$^{-1}$)[12a] while bridging ligands such as 4,4′-bipy, alkane-linked nitriles and tetrazoles will generally yield $J = 0$ cm$^{-1}$. Chloranilato or $THBQ^{2-}$ bridging leads to ferromagnetic coupling, $J \approx +0.7$ cm$^{-1}$, an $Fe^{II}$(TpyA) example of the latter bridge showing simultaneous ferromagnetic coupling and spin crossover in its magnetic moment data.[13c] The "half" crossover $Fe^{II}$(μ-bpym) compound also showed simultaneous HS-HS antiferromagnetic coupling at low temperatures below the spin transition.[6,9,15] Real et al. interpreted the thermal and photoexcited crossover behaviour in the bpym bridged family in terms of a synergy between coupling and spin crossover.[6,9,10,15] Indeed, they have been able to move the $T_{1/2}$ point by applying hydrostatic pressure to the compounds. Applied pressure is known to affect the volume change intrinsic to the HS to LS spin change but its effect upon exchange coupling, while of much current interest, is yet to be elucidated.

In the majority of dinuclear $Fe^{II}$ compounds reported, the spin transition dominates any spin-spin coupling so that, for example in the HS-HS region of magnetic moment, above $T_{1/2}$, in the μ-pypz, μ-bpypz and μ-bpytz species there is little evidence of any decrease due to antiferromagnetic $S$ = 2, $S$ = 2 coupling. Much stronger antiferromagnetic or ferromagnetic coupling, along good superexchange N-donor pathways such as found in μ-$N^{3-}$, μ-$N_3^-$ or μ-$CN^-$ bridging has yet to be achieved in SCO clusters. The CN-bridged square cluster of Oshio[30] and Vahrenkamp[29] had intervening LS $[Fe(bipy)_2]$ groups separating the two SCO $[(tpa)Fe(NC)_2]$ coordination spheres, which was fortuitous since direct Fe(CN)Fe bridging will usually lead to LS $Fe^{II}$ (≈ diamagnetic) at the carbon end, depending on the other coligands present.

## 3.4. LIESST Effect in Dinuclear $Fe^{II}$ Spin Crossover Compounds

Our LIESST work has, to date, been largely on mononuclear $Fe^{II}$ bis(terdentate), $[Fe^{II}N_6]$, compounds, and some unexpected results have been found for meridionally[48] and facially ligated[49] chelate complexes, particularly in regard to the relationship $T_{LIESST} = T_o - 0.3T_{1/2}$. Lètard et al. had found that from some 60 mononuclear SCO complexes studied, families of them followed four different $T_o$ lines according to the inner coordination environment around $Fe^{II}$.[50] Our bis(terdentate) complexes,[48,49] and also, very recently, the $[Fe(N_2O_2)(py)_2]$ Jäger-type complexes[12b] were found to follow the $T_o$ = 100 K line, rather than the 150 K line hitherto followed by many other bis(terdentate) (meridional) compounds.[51] Flexibility in the ligand backbones, particularly when $CH_2$ groups separated the inner and outer pyridyl/pyrazole rings, was thought to influence this unexpected behaviour. Further influences on the magnetic, structural and LIESST behaviour of our bis(terdentate) chelates were brought about by the presence of solvate molecules and polymorphism.[48,49] In the case of the facially coordinated, mixed-ligand tris(pyrazolymethane) chelates, we are presently extending these in to dinuclear $Fe^{II}$ derivatives by means of aryl ether groups linking $pz_3CH$ chelators together, so that the magnetism and LIESST effects can be probed and compared to the mononuclear complexes.

In the dinuclear complex $[Fe_2(ddpp)_2(NCS)_4]\cdot 4CH_2Cl_2$,[38] the LIESST effect under 514.5 nm irradiation, shown in Figure 9 (and Figure 10) was not complete, but only ca. 40% of the metastable HS state was populated at 10 K ($T_{LIESST} \approx 50$ K).[52] Interestingly, no LIESST was observed in the partially desolvated phase $[Fe_2(ddpp)_2(NCS)_4]\cdot 1CH_2Cl_2$. A much higher degree of photoconversion, from the "half" $\chi_M T$ value to the HS value, was found for the 4,4′-bipy-bridged complex $[(3\text{-bpp})(NCS)_2Fe(\mu\text{-}4,4'\text{-bipy})Fe(NCS)_2(3\text{-bpp})]\cdot 2MeOH$ using 647 nm irradiation at 10 K ($T_{LIESST}$ = 72 K).[40] Preliminary LIESST studies, using Mössbauer methods, on the μ-pypz complex, $[(py)(NCX)(pypzH)_2Fe^{II}(\mu\text{-}pypz)_2Fe^{II}(pypzH)_2(NCX)(py)]\cdot 2H_2O$ did not show any evidence for metastable HS-HS states after irradiation with green laser light at low temperatures.[53] This might be because of sample-thickness effects since the closely related μ-bpypz compounds, also having one-step HS-HS → LS-LS spin transitions, showed strong LIESST from the LS-LS states when measured by diffuse reflectance, magnetic susceptibility and Raman spectral

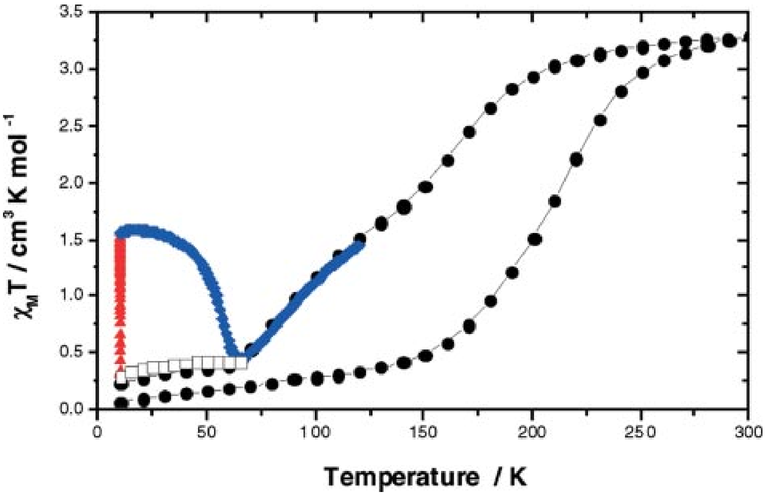


Figure 9. Effect of LIESST on the $\chi_M T$ values for $[Fe_2(ddpp)_2(NCS)_4]\cdot 4CH_2Cl_2$. Solid circles, top curve = data recorded in cooling and warming modes without irradiation. Red triangles = data recorded during irradiation at 10 K ($\lambda$ = 514.5 nm) for 2 h. Blue diamonds = data recorded in warming mode, up to 120 K, with the laser turned off after irradiation; $T_{LIESST}$ = 50 K. Solid circles, bottom curve = thermal data in cooling and warming mode for $[Fe_2(ddpp)_2(NCS)_4]\cdot 1CH_2Cl_2$. No LIESST was observed in this case.[52]

methods.[18a,54] Our μ-bpytz analogues, and other dinuclear systems, will be investigated by reflectance and susceptibility techniques, in collaboration with Létard.

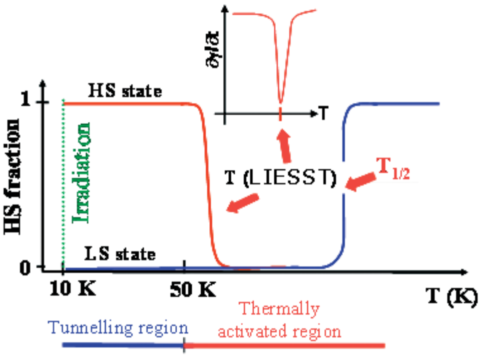


Figure 10. The various temperature and irradiation (LIESST) regions used to interpret Figure 9 with $T_{LIESST}$ (also shown as 1st derivative) and $T_{1/2}$ shown.

The most studied dinuclear SCO compounds, for their LIESST properties, are the bipyrimidine-bridged species. Since the LIESST features have recently been reviewed,[9,10] only a brief summary of pertinent points is given here for completeness. The first reports were by Létard, Real, Kahn et al.[55] The most recent work, by Real and Bousseksou and co-workers, has used irradiation by visible and IR wavelengths and measurements by FT IR and Raman spectroscopy, X-ray diffraction (single crystal and PXRD) and magnetic susceptibility (SQUID) methods.[10] Emphasis has been on the two-step spin-transition compound $[(NCS)_2(bt)Fe(\mu\text{-bpym})Fe(bt)(NCS)_2]$, its NCSe analogue and the "half" SCO complexes $[(NCX)_2(bpym)Fe(\mu\text{-bpym})Fe(bpym)(NCX)_2]$, where X = S or Se. Zero-field and applied-field Mössbauer studies of the LIESST effect ($\lambda$ = 514 nm) in $[(NCS)_2(bt)Fe(\mu\text{-bpym})Fe(bt)(NCS)_2]$, starting from the LS-LS ground state, showed that the excited spin states corresponded to both the HS-HS and HS-LS pairs.[21] Kinetic studies showed that the metastable HS-HS state relaxed back to both HS-LS and LS-LS states at 4.2 K, while the HS-LS excited pairs relaxed back to the ground state LS-LS pairs. An earlier susceptibility study of the LIESST effect in this complex,[55] using red-light irradiation ($\lambda$ = 647.1 nm and 676.4 nm), summarised in a recent review,[10] showed only the HS-HS excited state being generated. The temperature dependence of $\chi_M T$, after irradiation, indicated synergy between the LIESST effect and intradinuclear antiferromagnetic coupling since the plot followed the thermal population expected for the pair states $S$ = 0,1,2,3,4 generated by 2:2 (HS-HS) coupling. FTIR and Raman spectral studies confirmed the formation of HS-HS excited states in red-light irradiation.[56] While the descriptions of the excited pair states formed in $[(NCS)_2(bt)Fe(\mu\text{-bpym})Fe(bt)(NCS)_2]$ upon irradiation, and after subsequent relaxation, are somewhat confusing to follow,[10] the conclusions from the Mössbauer work and the susceptibility and vibrational spectral work appear to be self-consistent. The relaxation mechanism was interpreted in terms of the process HS-HS → HS-LS → LS-LS, the intermediate HS-LS state being confirmed in the Mössbauer spectra.[21] In a related compound $[(NCS)_2(phdia)Fe(\mu\text{-phdia})Fe(phdia)(NCS)_2]$, no HS-HS excited states were observed but only HS-LS and LS-LS following irradiation with 488 nm light, the HS-LS pairs being quite stable.[10,57]

An important advance in the photomagnetic properties of $[(NCS)_2(bt)Fe(\mu\text{-bpym})Fe(bt)(NCS)_2]$ has been the ability to selectively photoswitch from the LS-LS state to metastable HS-LS or HS-HS states using IR light of wavelength 1342 nm or red light of 647 nm, respectively, the details being recently reviewed.[10] This selectivity has been confirmed by crystal structures, solved at 23 K, of the HS-LS

(1310 nm) and HS-HS (808 nm) photoinduced states, supported by temperature-dependent unit-cell parameter measurements.[58] Good agreement was noted between the Fe–N bond lengths, Fe···Fe separations and the octahedral distortion parameter, $\Sigma$, found in the photoinduced (kinetically trapped) states and in the thermally generated equivalent (thermodynamically stable) states. These studies are leading to the possible development of multi-stepped molecular switches since reversible changes between the photoinduced HS-HS, HS-LS, HS-HS states was achieved using the sequence 808, 1310, 808 nm irradiation, as judged by time-dependent unit-cell volume measurements.[58] Similar switching results have recently been observed in the analogue $[(NCSe)_2(bt)Fe(\mu\text{-bpym})Fe(bt)(NCSe)_2]$,[59] the IR light irradiation yielding HS-LS excited states rather than the HS-HS state found earlier using visible light.[60]

## 4. Dinuclear Iron(III) $d^5$–$d^5$ Spin Crossover Compounds

While the first known mononuclear SCO compounds of $Fe^{III}$ contained the $S_6$-donor set from three dithiocarbamate ligands,[1,61] the majority of examples contain N,O-donor–donor combinations, often within Schiff base chelates.[4a,14] There are, to date, many fewer dinuclear $Fe^{III}$ compounds known than for $Fe^{II}$, and the $S = 5/2 \rightarrow S = 1/2$ transitions are generally gradual in nature.[62] As indicated above, a 4,4′-bipy-bridged complex, $[(saldpt)Fe(\mu\text{-}4,4'\text{-bipy})Fe(saldpt)](BPh_4)_2$, shows a gradual, one-step $S = 1/2 \rightarrow S = 5/2$ transition starting above 120 K but not fully HS-HS at 300 K ($T_{1/2} \approx 280$ K). Boca et al.[63] used an Ising model to fit the magnetic data on this and two other 5-substituted sal analogues, yielding $E(\text{HS} - \text{LS})$ of 1300 K (no cooperativity parameter included), and with a small exchange coupling, $J_{(S = 1/2) - (S = 1/2)}$ of $-2\ \text{cm}^{-1}$ included to account for a decrease in $\mu_{\text{eff}}$ at low temperature. No allowance was made for orbital degeneracy/spin orbit coupling in the $^2T_{2g}$ parent state of the $S = 1/2$ levels. Hayami et al.[64] reported the structures and magnetism of related dinuclear compounds, with saldpt or (salen)(L) (L = $H_2O$ or imidazole) end capping and azpy or tvp as the dipyridyl bridges. The salen derivatives remained HS-HS at all temperatures while the saldpt compounds showed gradual crossover of the magnetic moments above 150 K, supported by Mössbauer spectroscopic data. Later, using the salMedpt end cap and tvp as bridge, Matsumoto et al.[65] observed a full two-step HS-HS → HS-LS → LS-LS transition, with the structure at the plateau temperature providing evidence for HS $Fe^{III}$ and LS $Fe^{III}$ geometries in the dinuclear moiety. They had also noted a more gradual two-step transition, incomplete in the LS-LS region, for a 3-MeOsalMedpt analogue, the structure of which taken at the plateau temperature showed HS and LS $Fe^{III}$ centres in the dinuclear molecules.[66] These HS and LS sites independently formed weak layers in the packing diagram that stack alternately. In a further recent extension, using the 3-MeOsaldpt pentadentate ligand, and the bis(imidazole) bridge [bimb; earlier labelled tdim in 1-D $Fe^{III}$(salen) species],[67] a two-step transition was observed with $T_{1/2(1)} = 60$ K and $T_{1/2(2)} = 90$ K, and this was ascribed to a quasi-1-D packing motif involving π–π interactions. No thermal hysteresis was observed in any of these dinuclear systems.

Our recent, contemporaneous work on 1-D chains of type [Fe(salen)(base)](Y) and [Fe(acen)(base)](Y), where Y is $ClO_4^-$, $PF_6^-$, $BF_4^-$, $BPh_4^-$ and base is a two-connecting di-pyridyl or di-imidazole, has yielded a "chain of dinuclears" in the case of $[\{Fe^{III}(acen)\}_2(\mu\text{-tvp})(tvpH)(tvp)](\mu\text{-tvpH})(BPh_4)_4\cdot 2MeOH$. The monoprotonated $tvpH^+$ cations, one bonded to Fe at its other pyridine N atom while the other is not covalently bonded, act to link the dinuclear moieties together through weak NH···N(tvp) hydrogen bonding. Magnetic data show a gradual one-step LS-LS → HS-HS crossover beginning above 200 K and incomplete at 350 K, with no hysteresis.[68]

## 5. Dinuclear Cobalt(II) $d^7$–$d^7$ Spin Crossover Compounds

Kahn and Zarembowitch first isolated $Co^{II}$ SCO compounds using the dinucleating $(fsa)_2en^{2-}$ ligand, the latter containing both an $N_2O_2$ Schiff base pocket and an $O_4$ phenolato/carboxylato pocket with two *trans*-phenolato O-donors providing the bridges.[69] While many homo- and heterodinuclear derivatives were investigated for their magnetic exchange properties, the $Co^{II}$ system was limited to mononuclear species containing the SCO centre in the $N_2O_2$ pocket.

Brooker designed a different dinucleating macrocyclic ligand, $L^2$ that incorporated two pyridazine N,N-bridges joining the two $Co^{II}$ ions in a coplanar manner, with 1,3-propanediylbis(imino) N-donor end groups completing the equatorial planes. Axial ligands such as $NCS^-$, $SCN^-$, MeCN were used to tune the spin state on the $Co^{II}$ centres, the majority of such compound,[43,70] as well as their triazolato analogues[71] and acyclic 2-aminoethylpyridine derivatives,[72] displaying HS-HS behaviour at all temperatures, with weak antiferromagnetic coupling occurring across the $\{Co(N,N)_2Co\}$ bridges. In the particular case of $[Co_2L^2(NCS)_2(SCN)_2]$, the first simultaneous observation of SCO and antiferromagnetic coupling was clearly observed in the magnetic moment plot.[73] The spin transition was gradual, beginning above 250 K.

## 6. 1-D Chains of $Fe^{II}$, $Fe^{III}$ and $Co^{II}$ Exhibiting Spin Crossover

The tris(μ-4-R-1,2,4-triazole) 1-D $[Fe^{II}(4\text{-R-}1,2,4\text{-triazole})_3](Y)_2$ chains, much studied by Lavrenova,[74a] Kahn,[74b] Garcia and co-workers,[75] provide the iconic reference state for 1-D SCO materials, not only because of their room-temperature spin transitions and wide thermal hysteresis, but also because they came very close to commercial reality as data storage and display devices.[3,76] Recently, in other device-related work, photo-responsive molecular wires were obtained in solutions of $Fe^{II}$ 1-D analogues containing lipophilic $C_{12}$ chains on azobenzene R groups substituted at the 4-position.[77] At a more fundamental level, muon spin relaxation measurements have been made on the R = $NH_2$ derivative (nitrate salt; $T_{1/2}$ = 329 K, $\Delta T$ = 34 K) to probe the dynamics of spin change and the origins of the high cooperativity.[78] The main thing missing among the many R-substituted and Y-varied examples synthesised, including "ligand-alloy" materials, is a crystal structure, although some were solved as $Cu^{II}$ analogues,[79,80] with the 1-D structure for the $Fe^{II}$ compounds then deduced from XANES, EXAFS and powder diffraction methods. A recent paper of Gütlich, Gaspar et al.[80] employed such methods for a 4-(benzylamido)-substituted (triazole)$Fe^{II}$ chain for which the corresponding $Cu^{II}$/Y = $CF_3SO_3^-$ salt had its crystal structure solved and a lack of chain–chain interactions was noted. Three different anions were used for the $Fe^{II}$ species, the compounds being all hydrated, and, apart from one ($CF_3SO_3^-$ salt) that was LS at 295 K ($T_{1/2} \approx 340$ K), the other salts displayed an abrupt one-step spin change at ≈ 230–250 K with a hysteresis width of ca. 10 K, the latter value being lower than for other 4-R substituents. Interestingly, removal of the hydrated water gave 1-D (presumed) materials displaying much more gradual transitions, with lower $T_{1/2}$ values, compared to the hydrated parent, one behaving HS at all temperatures.

A key, early postulate to emerge from the triazole chain work was that such covalently bridged chains would, in comparison to mononuclear analogues, show enhanced cooperativity between the spin centres along the chains (e.g. leading to abrupt transitions having wide hysteresis loops, with distinct colour changes). Our approach has been to expand the small data base of 1-D SCO families to include other kinds and numbers of bridging groups leading, for example, to larger Fe···Fe separations, different bridge rigidity/flexibility and different structural nuances around $Fe^{II}$, compared to the triazole family, as well as to try and create chain–chain interactions in the crystal phase. Emphasis, to date, has been on the use of two-connected dipyridylamine (dpa) chelators, with connecting (linking) groups generally being heterocyclic rings and varied widely in the nature of their substituents. Two anions, $NCX^-$, have been used to complete the $Fe(N)_6$ coordination environments.

Thus, using the bis(dpa) ligand, 2-chloro-4,6-bis(dipyrid-2-ylamino)-1,3,5-triazine (cddt; Scheme 1), a range of differently solvated 1-D compounds was synthesised; $[Fe(NCS)_2(cddt)]\cdot 1/2(CHCl_3)\cdot H_2O$, $[Fe(NCS)_2(cddt)]\cdot 2MeOH$ (polymorphs a and b), $[Fe(NCSe)_2(cddt)]\cdot 2MeOH$[23] (Figure 11). The magnetic data for the two methanol solvates are shown in Figure 12, the NCS (b) complex displaying a somewhat unusual and subtle two-step-like incomplete transition, while the NCSe complex showed a full one-step crossover at a higher $T_{1/2}$ value of 220 K [cf. ≈ 200 K for the high-temperature step in the NCS (b) compound]. No thermal hysteresis was present. Having confirmed that the unusual shape of $\chi_M T$ vs. $T$ for the NCS (b) complex, with a very broad "step" at ca. 100 K, was reproducible and intrinsic to the material, the use of variable-temperature powder synchrotron XRD methods then yielded precisely the same curve as did the susceptibilities (Figure 13). Non-linearity was also observed in the temperature dependence of the unit-cell axes, particularly in *c* (Figure 13), with a minimum at ca. 200 K. This axis is the one along which the 1-D chains are orientated, and thus most sensitive to the spin transition. Non-linear thermal expansion behaviour was also observed along *a* and *b*, and we believe this is associated with the contraction of the Fe–N bonds oriented in the *ab* plane, as well as with intermolecular interactions including π–π interactions. Indeed, $[Fe(NCS)_2(cddt)]\cdot 2MeOH$ (b) shows π–π interactions between a pyridyl ring coordinated to Fe(1) and its symmetry-generated ring on the adjacent chain. The adjacent Fe(2) in the chain shows only very weak such interactions. These π–π interactions are not present in polymorph a, the latter not showing SCO with the Fe atoms remaining HS at all temperatures. Most interestingly, at 123 K, Fe–N lengths and octahedral distortions, $\Sigma$, around Fe(1) and Fe(2), for polymorph b, show that the chains have alternating Fe(1; LS), Fe(2; HS), Fe(1; LS), Fe(2; HS). spin states, in accord with the magnetic data.

As is commonly found in crystalline mononuclear and dinuclear SCO systems, other non-covalent interactions play a part in this family of 1-D materials. $[Fe(NCS)_2(cddt)]\cdot 2MeOH$ (b), and (a) show hydrogen bonding between one of the MeOH oxygen atoms and a sulfur atom of NCS, with polymorph a having one of its two crystallographically distinct NCS groups disordered at S with only one of its two positions involved in hydrogen bonding, as well as showing S···S interactions with a symmetrically related NCS group.[23] Compound $[Fe(NCSe)_2(cddt)]\cdot 2MeOH$ is isomorphous to polymorph a of the NCS derivative and has two distinct Fe atoms with disorder in the NCSe group and Se···Se interactions noted for one Se site to the adjacent chain (Figure 11). No π–π interactions were present in the NCSe compound, and the one-step HS → LS spin transition is primarily influenced by the stronger ligand-field of NCSe compared to NCS. Further perusal of the multifarious structural features of this 1-D family, shows that the HS compound $[Fe(NCS)_2(cddt)]\cdot 1/2(CHCl_3)\cdot H_2O$ displays cddt Cl···Cl chain–chain interactions and a similar intrachain structure to that in $[Fe(NCS)_2(cddt)]\cdot 2MeOH$ (a) and (b), but different to that in $[Fe(NCSe)_2(cddt)]\cdot 2MeOH$. Crystal packing of the chains and position of guest solvent molecules also show subtle differences between the four family members.

Our recent extensions of the bis(dpa) ligand systems to include a pyrimidine-linked version, 2,4-bis(2′,2′′-pyridyl)-pyrimidine (bdpp; Scheme 1), has yielded 1-D compounds with even more intriguing properties, particularly in regard to the observation of two-step spin transitions for the first time in unidimensional compounds.[81] Detailed variable-temperature structural work on $[Fe(NCS)_2(bdpp)]$, polymorphs a (triclinic) and b (monoclinic), and on $[Fe(NCSe)_2(bdpp)]$, in conjunction with magnetic and LIESST studies have revealed new insights in to the nature of the spin state

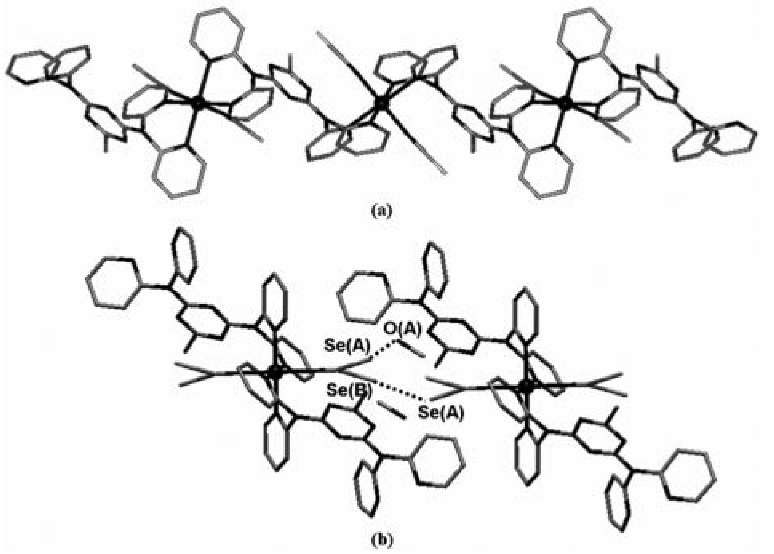


Figure 11. (a) General polymeric 1-D chain structure observed in the materials $[Fe(NCS)_2(cddt)]\cdot 1/2(CHCl_3)\cdot H_2O$, $[Fe(NCS)_2(cddt)]\cdot 2MeOH$ (polymorphs a and b) and (b) $[Fe(NCSe)_2(cddt)]\cdot 2MeOH$ illustrating the A and B positions of the disordered selenium atoms, the Se(A)···Se(B) interactions between adjacent chains and the Se(A)···O interactions are shown with dotted lines. Iron(II) centres are shown as black spheres, hydrogen atoms have been omitted. Reproduced with permission from ref.[23]

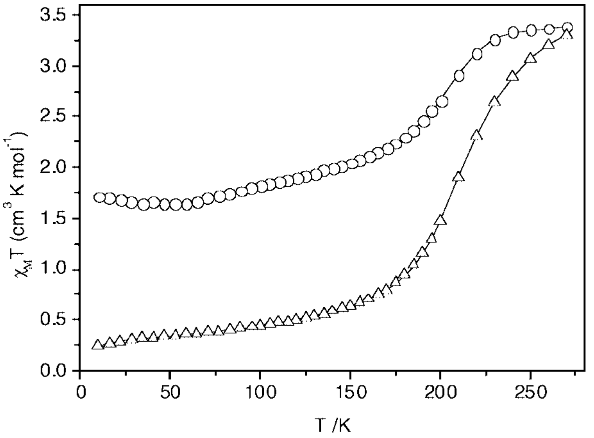


Figure 12. $\chi_M T$ vs. temperature for (open circles) $[Fe(NCS)_2(cddt)]\cdot 2MeOH$ (b) and (triangles) $[Fe(NCSe)_2(cddt)]\cdot 2MeOH$. Reproduced with permission from ref.[23]

and structure at the intermediate plateau (IP) temperature. $[Fe(NCS)_2(bdpp)]$ (b) remains HS at all temperatures whereas $[Fe(NCS)_2(bdpp)]$ (a) shows a full two-step SCO ($T_{1/2(1)}$ = 135 K and $T_{1/2(2)}$ = 90 K). The key structural difference is that polymorph a displays interchain π–π interactions and polymorph b does not, although polymorph b does show S···S contacts. Structural analysis of polymorph a at 25 K (LS-LS), 123 K(LS-HS) and 250 K (HS-HS) reveals two distinct $Fe^{II}$ centres at each temperature, with alternating but ordered HS and LS $Fe^{II}$ sites at the IP temperature. In contrast, $[Fe(NCSe)_2(bdpp)]$ also shows a two-step transition at higher temperatures because of the stronger ligand field of $NCSe^-$ ($T_{1/2(1)}$ = 200 K and $T_{1/2(2)}$ = 125 K). It has one unique $Fe^{II}$ centre at temperatures 90 K (LS), 150 K (LS/HS) and 250 K (HS) with an averaged LS/HS character at the IP temperature. Of great interest are the planes of diffuse scattering observed in the crystal diffraction patterns at 90 K and 150 K, lying between the Bragg peaks, and indicative of long-range ordering of the $Fe^{II}$ centres present in one direction but not in the other two. The ordering occurs along the direction of the 1-D chains (Figure 14). There is no diffuse scattering apparent at 250 K suggesting a rare disorder/order structural transition is occurring on lowering the temperature and associated with the two-step SCO behaviour. $[Fe(NCSe)_2(bdpp)]$ also shows interchain Se···Se interactions and twofold disorder in the C and Se atoms of the NCSe ligands. We were fortunate to gain these new insights from two members of this small family. Ongoing work includes further variations being made in the nature of the bis(dpa) linking ligand.

Other 1-D $Fe^{II}$ SCO materials include, of course, the tris(bridged) 4-R-1,2,4-triazole compounds, with their abrupt spin transitions and wide hysteresis gaps at room temperature. Some advances were mentioned above, and reviews have been written recently.[75] The related bis(triazole) and bis(tetrazole) ligands such as 1,2-bis(tetrazol-1-yl)propane (btzp) form polymeric 1-D compounds of type $[Fe(btzp)_3](ClO_4)_2$, displaying a gradual spin transition,[82] while a longer alkyl spacer in the butyl analogue, $[Fe(btzb)_3](PF_6)_2$, gives a more rigid 3-D net structure and a more abrupt SCO.[83] The more bulky 1,2-bis(tetrazol-1-yl)-2-methylpropane ligand (btzmp) yields a 1-D structure of different stoichiometry that involves double btzmp bridging as well as two unidentate btzmp groups on each $Fe^{II}$ viz. $[Fe(\mu\text{-}btzmp)_2(btzmp)_2](ClO_4)_2$. In this material a very abrupt HS → LS spin transition is observed with $T_{1/2}$ = 133 K and a narrow hysteresis gap $\Delta T$ of 3 K.[84] The spin transition is accompanied by an order/disorder transition

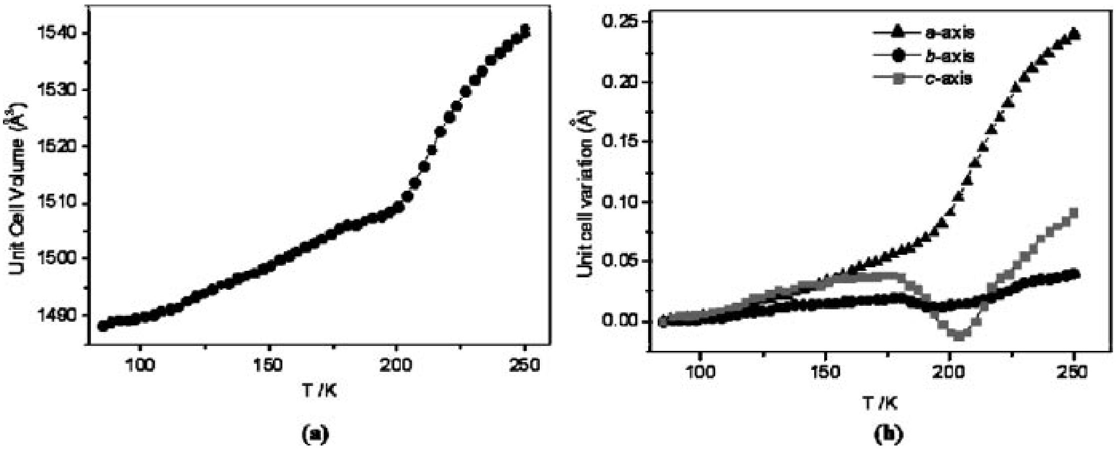


Figure 13. (a) Unit-cell volume variation and (b) relative change in unit-cell parameter variation vs. temperature for the spin transition in [Fe(NCS)$_2$(cddt)]·2MeOH (b) over the range 270–85 K obtained by synchrotron powder diffraction. Reproduced with permission from ref.[23]

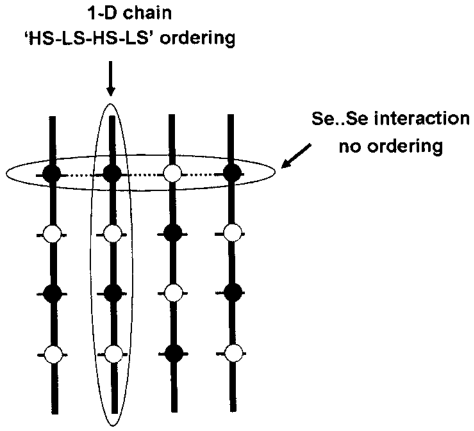


Figure 14. Schematic diagram of the "HS-LS-HS-LS" ordering of the iron(II) centres along the 1-D chains (101) for [Fe(NCSe)$_2$-(bdpp)] at the intermediate plateau temperature. Highlighted also is the random ordering of adjacent iron(II) centres along the directions of Se···Se interactions (110 and $1\bar{1}0$). The HS and LS states of iron(II) centres are represented as white and black spheres, respectively. The 1-D chains are represented as thick black lines and the NCSe$^-$ ligands as thin black lines.[81]

of the ClO$_4^-$ anion. The crystal packing is notably different in this bztmp example compared to the packing in the less hindered tris(btzb), -(btzp) and -(endi) (ethane-linked)[85] cases, and this is partly responsible for the increased cooperativity.

Real and Bousseksou and co-workers have described the structural, magnetic and Mössbauer spectral properties of 4,4′-bipy-bridged polymeric compounds.[86] In [(NCX)$_2$(bt)-Fe$^{II}$(μ-4,4′-bipy)], where X = S and Se, there are two structurally distinct Fe atoms, in separate chains, but each Fe has two *trans* NCX groups, two *cis* nitrogen atoms from bt (bithiazoline) and two *trans* nitrogen atoms from the bridging 4,4′-bipy ligands. It is interesting to note in passing that, in order to "snip out" a dinuclear moiety from such a 1-D chain as in the above-mentioned example by Rosa et al.,[40] a meridional N$_3$ terdentate chelate, 3-bpp, was used, rather than the bidentate bt, and the Fe/4,4′-bipy ratio used in the synthesis was 2:1 rather than 1:1. Magnetic and Mössbauer data for these two 1-D complexes show very incomplete and gradual SCO involving 12% (NCS) and 20% (NCSe) of the Fe$^{II}$ ions only, above 62 K and 72 K, respectively, a behaviour that is quite unlike the 1-D species described above. Below these temperatures a plateau was noted in $\chi_M T$ before rapid decreases that were due to zero-field splitting of the HS states. The data were interpreted in terms of near degenerate HS and LS states ($\Delta$ = 65–85 cm$^{-1}$) and an Ising-like model was employed to account for the population of vibrational levels as well as describing a mass effect for Se vs. S.[86] Precursor compounds [(NCX)$_2$(H$_2$O)$_2$Fe$^{II}$(μ-4,4′-bipy)]·4,4′-bipy contained 1-D chains that expanded their dimensionality to 2-D layers by hydrogen bonding between the *trans* H$_2$O molecules in adjacent 1-D chains and the non-coordinated 4,4′-bipy molecules. The FeN$_4$O$_2$ coordination spheres remain HS at all temperatures.[86]

Other 4,4′-bipy-bridged 1-D Fe$^{II}$ SCO compounds have been structurally characterised in order to understand their solid-state magnetic and cooperativity features. Kaizaki et al. utilised their dinuclear Fe$_2$(bpypz)$_2$ designs to include 4,4′-bipy instead of pyridine as the *trans*-axial ligands, thus forming 1-D "chains of dinuclears", in [Fe$^{II}_2$(NCS)$_2$(μ-bpypz)$_2$(μ-4,4′-bipy)]·MeOH;[18e] π–π contacts were apparent in the crystal packing between the bpypz ligands in adjacent chains. As in the parent dinuclear py compound, an abrupt one-step HS-HS → LS-LS spin transition occurred at $T_{1/2}$ = 162 K. Weber et al.[12f] observed a full and abrupt spin transition, with hysteresis, in a powdered sample of the Schiff base compound [Fe(N$_2$O$_2$)(μ-4,4′-bipy)] ($T_{1/2}$ = 228 K, $\Delta T$ = 18 K). Elastic interactions between the chains, spaced some 6 Å apart and much closer than the Fe···Fe intrachain distances (11.5 Å), were held responsible for the cooperativity observed.

A related linear-chain 8-aminoquinoline complex [Fe-(aqin)$_2$(μ-4,4′-bipy)](ClO$_4$)$_2$·2EtOH displayed a gradual HS → LS transition with $T_{1/2}$ = 220 K and no associated hysteresis; π-stacking and ligand-to-$ClO_4^-$ hydrogen bonding yields a sheet-like packing of the chains, and these interactions contribute to the weak cooperativity.[87] Two 2-(2-pyridyl)imidazole ligands occupied *cis* positions around $Fe^{II}$ in the zig-zag chain compound of similar stoichiometry to the above, [Fe(pyim)$_2$(μ-4,4′-bipy)](ClO$_4$)$_2$·2EtOH,[88] compared to the *trans* disposition in the linear aqin compound. The $T_{1/2}$ value of the gradual transition noted for this compound was similar (205 K) to that of the aqin derivative, and the interchain effects were similar in origin in both cases. Matouzenko and co-workers have extended their family of 1-D zig-zag species to include [Fe(pyim)$_2$(μ-bpen)](ClO$_4$)$_2$·2EtOH, where bpen is 1,2-bis(4-pyridyl)ethane (the ethene analogue was also studied). The chains are stacked through π–π interactions and the gradual, one-step spin transitions, and their $T_{1/2}$ values, have been corroborated by DFT calculations of the LS-HS energy gaps that are, in turn, influenced by the nature of the bridging dipyridyl ligand.[89] For these systems, crystal structures solved above and below $T_{1/2}$ retained the same space group, and the constituent $Fe^{II}$ centres within the chains all showed identical and typical HS and LS geometrical features with none of the HS-LS-HS-LS- ordering of the kind observed in some of our dpa-linked (cddt and bdpp) 1-D species, described above.[23] Understanding why these differences occur in these 1-D species, below the $T_{1/2}$ temperatures remains a formidable challenge.

Two-connecting di-pyridyl ligands of the type shown in Scheme 1, but containing a C–C linker, have been used to make 1-D species of type [Fe(NCX)$_2$(bpen)$_2$] [X = S, Se, BH$_3$; bpen = 1,2-bis(4-pyridyl)ethane].[90] They showed a number of solid-state features such as supramolecular isomers, solid-to-solid transformations, changes in spin state and $T_{1/2}$ values and the ability to enclathrate guest molecules such as biphenyl.

A recent paper by Aromi and Gamez and co-workers[91] described a 1-D "half" SCO material ($T_{1/2} \approx 310$ K), [Fe$_3$(dpya-triz)$_2$(EtCN)$_4$(BF$_4$)$_2$](BF$_4$)$_4$·4EtCN, made up of dimeric {FeN$_4$(NCEt)$_2$}$_2$ moieties in which the N$_4$-donors are from two dpya fragments (labelled elsewhere and herein as dpa) in the 2,6-positions of a tris(dipyridylamine)-substituted 1,3,5-triazine ring. The remaining dpya group at the 4-position is linked into a 1-D chain by *trans*-(FBF$_3$)$_2$Fe$^{II}$ centres. Notably, this EtCN solvate readily substituted EtCN by atmospheric water to give an HS material. The porous features of the crystals led to sorption of propanol or acetonitrile, the latter solvate also showing partial SCO.

Linking of chelated $Fe^{II}$ moieties at a remote N-donor position of the chelator, by $Fe^{II}$ centres, of the kind just described has recently yielded a number of metallosupramolecular 1-D SCO materials. Thus, Ruben et al. have used a 2,6-bis(1-pyrazolyl)pyridine meridional terdentate (terpy-like) ligand, $L^3$, which has a 4-pyridyl N-donor in the 4-position of the central pyridyl ring.[92] Monoprotonation of the ligand at the 4-pyridyl "backside", in [Fe(L$^3$)$_2$H](ClO$_4$)$_3$·MeOH, formed a hydrogen-bonded N–H···N chain that shows a gradual SCO with $T_{1/2}$ = 286 K ($\Delta T$ = 2 K). This kind of hydrogen bonding is rather like that observed in our "chain-of-dimer" Fe$^{III}$(acen)/tvp/tvpH structure described above.[68] An extension of this ligand design, in which two of the $N_3$ terdentate chelators were joined at the central pyridine 4-position by a *para*-substituted benzene ring ($L^4$), yielded another metallosupramolecular chain, [Fe(L$^4$)](BF$_4$)$_2$, though not structurally characterised.[92b] It showed an enhanced $T_{1/2}$ value of 323 K and $\Delta T$ of 10 K. Hayami and co-workers had earlier used the 4-pyridyl-substituted terpy ligand to make 1:1 chain species, [Co(pyterpy)(Cl)$_2$]·MeOH, with "head-to-tail" coordination in the 1-D chain, and an overall 3-D network involving π–π contacts between the chains. It remained HS $d^7$ at all temperatures, whereas a structurally uncharacterised ·2H$_2$O adduct displayed an abrupt spin transition with $T_{1/2}$ = 223 K ($\Delta T \approx 1$ K).[93]

In our Fe$^{II}$(pypz) work, as well as the covalently pypz$^-$-bridged dinuclear compounds, described above,[5a,16] we also isolated neutral ligand (pypzH) chelated species, [Fe(pypzH)$_2$(NCS)$_2$](μ-H$_2$O), that formed 1-D motifs by hydrogen bonding between a hydrated water O atom and adjacent pyrazole NH hydrogen atoms of the pypzH ligands in neighbouring molecules.[17]

The $N_2O_2^{4-}$ tetradentate Jäger ligand has been used by Müller et al.[94] to make hydrogen-bonded 1-D iron(II) SCO materials of the formula [Fe(N$_2$O$_2$)(imidazole)$_2$] involving (imidazole)NH···O=COEt(L) interactions between neighbouring molecules. A vacuum-dried sample, [Fe(N$_2$O$_2$)(imidazole)$_{1.8}$], showed an abrupt spin transition at $T_{1/2}$ = 330 K with hysteresis ($\Delta T \approx 4$ K). Use of the regular solution model gave a best-fit value of the cooperativity parameter, $\Gamma$, of ≈ 495 cm$^{-1}$.

As indicated earlier, we have explored 1-D iron(III) Schiff base crossover systems using a large range of di-pyridyl type bridges.[68] Matsumoto and co-workers have recently solved the structure, at three temperatures, of [Fe(acen)(bpyp)](BPh$_4$),[95] a complex first reported by Maeda et al.,[96] both groups observing the same, gradual $S = 5/2$ to $S = 1/2$ transition centred at ca. 200 K, with no hysteresis. The structure, solved at approximately the $T_{1/2}$ temperature, showed alternating zig-zag chains, each chain having equivalent but different Fe$^{III}$ sites that are all in spin states HS or all LS, a quite different situation to that observed by us for the Fe$^{II}$ chains [Fe(NCS)$_2$(cddt)]·2MeOH (b)[23] and [Fe(NCS)$_2$(bdpp)] (a).[81] In fact, the two inequivalent Fe sites persist in the LS and the HS structures, solved at 108 K and 296 K, respectively. A zig-zag chain structure was also observed by Matsumoto et al. in [Fe(salophen)(tdim)], a complex in which the two-connecting bridge was 1,1′-tetramethylenediimidazole.[97] Two different configurations of the imidazole rings around each Fe$^{III}$ were found with an occupation ratio of 0.65 to 0.35. This was felt to influence the partial spin transition noted at ca. 80 K, the magnetic moment plot being reminiscent in shape of those obtained for [(NCX)$_2$(bt)Fe$^{II}$(μ-4,4′-bipy)].[86] Whereas the latter was explained in terms of near degenerate HS and LS states, plus vibrational effects, the Fe$^{III}$ system was explained by assuming that the Fe site in one configuration remained HS while the other showed SCO as the temperature was varied. Mössbauer and EPR spectroscopic data gave support for this analysis.

In the context of 1-D hydrogen-bonded SCO species, it is important to mention the work of Törnroos, Bürgi and co-workers on the well-known[98] tris(2-picolylamine)-iron(II) mononuclear compounds of formula $[\mathrm{Fe^{II}(2\text{-pic})_3}](\mathrm{Cl})_2\cdot\mathrm{S}$ (S = 2-propanol[99] and ethanol[100]). The crystal packing reveals 1-D zig-zag chain motifs and 2-D hydrogen-bonded arrays, respectively. Multiple X-ray crystal structures, at many temperatures, were obtained by use of synchrotron sources, thus enabling a detailed understanding of structural phase transformations to be achieved and correlated with areas of the spin-transition curve at these temperatures. Features such as superlattice diffraction patterns, multiple phase coexistence and the consequent ordering of, say, HS molecules or the disorder of HS and LS molecules, in intermediate phases, were revealed. The transition curve for the propanol solvate was most unusual, with five zones delineated and with hysteresis occurring over a limited temperature region.[99] In this solvate, ordering occurs near 95% of HS concentration, with the complexes in one zig-zag (hydrogen-bonded) chain being nearly all HS while those in the next chain are made up of a disordered mixture of HS and LS states. In contrast, the ethanol solvate forms a 2-D layer "chessboard" pattern with nearly complete ordering at only 50% HS concentration.[100] These kinds of details are of a similar precision to those described above for our 1-D covalently bridged compound $[\mathrm{Fe(NCSe)_2(bdpp)}]$.[81]

Studies of the LIESST effect have been made on very few 1-D species. The "chain of dinuclears" $[\mathrm{Fe^{II}_2(NCS)_2(\mu\text{-}bpypz)_2(\mu\text{-}4,4'\text{-}bipy)}]\cdot\mathrm{MeOH}$ showed a distinct LIESST following green-light irradiation (532 nm) at 4 K and measured by susceptibilities ($T_{\mathrm{LIESST}}$ = 54 K), or by use of 632.8 nm irradiation at 10 K and measuring the Raman spectral intensities in the range 10–100 K, of the NCS ν(CN) band, the position of which is sensitive to being in HS or LS states.[18e] A synergy between the weak antiferromagnetic exchange, across the pyrazolato bridges of the dinuclear moieties (but not by 4,4′-bipy pathways), and the spin-state change, was proposed to explain the shape of the susceptibility temperature dependence, obtained upon warming above 4 K, following light irradiation. This temperature region of the LIESST magnetism plot for our 1-D compound $[\mathrm{Fe(NCS)_2(bdpp)}]$(a), with $T_{\mathrm{LIESST}}$ = 55 K, following green light irradiation at 10 K, was ascribed to zero-field splitting of the HS $\mathrm{Fe^{II}}$ centres rather than to spin-exchange coupling;[81] 62% of the $\mathrm{Fe^{II}}$ sites were trapped in the metastable HS state in this compound compared to 43.5% trapped by quench cooling in the absence of photoirradiation (so-called TIESST effect). Interestingly, the sister compound, $[\mathrm{Fe(NCSe)_2(bdpp)}]$, did not show thermal trapping after quench cooling, a feature that often signifies unsuccessful LIESST, but the LIESST effect was clearly observed, and 53% of HS states were trapped, with $T_{\mathrm{LIESST}}$ being 49 K. Only one $T_{\mathrm{LIESST}}$ value was noted in these two two-step SCO 1-D compounds, whereas we observed two such values in a recent two-step monomer.[48]

## 7. Nature of the Spin Transition in Dinuclear and 1-D Chain Compounds

This summary addresses points (ii) and (iii) of the Introduction and looks at the current understanding of the nature of the spin transition in dinuclear and 1-D systems. Beginning with dinuclear compounds, we have seen that the pioneering work on $\mathrm{Fe^{II}}$(μ-bpym) compounds by Real[15] and Kahn[6] and their groups has inspired others, including ourselves, to contribute to this area. This Microreview shows that big strides have been made over the last decade in making new compounds, with different bridging and end groups, that not only show the full two-step transition and the half transition observed for members of the μ-bpym family, but also display full one-step HS-HS to LS-LS transitions, as in some, but not all, of the μ-bpypz and μ-bpytz families and in one μ-bpym example. This begs the question, why do these differences occur? We will offer suggestions below. Perhaps not noticed as much as it should have, has been the observation of full two-step transitions in dinuclear $\mathrm{Fe^{III}}$ complexes together with structural evidence for ordered HS-LS (intermediate) spin states at the IP temperature.[64] Returning, however, to the $\mathrm{Fe^{II}Fe^{II}}$ systems, there are now structurally characterised examples that yield pair spin states of the following kinds as the temperature is lowered: (a) HS-HS → LS-LS, (b) HS-HS → HS-LS (structurally ordered, half crossover), (c) HS-HS → HS-LS → LS-LS (structurally ordered HS-LS, full crossover), (d) HS-HS → 0.5[(HS-HS) + (LS-LS)] → LS-LS (structurally ordered, half crossover, with only half the HS-HS molecules undergoing full SCO), (e) HS-HS → HS/LS → LS-LS [structurally disordered (averaged) at the IP temperature, full crossover]. There are also density functional theoretical calculations that use crystal structure data on the dinuclear μ-bpym and μ-pypz molecules as input to confirm (predict?) situations (a) and (d)[101] and regular solution-model calculations that simulate the $\gamma_{\mathrm{HS}}$ vs. $T$ plots and yield the cooperativity parameter, $\Gamma$. Other theoretical models for two-step transitions have been summarised by Bousseksou et al.[10]

Recent, detailed structural and Mössbauer spectral analyses of the μ-bpym complex, $[\mathrm{(NCS)_2(bt)Fe(\mu\text{-}bpym)Fe(bt)(NCS)_2}]$, at 293, 240, 175 (IP region) and 30 K, together with variable-temperature lattice parameter studies,[21] confirm that the two-step spin transition proceeds through transformation (e), with the HS/LS pairs dominating the IP region of temperature. Real et al.[21] searched hard for the presence of super-lattice reflections, analogous to those we saw in the 1-D system (above), $[\mathrm{Fe(NCSe)_2(bdpp)}]$,[81] but none were detected at 175 K for this two-step crossover compound, thus implying the disordered (averaged) {HS-LS ↔ LS-HS} structure, with observed, average Fe–N bond lengths. These authors suggest that synchrotron radiation studies might yet reveal super-lattice reflections, and thus ordering of the LS/HS states is not ruled out.[21] This group proposes that stabilisation of the HS-LS state is due to a synergy between intra- (elastic) and intermolecular cooperative interactions, i.e. short and long range. This leads to the IP region between the two steps and its width. Dilution (15%) into a Zn–Zn host showed a continuous one-step change, thus confirming a reduced cooperativity and weaker intermolecular effects. The elastic interactions within the dinuclear $[(NCS)_2(bt)Fe(\mu\text{-bpym})Fe(bt)(NCS)_2]$ molecules mean that as one Fe changes spin, this leads to a change in the energy gap between HS and LS levels of the second Fe, thus meaning the two Fe sites do not behave in an independent manner and the HS-HS, HS-LS and LS-LS states consequently appear.[9,21] Using this logic, the direct HS-HS to LS-LS spin transition [process (a)] in the μ-pypz and μ-bpyp(t)z compounds[5a,5b,18,19] would imply that these more rigid bridges produce a weaker elastic interaction and this leads to the two Fe atoms changing spin simultaneously. It does not explain the one-step transition in the dpa/μ-bpym complex, but this is much broader than it is in the pyrazolato- and triazolato-bridged materials.[32] Separating out the interdinuclear contributions from intradinuclear in such one-step compounds is hard to do with certainty, but it is possible to compare close intermolecular contacts in the structures of the HS-HS and LS-LS molecules. Presumably interdinuclear effects favour the LS-LS state in which they are stronger than in the HS-HS state. In the mechanism (d), 4-Phpy/μ-bpypz two-step compound,[18c] strong π–π contacts were deemed responsible for the "like-spin" pair {HS-HS + LS-LS} stabilisation. Compounds that follow mechanism (c), viz. $[Fe_2(ddpp)_2(NCS)_4]\cdot 4CH_2Cl_2$, not only display extensive intermolecular contacts, but the two Fe atoms within each dinuclear molecule are crystallographically slightly distinct in the HS-HS and LS-LS states, and grossly so in the HS-LS state, this structural inequivalence probably being sufficient to cause the two-step process and the ordered structure of the HS-LS molecules.[38]

In summary, there is not a "catch all" explanation for the spin-transition mechanism in dinuclear iron(II) [and iron(III) and cobalt(II)] SCO species in the solid state. We have seen that within iron(II) families that have a common bridge geometry, full one-step, full two-step and "half" SCO transitions are observable. Nevertheless, great advances have been made in the last few years to augment and complement knowledge of the spin-change mechanism first proposed, and later confirmed, for the bipyrimidine-bridged family. The full answer to why these differences occur within and between families remains a challenge for the future.

Our understanding of the spin-transition mechanism in covalently bridged iron(II) 1-D chain compounds has improved considerably in the last two years or so. There are, unfortunately, no crystallographic data on the tris(μ-4-R-1,2,4-triazole) chains whether at room temperature, where the hysteretic HS → LS spin transition occurs, or at higher or lower temperature, where the HS and LS states apply. Our 1-D species containing bis(dpa) bridging ligands have yielded the following spin-state changes without any thermal hysteresis being observed: (f) one-step HS → LS, (g) unusual two-step, incomplete (at the broad lower temperature step the ordered -HS-LS-HS-LS- spin states occur), (h) full two-step HS → HS/LS → LS (short-range disorder in HS/LS intermediate state but with long-range order along the 1-D direction evidenced by diffuse planes in diffraction pattern), (i) full two-step HS → HS-LS → LS with ordered -HS-LS-HS-LS- sites at the IP temperature and slightly different site symmetries at the HS and LS states. Other closely related members of the two bis(dpa) families studied to date show HS states at all temperatures. Interchain interactions of π–π, S···S, Se···Se types, and hydrogen bonding to solvate molecules, as well as disorder in $NCX^-$ coligands, all play roles in the spin-transition mechanism that are hard to define precisely. Other chains having 4,4′-bipy bridges show either type (f) one-step spin transitions or the unusual spin change, labelled (h) incomplete, gradual HS → LS in which HS and LS states are nearly degenerate, thus making vibrational effects important.[86] An $Fe^{III}$ 1-D chain displays a full two-step spin transition with another mechanism (i) HS → 0.5{all HS + all LS} → LS, with an ordered structure at the IP of consecutive chains being all HS $Fe^{III}$ and all LS $Fe^{III}$. It is analogous to the dinuclear spin change (d). A "chain of 4,4′′-bipy-linked dimers" in the μ-bpypz family follows mechanism (f) where HS is actually HS-HS and LS is LS-LS of the dimer moieties. A number of supramolecular, hydrogen-bonded 1-D chains of $Fe^{II}$, $Fe^{III}$ or $Co^{II}$ display rather abrupt transitions of mechanism (f), some with narrow hysteresis gaps, a doubly bridged bis(tetrazole)$Fe^{II}$ chain behaving likewise.

It can be seen, from the above, that the 1-D systems present a disparate array of spin changes and can thus be termed "a work in progress". The tris(μ-4-R-1,2,4-triazole)iron(II) chains presumably are categorised as (f), but whether the Fe sites all change spin, HS → LS, simultaneously or sequentially, and what effects chain–chain interactions have on the spin change, remain rather unclear. The chain–chain interactions will influence the cooperativity which is high in these compounds, as judged by the wide hysteresis loops. What has become clear from all the other 1-D systems summarised here, is that none of them display the same degree of cooperativity, with only a few showing abrupt SCO and associated narrow hysteresis loops. All have less rigid bridging and longer M···M separations between adjacent metal ions than does the tris(μ-4-R-1,2,4-triazole)iron(II) family. One might expect this to lead to it being easier to change geometry at each metal site as their spin states change, perhaps yielding higher cooperativity, the opposite of what is observed. However, set against this is the probable loss of or decrease in cooperativity in the more flexible chains since the spin change at one Fe will be less likely to affect the change at the neighbouring Fe. Put another way, elastic interactions between adjacent metal ions, across the flexible bridging groups, will be different to that in the tris(bridged) triazole system (here sharing faces of octahedra), the latter thus expected to show more abrupt transitions, as observed. The many and subtle chain–chain contacts noted in the bis(dpa) and 4,4′-bipy 1-D crystalline species presumably are, in most reported examples, not strong enough to create the high degree of cooperativity, as they, in combination with the elastic intrachain Fe···Fe interactions, do in the triazole-bridged family.

## 8. Future Directions

This area of research has a rich past, particularly in Europe and Australia, and, in the author's view, a challenging and exciting future. It provides a broad set of interests to those involved, ranging from ligand design, organic and metal-organic syntheses, structural chemistry to chemical physics and theory. In relation to the points in the Introduction we are pursuing new, covalently bridged dinuclear SCO compounds, to further probe the synergy question relating magnetic exchange to SCO. To date, the exchange coupling constants have been close to zero or weakly coupled, and there is a need for systems that have much stronger coupling. Major advances have been made in point (ii) in regard to characterising the structures of HS-LS species in both dinuclear and 1-D polynuclear materials with new evidence for structural ordering being described above. New 1-D compounds are being investigated to corroborate such findings.

Controlling or predicting the occurrence and degree of cooperativity in crystalline di- or polynuclear molecular SCO compounds [point (iii)] remains elusive even though much has been discovered about the intermolccular effects that underpin cooperativity. Apart from the 1-D tris(triazole)Fe$^{II}$ chains, the cooperativity (abruptness in spin transition, thermal hysteresis) is generally weak, across numerous families of compounds, and the early postulate of covalent bridging leading to increased cooperativity has not been borne out in practice. A quantum leap in thinking and system design is needed to try and quantify these cooperativity issues.

Point (iv), dealing with hitherto unknown hybrid materials such as SCO-SMM or related clusters, is being pursued and very exciting large SCO clusters have recently been isolated here by colleagues Batten and Duriska. Designs of covalently linked clusters containing, say, Mn SMM and Fe$^{II}$ SCO centres are being investigated in collaboration with Brechin and Jones (University of Edinburgh), with important new physics anticipated from such hybrid materials.

Finally, the photomagnetic work on polynuclear Fe$^{II}$ SCO systems has yielded important advances by other groups in regard to photoswitching and related phenomena in the dinuclear μ-bipyrimidine family, in which photoexcitation has proceeded from LS-LS and HS-LS states, and these have been combined with reverse LIESST from HS-HS states. There is much future scope for LIESST work on polynuclear systems of both Fe$^{II}$ and Fe$^{III}$, and we are presently investigating, with Létard, for example, dinuclear tris(pyrazolylmethane)iron(II) compounds for comparison to the mononuclear analogues mentioned briefly in section 3.4. The hybrid heterometallic SCO cluster materials, envisaged above, pose interesting possibilities in regard to their photomagnetic properties and spin switching, the latter being possible in both ground and excited states and perhaps able to affect the SMM hysteresis.

### Glossary of Ligand Labels and Symbols

The arrow symbol in, for example, HS-HS → LS-LS implies a reversible spin state change; this applies throughout. Labels and symbols are listed in Table 1.

Table 1. Abbrevations of ligand labels and symbols.

| | |
|---|---|
| acen$^{2-}$ | *N,N′*-bis(acetylacetoneiminato)ethylenediamine |
| 2,2′-bipy | 2,2′-bipyridine |
| 3-bpp | 2,6-bis(3-pyrazolyl)pyridine |
| bpym | bipyrimidine |
| bpypz$^-$ | 3,5-bis(2-pyridyl)pyrazolate |
| bpytz$^-$ | 3,5-bis(2-pyridyl)1,2,4-triazolate |
| bt | 2,2′-bithiazoline |
| $n$Bu$_4$N$^+$ | tetra(*n*-butyl)ammonium |
| bztpen | *N*-benzyl-*N,N′,N′*-tris(2-pyridylmethyl)ethylenediamine |
| CA$^{2-}$ | chloranilate |
| dabco | 1,4-diazabicyclo[2.2.2.]octane |
| DBQH$_2$ | 2,5-di-*tert*-butyl-3,6-dihydroxy-1,4-benzoquinone |
| dca$^-$ | dicyanamide |
| DMF | dimethylformamide |
| dpa | bis(2-pyridyl)amine |
| dpm | bis(2-pyridyl)methyl |
| EXAFS | X-ray absorption fine structure |
| HS | high spin |
| LS | low spin |
| LIESST | light-induced excited spin state trapping |
| 3-MeOsalMedpt | *N,N′*-bis[(3-methoxy)salicylaldiminato]-1,4-methyl,7-propylenetriamine |
| 1,10-phen | 1,10-phenanthroline |
| 4-Phpy | 4-phenylpyridine |
| pmat | 4-amino-3,5-bis{[(2-pyridylmethyl)amino]methyl}-4*H*-1,2,4-triazole |
| py | pyridine |
| pypzH | 3-(2-pyridyl)pyrazole |
| saldpt | *N,N′*-bis(salicylaldiminato)-1,4,7-propylenetriamine |
| salen$^{2-}$ | *N,N′*-bis(salicylaldiminato)ethylenediamine |
| salophen$^{2-}$ | *N,N′*-bis(salicylaldiminato)phenylenediamine |
| SCO | spin crossover |
| SMM | single molecule magnet |
| THBQH$_2$ | 2,3,5,6-tetrahydroxy-1,4-benzoquinone |
| tpa = TpyA | tris(2-pyridylmethyl)amine |
| XANES | X-ray absorption near edge spectroscopy |

**Note Added in Revision** (April 29, 2008): Some recent papers are worthy of note. In regard to sections 3.3 and 3.4, photomagnetic details of members of the $[(L)(NCS)Fe^{II}(\mu\text{-bpypz})_2Fe^{II}(NCS)(L)]$ family,[54] where L is pyridine (powder sample displaying SCO) and other substituted pyridines, reveal that the direct LIESST process at 10 K converts the LS-LS ground state to the HS-HS metastable state involving an antiferromagnetic interaction similar to that found in an HS-HS example, in which L = 3,5-Me$_2$py ($J = -1.45\ \mathrm{cm}^{-1}$). The HS-LS state could not be detected. In section 6 dealing with 1-D Fe$^{II}$ crossover materials, and their applications, Létard et al. have patented nanoparticles of the 4-R-1,2,4-triazole materials using surfactants. Applications are proposed in thermochromic pigments, data storage, optical limiters and contrast agents.[102] The alkane-linked (di-tetrazole)Fe$^{II}$ series of Linert and co-workers has been extended to include longer alkane linkers, viz. $C_{5-10,12}$, thus forming 3-D interpenetrated network structures that produce subtle effects on the spin transitions and LIESST effects with solvent inclusion and anion variations playing their parts.[103]

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