Influence of a thermochromic anion on the spin crossover of iron(II) trinuclear complexes probed by Mössbauer spectroscopy

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Abstract. The insertion of thermochromic anions (1 and 2) into triazole based iron(II) trinuclear spin crossover complexes [FeIII$_3$(hyetrz)$_6$(H$_2$O)$_6$](1 or 2)$_2$Cl$_2$ paves the way to a large panel of multifunctional materials. In addition to a gradual thermo-induced spin conversion of the central metal ion on cooling below room temperature, an unexpected split of the Mössbauer signal of the external iron(II) ions as well as pronounced relaxation phenomenon for the central HS iron(II) ion was discovered. This phenomenon is suggested to be induced by the tautomeric equilibrium between enol and keto forms of the anion.

1. Introduction
Spin crossover (SCO) is a highly versatile phenomenon which involves a complete electronic reorganization between a diamagnetic low-spin (LS) and a paramagnetic high-spin (HS) state, in iron(II) coordination compounds [1]. Many applications are thought in sensors [2] and displays [3] but the most promising field is presumably the development of new molecular switches for molecular electronics [3]. The large majority of iron(II) SCO compounds are made of mononuclear or large polynuclear units such as linear chains [2]. Some dinuclear and tetranuclear self-assemblies [4,5] were obtained by using ligands with specific coordination sites although trinuclears were synthesised with suitable metal/ligand ratios with 1,2,4-triazole ligands [6]. In these later model SCO complexes, only the central iron(II) ion, which is isolated from the terminal HS iron(II) ions, is SCO capable [6] (Figure 1a). In addition, the use of an alcohol substituted triazole such as 4-(2’-hydroxyethyl)-1,2,4-triazole (hyetrz) can lead to dense supramolecular networks which can modulate the SCO phenomenon thanks to steric and electronic factors [6]. A strong influence of the anion nature was also nicely demonstrated because of the sensitivity of the external iron(II) ions on the SCO of the central ion in the case of an anion-directed rigid supramolecular network [7]. In this work, novel thermochromic anions derivated from N-salicylidene aniline were introduced in 1,2,4-triazole based trinuclear compounds. The sodium salt of N-salicylidene p-aminobenzene sulfonate anion (1) and its bromo derivative (2) display thermochromism thanks to a thermo-induced tautomeric equilibrium between an uncoloured enol form and a yellow cis-keto form (Figure 1b) [8]. An indirect influence of the anion nature activated by temperature is proposed to explain the unusual Mössbauer features of the trinuclear complexes (3,4).
Figure 1. (a) Schematic view of a 4-R-1,2,4-triazole iron(II) trinuclear compound with
R = CH₂CH₂OH. (b) Sodium salt of the N-salicylidene p-aminobenzene sulfonate with R = H (1), Br
(2). The thermo-induced equilibrium between the uncoloured enol and the yellow cis-keto forms is
shown.

2. Results

1 and 2 was synthesized following the reported method [9]. Interestingly, the trinuclear compound
3, [FeII₃(hyetrz)₆(H₂O)₆](1)₄Cl₂, (Figure 1) was obtained although a ratio of one equivalent of iron(II)
chloride salt for three equivalents of hyetrz and two equivalents of the sodium salt of the anions 1 was
engaged in the reaction medium (methanol, technical grade). It strongly suggests that 1 prevents the
formation of the usually reported 1D chain [2].

3 was analysed by temperature dependent ⁵⁷Fe Mössbauer spectroscopy (Figure 2). At 145 K, the
central metal ion gives rise to two ⁵⁷Fe Mössbauer signals: a narrow doublet (δLS = 0.43(1) mm/s and
ΔEQ-LS = 3.2(2) mm/s) and a large quadrupole doublet (ΔEQ-HS-central = 2.66(4) mm/s) with a higher
isomer shift (δHS-central = 1.71(2) mm/s) which appears to be unusually large and higher than reported
values [7] (Table 1). These contributions are attributed to a LS iron(II) and a HS iron(II) produced by
a thermally induced HS ↔ LS spin conversion [10]. This is consistent with the FeII₄N₆ coordination
sphere which is very often encountered for SCO centres [1]. The external iron(II) ions have a N3O3
coordination sphere which is not suitable for SCO in the present case (Figure 1a). Surprisingly, for 3,
the external FeII₄HS-ext. Mössbauer contribution appears to be split into two slightly different doublets

| δ [mm/s] | T [K] | FeII₄LS | FeII₄Central | FeII₄HS-ext. | FeII₄HS-central |
|---------|-------|---------|-------------|-------------|----------------|
| 3       | 145(1) | 0.43(1) | 0.37(2)     | 1.16(1)     | 1.16(1)        |
|         | 175(1) | 0.45(2) | 1.12(1)     | 1.16(1)     | 1.16(1)        |
|         | 225(1) | 0.41(2) | 1.03(2)     | 1.17(1)     | 1.17(1)        |
|         | 275(1) | 0.40(4) | 0.81(7)     | 1.18(2)     | 1.40(3)*       |
| 4       | 145(1) | 0.33(3) | 1.12(6)     | 1.22(5)     | 1.22(5)        |
|         | 175(1) | 0.28(4) | 1.11(1)     | 1.17(1)     | 1.17(1)        |
| ΔEQ [%] |       |         |             |             |                |
| 3       | 145(1) | 0.32(2) | 3.1(8)      | 3.3(9)      | 3.3(9)         |
|         | 175(1) | 0.26(4) | 2.9(2)      | 3.3(2)      | 3.3(2)         |
|         | 225(1) | 0.20(4) | 3.0(2)      | 3.0(2)      | 3.0(2)         |
|         | 275(1) | 0.22(7) | 3.5(4)      | 3.5(4)      | 3.5(4)         |
| 4       | 145(1) | 0.1(3)  | 0(9)        | 0(9)        | 0(9)           |
|         | 175(1) | 0(9)    | 0(9)        | 0(9)        | 0(9)           |
| ΔEQ [%] |       |         |             |             |                |
| 3       | 145(1) | 0.14(1) | 0.16(4)     | 0.16(4)     | 0.16(4)        |
|         | 175(1) | 0.16(4) | 0.15(4)     | 0.15(4)     | 0.15(4)        |
|         | 225(1) | 0.12(3) | 0.14(5)     | 0.14(5)     | 0.14(5)        |
|         | 275(1) | 0.15(7) | 0.16(3)     | 0.22(3)     | 0.36*          |
| 4       | 145(1) | 0.27(3) | 0.32(5)     | 0.27(5)     | 0.27(5)        |
|         | 175(1) | 0.32(5) | 0.22(9)     | 0.22(9)     | 0.22(9)        |

Table 1. Temperature dependent ⁵⁷Fe Mössbauer parameters for 3 and 4. Isomer shift (δ) values are
given respective to α-Fe. * Fixed parameters. ΔEQ = quadrupole splitting. Δ/2 = half width at half
maximum.

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Figure 2. Temperature dependant ⁵⁷Fe Mössbauer spectra of 3 (top) and 4 (bottom).
labelled Fe\textsuperscript{II}\text{HS-Ext.1} and Fe\textsuperscript{II}\text{HS-Ext.2} (Figure 2). These two signals are detected at a lower isomer shift ($\delta_{\text{HS-ext.1}} = 1.14(1)$ mm/s and $\delta_{\text{HS-ext.2}} = 1.17(1)$ mm/s) and a higher quadrupole splitting ($\Delta E_{Q,\text{HS-ext.1}} = 3.15(8)$ mm/s and $\Delta E_{Q,\text{HS-ext.2}} = 3.39(4)$ mm/s) than for the central iron(II) HS ion because of the strongly different coordination spheres of these ions (Table 1). The difference between the two Fe\textsuperscript{II}\text{HS-Ext.} is clearly identified in the $\Delta E_Q$ values and translates the presence of two types of long-range molecular environments through a different H-bonding network at the end of the trinuclear entities.

The influence of temperature on 3 was analysed by \textsuperscript{57}Fe Mössbauer spectroscopy on warming over the temperature range 145-275 K (Figure 2). Mössbauer spectra of 3 are fitted best by the combination of the four contributions described above although the presence of a small amount of Fe\textsuperscript{III}\text{HS impurity is identified in the 275 K spectrum thanks to the higher $f$ factor of this iron site (Table 1). An optimization of Mössbauer parameters all together was successfully achieved for the 145(1) K spectrum but did not lead to a good fit for other spectra. Some parameters need indeed to be fixed during the optimization. A gradual and incomplete SCO phenomenon is clearly identified for the central metal ion because of the slow decrease of the Fe\textsuperscript{IILS-central} relative area fraction (from 22 to 7 %) compensated by a slow increase of the Fe\textsuperscript{IIHS-central} relative area fraction (12 to 29 %) (Figure 3a). The two Fe\textsuperscript{II}\text{HS-ext.} doublets seem to be involved in a thermal equilibrium although the error on their relative area fraction seems to be large. Fe\textsuperscript{II}\text{HS-ext.1} relative area fraction decreases from 33 to 18 % whereas the relative area fraction of Fe\textsuperscript{II}\text{HS-ext.2} increases from 32 to 43 % (Figure 3a). Interestingly, a large sensibility of the isomer shift values is noted for the Fe\textsuperscript{II}\text{HS-central} and Fe\textsuperscript{II}\text{HS-Ext. 1} (Table 1). Although this variation is supported by the presence of a second order Doppler effect, the modifications is higher than the expected ones. An influence of the thermo-sensibility of the anion could be invoked to explain this observation. Moreover, the half width at half maximum, $\Gamma/2$, of the central HS iron(II) ion increases on cooling and reaches a maximum at 225(1) K, before returning to a similar value on further cooling (Figure 3b). This dramatic line broadening reflects a pronounced relaxation phenomenon, that might be promoted by the tautomeric equilibrium between the enol and keto forms of the anion. Accurate population of respective species shall be derived using an appropriate relaxation model \cite{11} to fit our spectra in order to take into account the present dynamics.

Figure 3. (a) Evolution of the relative area fraction for 3 over the temperature range 140-275 K. (b) Evolution of $\Gamma/2$ for 3 over the same temperature range.

A second trinuclear SCO compound [Fe\textsuperscript{II}\text{3(hyetrz)}\textsubscript{3}(H\textsubscript{2}O)\textsubscript{6}][2]\textsubscript{2}Cl\textsubscript{2} (4) was prepared by mixing one equivalent of iron(II) chloride salt, three equivalents of hyetrz and two equivalents of the sodium salt of the anions 2 in methanol and investigated by Mössbauer spectroscopy from 145 K to 175 K. The presence of four iron(II) signals as in 3 is confirmed (Figure 2). The change of the anion from 1 to 2 leads to a significant change into some Mössbauer parameters. The Fe\textsuperscript{IILS} site is a singlet and has a lower isomer shift than for 3. The isomer shift of Fe\textsuperscript{IILS-central} increases and shows a lower quadrupole splitting (See Table 1). The SCO phenomenon is still observed with a decrease of the Fe\textsuperscript{IILS relative...
area fraction: from ~ 22 to 13 % and an increase of the Fe$^{II}_{HS-central}$ relative area fraction: from ~ 12 to 16 %, which appears to be less influenced by the anion equilibrium (Table 1). Although the isomer shifts of Fe$^{II}_{HS-ext.}$ do not differ much comparing 4 and 3, a large change in the relative Fe$^{II}_{HS-ext.1}$/Fe$^{II}_{HS-ext.2}$ ratio is observed (from 33/32 for 3 to 19/47 for 4 at 145(1) K). The variation of the relative area fraction of Fe$^{II}_{HS-ext.}$ sites with the temperature which was observed for 3 is preserved in 4.

3. Conclusion
The influence of a thermochromic anion was probed by $^{57}$Fe Mössbauer spectroscopy for this novel type of multifunctional material built with a triazole based trinuclear SCO compound, for the first time. The stabilization of the trinuclear pattern, revealed by a ratio Fe$^{II}_{central}$/Fe$^{II}_{ext.}$ of ~ 1/3, is the first consequence of the successful insertion of the organic anions 1 and 2 which is believed to prevent the formation of the 1D chain. A reaction mechanism involving a steric hindrance of anions must be considered. A second very interesting impact of the presence of the anions is highlighted by the splitting of the doublet corresponding to the Fe$^{II}_{HS-ext.}$ into two slightly different doublets (Fe$^{II}_{HS-ext.1}$ and Fe$^{II}_{HS-ext.2}$). This behaviour translates the presence of two slightly different molecular environments for the external metal ions. The electronic density of the organic anion has a strong influence on the relative area fraction of the two Fe$^{II}_{HS-ext.}$ doublets as shown by compound 4 where the anion was substituted by a bromide. Thus, a new type of multifunctional material which combines a thermo-sensitive anion and a SCO inorganic compound was synthesized, for the first time. A direct influence of the presence of the anion was revealed thanks to $^{57}$Fe Mössbauer spectroscopy. The communication between the anion and the complexes is thought to be favoured by the expected dense supramolecular network developed by these molecules [6]. Further studies on the incorporation of thermochromic anions into SCO networks are in progress in our laboratories.

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