DOI: 10.1002/ejic.200600365

The Two-Step Spin Conversion in a Supramolecular Triple Helicate Dinuclear Iron(II) Complex Studied by Mössbauer Spectroscopy

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Dedicated to Professor Hans-Georg von Schnering on the occasion of his 75th birthday

Keywords: Spin crossover / Molecular bistability / Supramolecular chemistry / Iron(II) dinuclear compounds / Two-step conversion / Mössbauer spectroscopy

The triple helicate dinuclear iron(II) complex, $[Fe_2(L)_3](ClO_4)_4\cdot 2H_2O$ (**1**), previously reported by Tuna et al. (*Chem. Eur. J.* **2004**, *10*, 5737), was prepared and characterised by detailed SQUID and ^{57}Fe Mössbauer measurements. Compound **1** exhibits a thermochromic two-step spin conversion at $T_{SC}^{(1)}$ ca. 240 K and $T_{SC}^{(2)}$ ca. 120 K, but does not switch its spin state further below 20 K as proven by Mössbauer spectroscopy. The sharp variation of the susceptibility below 20 K is due to zero-field splitting of the remaining iron(II) high-spin species. Applied field ^{57}Fe Mössbauer spectroscopy experiments at 4.2 K indicate that the gradual thermal spin conversion from [HS–HS] pairs to [LS–LS] pairs is complete for one half of the Fe^{II} active sites. The presence of a step tracked in the spin-conversion curve and through the variation of the Mössbauer parameters of an uncoupled iron(II) site call for the occurrence of an [LS–HS] intermediate spin state in the plateau region.

Introduction

The spin crossover (SCO) phenomenon presumably belongs to one of the most exciting and active field of research in molecular and coordination chemistry[1] as probed by the constantly increasing amount of papers.[2] This phenomenon has been observed for coordination compounds of 3d transition metals such as d^4 (Cr^{II}, Mn^{III}), d^5 (Fe^{III}, Mn^{II}), d^6 (Fe^{II}, Co^{III}) and d^7 (Co^{II}) ions.[3] Yet, most of the synthetic efforts and physical investigations have been carried out for Fe^{II} mononuclear complexes displaying a wide range of SCO behaviours.[1,2] Recently, synthetic approaches combining the tools of supramolecular and coordination chemistry have been developed because it was realised that bridging active sites through noncovalent and/or covalent bonds could enhance cooperative effects associated to the spin-state change of individual molecules.[4] Such strategy is appealing because it can lead to the observation of a bistability domain that is of great importance for potential applications.[5] It should, however, be used with caution as strong cooperative interactions between spin-changing molecules in the crystal lattice can disfavour, in some cases, the occurrence of spin-state crossover itself.[6,7] The understanding of complex magnetic behaviour as developed in SCO coordination polymers[8] requires a full understanding of the SCO occurring in much simpler compounds such as monomers and oligomers.[9–10] As such, dinuclear Fe^{II} complexes exhibiting a SCO between the high-spin (HS, $^5T_{2g}$) state and the low-spin (LS, $^1A_{1g}$) state in the liquid and solid state have been the subject of intensive preparation and investigations during the last three years.[11–19] The quest for new complexes is motivated by the understanding of the nature and the determination of the proportion of the existing spin pairs for these materials exhibiting gradual, abrupt or stepwise spin conversions. Another motivation stems from the possibility to combine both magnetic exchange and SCO phenomena in the same dinuclear unit[20] leading to multifunctional materials.[21]

Several modules have been used to link the active SCO sites in these binuclear systems: one bridging ligand such as μ-bpym (bpym = 2,2′-bipyrimidine)[11,12,17b] or μ-dicyanamide,[15] two ligands constituting a μ-pyrazolato[16,17] or μ-triazolato bridge,[18] or three benzimidazole bridging ligands leading to an helicate structure presenting a spin con-

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version in solution.[19] A new series of triple helicate dinuclear Fe^{II} complexes of the type $[Fe_2(L)_3]A_4 \cdot n$Solvent with A = PF_6^-, BF_4^- and ClO_4^- was also recently communicated.[22] L is a Schiff base resulting from the condensation of 3*H*-imidazole-4-carbaldehyde with 4,4′-methylenedianiline in methanol. Their crystal structure reveals that the Fe^{II} centres are in a six-coordinate pseudo-octahedral coordination environment bound to three imidazolimine units originating from three different ligand strands. Each ligand strand binds to two metals, and the three ligands wrap around the metal–metal axis leading to a triple helical dinuclear structure (Figure 1). CH···π interactions are noted in the centre of the helix, the Fe···Fe distance being of 11.584(3) Å.[22] These compounds, that were investigated by SQUID measurements over the temperature range 1.8–340 K, where shown to display a thermally induced spin-state conversion. The perchlorate complex of formula $[Fe_2(L)_3](ClO_4)_4 \cdot 2H_2O$ (**1**) attracted our special interest, because it was reported to exhibit a two-step spin conversion with one gradual step at $T_{sco} \approx 180$ K and another very abrupt spin conversion was proposed to take place below ca. 20 K. On this basis, the authors concluded on the existence of a "tristability" phenomenon[22] although no hysteresis effect was observed. Our attention has been drawn to this compound for two main reasons:

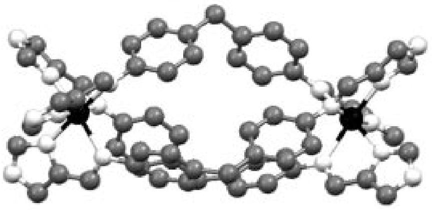

Figure 1. View of the triple-helicate cation in complex **1** adapted from ref.[22]. Hydrogen atoms and perchlorate anions are omitted for clarity. White and grey small spheres correspond to nitrogen and carbon atoms, respectively. The larger black spheres correspond to Fe^{II} ions.

(i) To our experience it is very unlikely, for kinetic reasons, that thermal spin conversion occurs at such low temperatures as below 20 K. The sharp decrease of the $\chi_M T$ values below 20 K may be rather due to zero-field splitting (ZFS) of the approximately 50 % of the Fe^{II} ions in the HS state still present in the plateau around 50 K.

(ii) The spin conversion observed between 260 and 50 K gives rise to the question whether it takes place simultaneously in the Fe^{II} dinuclear units, viz. via [HS–HS] ↔ [LS–LS] pairs, or via the intermediate [HS–LS] pairs in the sequence [HS–HS] ↔ [HS–LS] ↔ [LS–LS], as demonstrated to occur in other dinuclear Fe^{II} complexes.[11a,12,14]

We thus re-synthesised and characterised compound **1** in order to clarify its thermally induced spin conversion by a set of precise SQUID and ^{57}Fe Mössbauer measurements over the temperature range 1.8–300 K. The full differentiation of the existing spin pairs is not a routine exercise, and can only be solved using applied field Mössbauer spectroscopy,[23] which has also been carried out at 4.2 K.

Results

Synthesis and Characterisation

Complex **1** was prepared according to the described procedure.[22] The ligand L was first obtained as shown by ^{1}H NMR and IR spectroscopy. The complex was also successfully obtained, as an orange powder, as shown by electrospray ionisation mass spectrometry (ESI), C,H,N analysis, IR and UV/Vis spectroscopy. No thermogravimetric measurement was carried out due to the presence of perchlorate anions in this complex. The use of ^{57}Fe Mössbauer spectroscopy (vide infra), confirmed the nonoxidation of this material since no ferric species were observed for this Fe^{II} compound. Interestingly, this material reveals a distinct colour change on cooling from orange (293 K) to wine brown (77 K). This reversible thermochromic phenomenon was not previously reported.[22]

Magnetic Susceptibility Measurements

The magnetic data were collected every K over the temperature range 300–1.8 K on cooling and warming modes with an applied field of 10 kOe. The temperature dependence of the molar magnetic susceptibility is displayed in Figure 2 in the form of a $\chi_M T$ vs. T plot, χ_M being the molar magnetic susceptibility corrected for diamagnetic contributions and T the temperature. At room temperature, $\chi_M T$ is equal to 7.23 cm^3 mol^{-1} K, which indicates Fe^{II} ions in the HS state with a g value of 2.197. As T is lowered, $\chi_M T$ initially remains constant down to ca. 280 K and then smoothly decreases in two steps as a result of a HS to LS conversion, reaching a plateau value of 3.43 cm^3 mol^{-1} K at 66 K. The conversion is thus incomplete, ca. 50 % of molecules remaining in the HS state. Between 65 and 30 K, the $\chi_M T$ product decreases very slightly, a behaviour that might be attributed to weak antiferromagnetic interactions between paramagnetic spin carriers, as confirmed by applied field ^{57}Fe Mössbauer spectroscopy. Below 20 K, $\chi_M T$ decreases sharply and falls to 0.96 cm^3 mol^{-1} K at 1.8 K. This behaviour can be attributed to the presence of ZFS splitting due to spin-orbit coupling of the HS Fe^{II} ions, and the preferred Boltzmann population of the lowest levels with decreasing temperatures. The absence of any spin-state crossover at this temperature is unambiguously demonstrated by zero-field ^{57}Fe Mössbauer spectroscopy (see next section). The spin conversion occurs in two steps with transition temperatures near 240 K and 120 K, respectively. It is of interest to note that the mean transition temperature around 180 K roughly corresponds to the transition temperature deduced from the gradual spin conversion of the first step presented in.[22] As T is increased, the same magnetic behaviour was observed indicating no hysteresis effect in none of the spin conversion branches. This measurement thus confirms the absence of a bistability domain for **1** and does not support the tristability behaviour interpreted in ref.[22]. The calculated $\chi_M T$ values for the nonsolvated dinuclear complex in ref.[22] of 7.70 cm^3 K mol^{-1} and

3.81 $cm^3\,K\,mol^{-1}$ at room temperature and 66 K, respectively, are noticeably higher than in Figure 2 of the present study. These magnetic data were not calculated for the non-solvated complex as indicated in the caption to Figure 1 in ref.[22] because considering the molecular mass (1718.93 $g\,mol^{-1}$) and diamagnetic correction (–220.68·$10^{-6}\,cm^3\,mol^{-1}$) for the crystals of $[Fe_2(L)_3](ClO_4)_4$·4MeOH·H_2O, we could fully recover the magnetic data presented in ref.[22]. The calculations in ref.[22] are thus not correct because these SQUID measurements were performed on powders of $[Fe_2(L)_3](ClO_4)_4$·$2H_2O$ as done in our study.

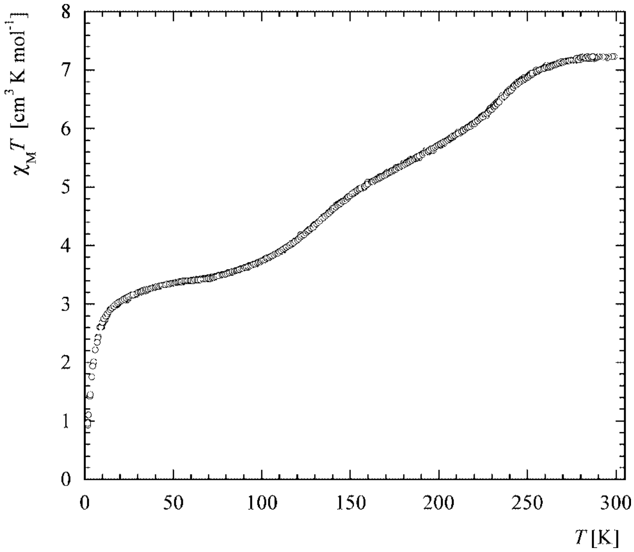

Figure 2. $\chi_M T$ vs. T plot for **1** over the 300–1.8 K range.

Zero-Field ^{57}Fe Mössbauer Spectroscopy

^{57}Fe Mössbauer spectra were recorded for **1** at variable temperatures between 300 K and 4.2 K. Selected spectra are displayed in Figure 3, and detailed values of the Mössbauer parameters at 19 temperatures deduced from least-squares fitting procedures are listed in Table S1 (supp. inf.; for supporting information see also the footnote on the first page of this article). The spectrum at 300 K could be fitted best with two quadrupole doublets. The isomer shift, δ, is 0.98 mm/s for both doublets, the quadrupole splitting, Δ, is 1.20 mm/s and 0.79 mm/s, respectively. Both signals refer to Fe^{II} in the HS state, one denoted as HS(A) with area fraction of ca. 10% and the other as HS(B) with area fraction of ca. 90%. This result is consistent with the magnetic measurements recorded at 300 K that also indicated 100% of HS Fe^{II} ions. On decreasing the temperature the quadrupole splitting of these two Fe^{II} HS species increases (see Figure 4); this is typical for Fe^{II} HS species, where the electric field gradient is dominated by the temperature-dependent valence-electron contribution. The difference between the quadrupole-splitting values of HS(A) and HS(B) is caused by different lattice contributions of opposite sign to that of the valence-electron contributions. The HS(B) signal loses intensity on lowering the temperature at the favour of

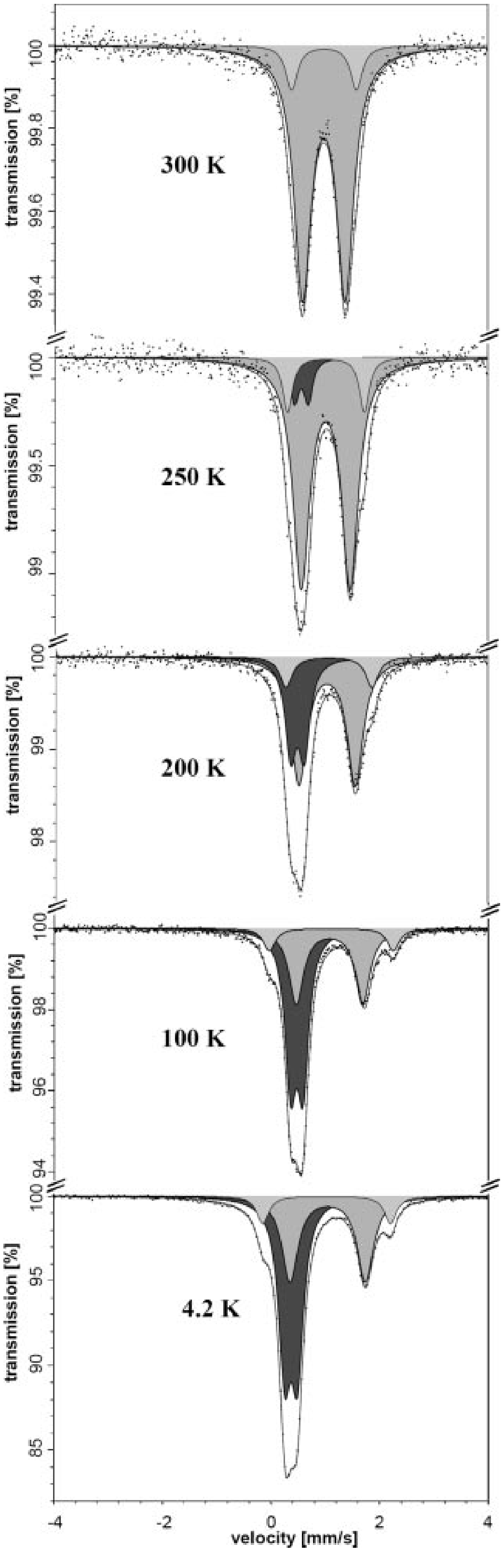

Figure 3. Selected ^{57}Fe Mössbauer spectra for **1** over the temperature range 300–4.2 K. The integrals of HS species (A and B) are filled in light grey and grey, respectively, and the LS species (B) in black.

a new signal, a poorly resolved quadrupole doublet with parameter values δ = 0.57 mm/s and Δ = 0.25 mm/s typical of iron(II) in the LS state, LS(B) that is seen from 270 K downwards. Thus HS(B) undergoes partial thermal spin conversion to reach a plateau, that is also seen in the $\chi_M T$ curve, corresponding to ca. 40% HS(B) and ca. 50% LS(B) at 4.2 K, while the ca. 10% of HS(A) remains essentially constant over the whole temperature range (Figure 5). The partial spin conversion is completed at about 80 K as noted in the $\chi_M T$ curve. The spectrum obtained at 4.2 K shows, in comparison to the spectrum at 61 K, that the strong decrease of the $\chi_M T$ values to very low temperatures, seen in Figure 2, is not caused by a further decrease of the HS molar fraction and, therefore, not caused by a spin transition. The ZFS with increasing Boltzmann population of the lowest electronic levels on lowering the temperature is responsible for the abrupt decrease below 20 K.

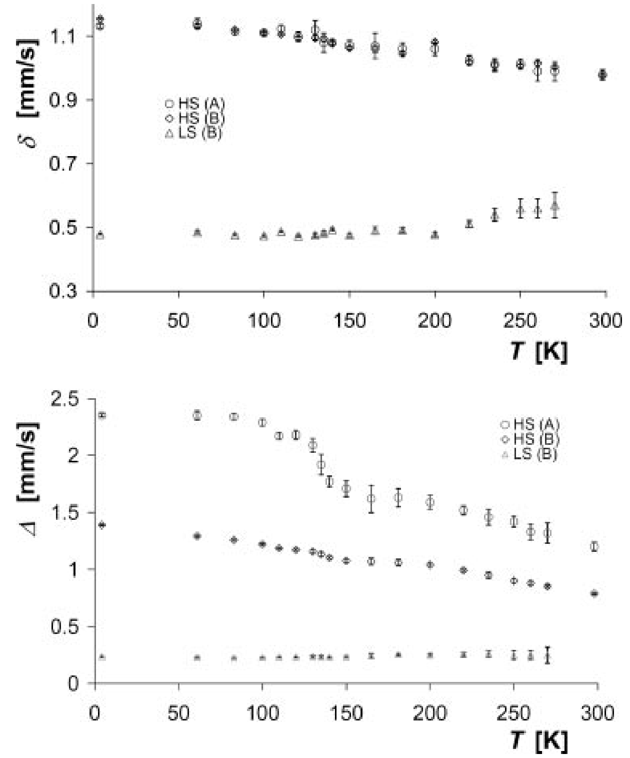

Figure 4. Temperature dependence of isomer shift (δ) and quadrupole splitting values Δ for site A: ○ (HS) and site B: ◊ (HS), Δ (LS) in **1** over the temperature range 300–4.2 K.

The SCO dinuclear units are thus represented by the HS(B) site. But the nature of the HS(A) site should be discussed. The HS(A) site does not refer to an impurity as a result of oxidation because no ferric species were detected (the isomer shift corresponds to Fe^{II} ions[24] and signal A is present over the whole temperature range of investigation – see Figure 5). It cannot be attributed to the iron starting material, too, for two reasons: (i) The isomer shift of HS(A) is exactly the same as the one of the dinuclear units HS(B) (see Figure 4) (ii) We did not observed a gradual replacement of the lines for this site between ca. 200 K and 250 K, as reported for $[Fe(H_2O)_6](ClO_4)_2$.[25] Therefore, HS(A) should correspond to nonswitched complexes that could be either $[Fe_2L_3]^{4+}$ dinuclear units or dinuclear units with one vacant metal centre. Applied field Mössbauer experiments (see next section) have revealed that these species are uncoupled at 4.2 K. We thus favour the hypothesis of the presence of mononuclear species, that is interestingly supported by the detection of mononuclear species in the ESI analysis of **1**.

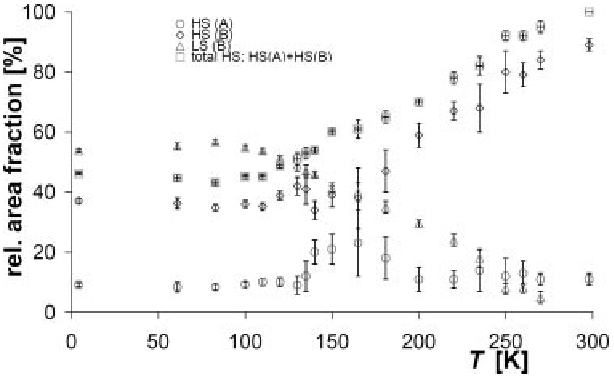

Figure 5. Temperature dependence of the relative area fraction for site A: ○ (HS) and site B: ◊ (HS), Δ (LS) in **1** over the temperature range 300–4.2 K. The HS molar fraction (□) is also given.

Applied Field ^{57}Fe Mössbauer Spectroscopy

To answer the second question of this study, whether the spin conversion occurs via intermediates of [HS–LS] pair formation or directly from [HS–HS] to [LS–LS] pairs, we have performed a ^{57}Fe Mössbauer experiment in applied parallel magnetic field (50 kOe) at 4.2 K (Figure 6), as the zero-field Mössbauer spectrum gives only access to the fraction of HS and LS components, irrespective of the nature of the spin pairs involved. The effective hyperfine magnetic field H_{eff} at the iron nuclei of a paramagnetic nonconducting sample in an external field H_{ext} may be estimated as $H_{\text{eff}} \approx H_{\text{ext}} - [220 - 600(g-2)]\langle S \rangle$, where $\langle S \rangle$ is the atomic spin moment and g the Landé splitting factor.[26,27] The difference between the expectation values of S for Fe^{II} in the LS and in the HS states in [LS–LS], [HS–LS] and [HS–HS] pairs enables one to distinguish unambiguously between the dinuclear units consisting of two possible spin states in an external magnetic field.[11a] To do so, the strength of the external magnetic field should be sufficiently high, and the temperature sufficiently low, in order to avoid magnetic relaxation taking place within the characteristic time window of a Mössbauer experiment ($\approx 10^{-7}$ s). The black spectrum with area fraction of 57% refers to Fe^{II}–LS split by a local effective field of 49.4 kOe, which corresponds to the applied magnetic field of 50 kOe, as expected for $\langle S \rangle = 0$ of the LS centres in the [LS–LS]. The grey doublet with area fraction of 37% shows considerable line broadening arising from the interaction with the external field. The value of the effective field calculated from this spectrum is 13 kOe. The two iron HS centres of the [HS–HS] pairs are antiferromagnetically coupled and the resulting spin ladder is thermally populated leading to the expectation value <S> of ca. 0.4, derived from the formula above. This value results from a weak antiferromagnetic coupling between the two HS Fe^{II} centres of the dinuclear species. The light-grey magnetically split spectrum with area fraction of ca. 6% is typical for uncoupled Fe^{II}–HS centres with S = 2 each. This fraction corresponds to the HS(A) site. The calculated effective field is 56 kOe. Thus, no [HS–LS] pairs were detected at 4.2 K.

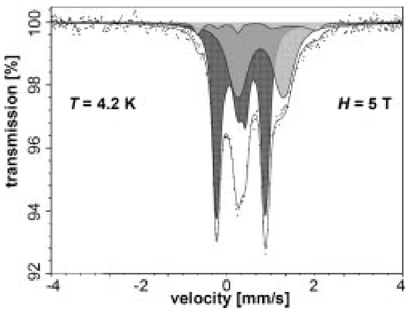

Figure 6. ^{57}Fe Mössbauer spectrum of **1** recorded at 4.2 K in an external magnetic field of 50 kOe. The signals in black, grey, and light grey refer to LS ions in [LS–LS] pairs, HS ions in [HS–HS] pairs and to uncoupled HS ions, respectively.

Discussion

The field experiments at 4.2 K may call for the occurrence of thermal spin conversion in the present triple helicate dinuclear system directly from [HS–HS] to [LS–LS] species, contrary to what was observed for the series $\{[Fe(L)(NCX)_2]_2(\mu\text{-bpym})\}$ (L = bpym, X = S or Se) and (L = bt = 2,2′-bithiazoline and X = S)[23] and for $\{[Fe(phdia)(NCS)_2]_2(phdia)\}$ (phdia = 4,7-phenanthroline-5,6-diamine)[14] using the same physical method. According to Real, the predominant factor that determines the existence of [HS–LS] pairs is the strength of intermolecular interactions in these compounds.[28] Indeed, weak intermolecular interactions were taken responsible for the direct [HS–HS] to [LS–LS] transformation observed by applied field Mössbauer spectroscopy in $\{[Fe(dpa)(NCS)_2]_2(bpym)\}$ (dpa = 2,2′-dipyridylamine),[13] but such interactions can be hardly evaluated because this material was not structurally characterised. This is in line with a density functional theory (DFT) study recently reported by Zein and Borshch.[29] These authors have studied the energetics of five binuclear SCO complexes exhibiting different ligand-field strength and different structural arrangements of the bridging ligands. It could be shown that spin transition via the intermediate [HS–LS] pairs occurs only in those cases, where the energy of the [HS–LS] pairs lies below the halfway point between the energies of [LS–LS] and [HS–HS] states. Favourable for this to occur seems to be a planar bridging structure. On the contrary, a strong distortion of the bridging ligand breaks the electronic communication between the metal centres and destabilises the [HS–LS] spin-state shifting it above the halfway point. In such systems, a direct spin transition from [HS–HS] to [LS–LS] is expected and has indeed been observed on the basis of X-ray measurements, for two other binuclear complexes: $[(pypzH)(NCSe)Fe(\mu\text{-pypz})_2Fe(NCSe)(pypzH)]\cdot 2H_2O$ displaying an abrupt spin transition[17a] and $[\{Fe(NCBH_3)(4\text{-phpy})\}_2(\mu\text{-bpypz})_2]$ (4phpy = 4-phenylpyridine) presenting a stepwise transition.[16a] This also appears to be the case in the triple helicate system under study that displays a gradual spin conversion despite the fact that all noncoordinated species (perchlorate anions, water and methanol solvent molecules) are involved in hydrogen bonding with the triple-helicate cation in the crystal structure of $[Fe_2(L)_3](ClO_4)_4\cdot 4MeOH\cdot H_2O$.[22] The use of the very flexible L thus does not propagate efficiently cooperative effects associated with the spin-state change within the dinuclear unit as earlier observed for some Fe coordination polymers exhibiting a gradual SCO behaviour.[30] Interestingly, according to the above mentioned DFT calculations,[29] the step in the spin conversion curve around 180 K (see Figure 2) calls for the presence of an intermediate spin state involving [LS–HS] pairs. This situation is supported by the Zero-field Mössbauer study looking at the evolution of the HS(A) fraction as well as its Mössbauer parameters. On cooling, in the region slightly below the step, the quadrupole splitting increases rather abruptly and follows from then on the usual increase of the quadrupole splitting with decreasing temperature (Figure 4). The jump in quadrupole splitting falls together with the formation of the [LS–LS] pairs. If we consider that the transition would directly occur from [HS–HS] to [LS–LS], we would then rather expect a continuous increase in quadrupole splitting as is commonly observed for iron(II) HS compounds. The ca. 50% gradual spin conversion of **1** thus occurs via [LS–HS] pairs formation and is complete for the involved fraction since these pairs are not present at 4.2 K. A quantitative evaluation of the population of these mixed species could not be obtained by applied field Mössbauer spectroscopy due to the high temperature range of the plateau (≈ 180 K) that would have prevented the trapping of the sample to 4.2 K by rapid cooling. During the pronounced change of the quadrupole splitting of HS(A) the area fraction of this site increases and decreases again (see Figure 5). This indicates transient stiffening of the nearby lattice which shows that these HS sites, although presumably not directly linked to the dinuclear complexes, may take part in the cooperative elastic interactions accompanying the spin conversion process.

Conclusions

The spin-state-crossover phenomenon in $[Fe_2(L)_3](ClO_4)_4\cdot 2H_2O$ (**1**) investigated by precise SQUID magnetic measurements performed over the temperature range (300–1.8 K) occurs in two steps at ca. 240 K and ca. 120 K. ^{57}Fe Mössbauer data recorded at 4.2 K have demonstrated that half of the Fe^{II} ions remains in the HS state, and that the second drop of $\chi_M T$ observed below ca. 20 K cannot be attributed to a spin-state conversion. The absence of any hysteresis effect also disapproves the "multistability" character reported for **1**,[22] and confirms the noncooperative character of the spin conversion. Applied field Mössbauer measurements demonstrate the occurrence of a complete thermal spin conversion for half of the iron(II) ions from [HS–HS] to [LS–LS] species because no [LS–HS] species were identified at 4.2 K. The mechanism of this spin-state conversion should, however, involve [LS–HS] species that should be responsible of the presence of the plateau around 180 K in the magnetic measurements (Figure 2) and which are sensed in the Mössbauer parameters of an uncoupled iron(II) site. Further experiments are planned to confirm the presence of these mixed species in this novel system.

Experimental Section

General: All reagents and solvents were used as received from commercial sources. ^{1}H NMR spectra were recorded with a Gemini 200–92, 200 MHz spectrometer. The solvent residual peak has been set as a reference. CHN analyses have been performed by the Zentrale Analytik of the Institute für Organische Chemie (Mainz). IR spectra were collected with a BioRad FTS-135 spectrometer using KBr pellets. UV spectra in solution were recorded with a Cary 50 spectrometer and diffuse reflectance spectra on solids were recorded with a CARY 5E spectrophotometer using polytetrafluoroethylene as a reference. Mass spectra were recorded with a Thermo Finnigan LCQ Ion Trap spectrometer using ESI mode and detecting positive ions. Magnetic susceptibilities were measured over the temperature range 1.8–300 K with a cooling and heating rate of 2 K/min with a Quantum Design MPMS*XL* SQUID magnetometer equipped with a 50-kOe magnet operating at 10 kOe. Magnetic data were corrected for diamagnetic contributions, which were estimated from Pascal's constants. ^{57}Fe Mössbauer spectra were recorded in transmission geometry with a conventional constant-acceleration spectrometer with a room temperature ^{57}Co(Rh) source over the temperature range (300–83 K). The samples were sealed in a Plexiglas sample holder. For the 4.2 K experiment, the samples were mounted in a helium-bath cryostat with a ^{57}Co(Rh) source that was kept at 4.2 K. A superconducting magnet was applied to create a magnetic field directed parallel to the wave vector of the γ-quanta. The spectra were fitted to Lorentzians using Recoil 1.05 Mössbauer Analysis Software[31] assuming equal Debye–Waller factors of the HS and LS states of the Fe^{II} ions. All isomer shifts refer to natural Fe at room temperature.

Synthesis of L: The L ligand has been prepared as a white solid by a condensation reaction of 4,4′-methylenedianiline and 3*H*-imidazole-4-carboxaldehyde in methanol according to ref.[22]. ^{1}H NMR (200 MHz, DMSO, 25 °C): δ = 8.43 (s, 1 H, H^{im}), 7.82 (s, 1 H, H$^{2/4}$); 7.64 (s, 1 H, H$^{2/4}$), 7.24 (d, J = 7.6 Hz, 2 H, H^{Ph}), 7.15 (d, J = 7.6 Hz, 2 H, H^{Ph}), 3.96 ppm (s, 1 H, CH$_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3021 (w), 2907 (w), 2827 (*w*), 1629 (vs), 1600 (s), 1541 (vw), 1501 (s), 1437 (m), 1414 (*w*), 1351 (w), 1330 (*w*), 1299 (w), 1222 (*m*), 1201 (*w*), 1170 (w), 1148 (sh), 1109 (w), 1093 (m), 1014 (w), 990 (m), 977 (sh), 918 (w), 873 (m), 844 (m), 808 (w), 787 (w), 753 (w), 709 (w), 622 (s), 601 (w), 539 (m) cm^{-1}.

Synthesis of 1: The complex [Fe$_2$L$_3$](ClO$_4$)$_4$·2H$_2$O was prepared as an orange powder according to a procedure slightly adapted from that in ref.[22] substituting the addition of LiClO$_4$ by Fe(ClO$_4$)$_2$·6H$_2$O to avoid the presence of unwanted cationic species and a few mg of ascorbic acid to prevent oxidation of Fe^{II} ions. Yield: 0.097 g (67%). C$_{63}$H$_{58}$Cl$_4$Fe$_2$N$_{18}$O$_{18}$ (1608.77): calcd. C 47.04, H 3.63, N 15.67; found C 47.10, H 3.67, N 15.58. IR (KBr): $\tilde{\nu}$ = 3131 (br), 2932 (w), 2853 (w), 1620 (vs), 1599 (s), 1558 (w), 1540 (w), 1506 (s), 1501 (sh), 1437 (m), 1294 (m), 1232 (w), 1207 (w), 1090 (vs), 1009 (m), 935 (vw), 892 (m), 861 (w), 814 (m), 756 (w), 708 (w), 625 (s), 544 (w) cm^{-1}. UV/Vis (PTFE): λ_{max} = 470 nm (MLCT), 880 nm (^{5}E←^{5}T$_2$). UV/Vis (MeCN): λ_{max} = 282 (π–π*), 306 (π–π*), 460 (MLCT), 825 (^{5}E←^{5}T$_2$). ESI-MS (MeCN): m/z = 1473 [Fe$_2$(L)$_3$(ClO$_4$)$_3$]$^+$, 1118 [Fe$_2$(L)$_2$(ClO$_4$)$_3$]$^+$, 817 [Fe$_2$(L-H)(L-2H)]$^+$, 686 [Fe$_2$(L)$_3$(ClO$_4$)$_2$]$^{2+}$, 636 [Fe$_2$(L)$_2$(L-H)(ClO$_4$)]$^{2+}$, 586 [Fe$_2$(L)(L-H)$_2$]$^{2+}$, 459 [Fe$_2$(L)(L-H)(ClO$_4$)]$^{2+}$, 409 [Fe(L-H)]$^+$, 355 [HL]$^+$. The synthesis carried out with the same reagents as in ref.[22] led to the same analytical results.

CAUTION! No problems were encountered during the preparation of the perchlorate complex described in this work. However, suitable care must be taken when handling such potentially explosive materials.

Supporting Information (see footnote on the first page of this article): Overview of the ^{57}Fe-Mössbauer parameters for **1**.

Acknowledgments

This work was partly funded by the Deutsche Forschungsgemeinschaft (Priority Programme No.1137, Molecular Magnetism, and the CNRS-DFG project Gu 95/59), the Fonds der Chemischen Industrie, the Materialwissenschaftliches Forschungszentrum der Universität Mainz and the Fonds Special de Recherche de l'Université Catholique de Louvain.

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Received: April 24, 2006