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Study of thermal spin crossover in [Fe(II)(isoxazole)₆](BF₄)₂ with Mössbauer spectroscopy

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Abstract

⁵⁷Fe Mössbauer spectroscopy of the mononuclear [Fe(II)(isoxazole)₆](BF₄)₂ compound has been studied to reveal the thermal spin crossover of Fe(II) between low-spin ($S = 0$) and high-spin ($S = 2$) states. A temperature-dependent spin transition curve has been constructed with the least-square fitted data obtained from the Mössbauer spectra measured at various temperatures in the 240–60 K range during the cooling and heating cycle. The compound exhibits a temperature-dependent two-step spin transition phenomenon with T_{SCO} (step 1) = 92 and T_{SCO} (step 2) = 191 K. The compound has three high-spin Fe(II) sites at the highest temperature of study; among them, two have slightly different coordination environments. These two Fe(II) sites are found to undergo a spin transition, while the third Fe(II) site retains the high-spin state over the whole temperature range. Possible reasons for the formation of the two steps in the spin transition curve are discussed. The observations made from the present study are in complete agreement with those envisaged from earlier magnetic and structural studies made on [Fe(II)(isoxazole)₆](BF₄)₂, but highlights the nature of the spin crossover mechanism.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Research activities in the area of Fe(II) spin crossover materials have been stimulated in recent years with the objective of developing molecular switching units on the nanoscopic

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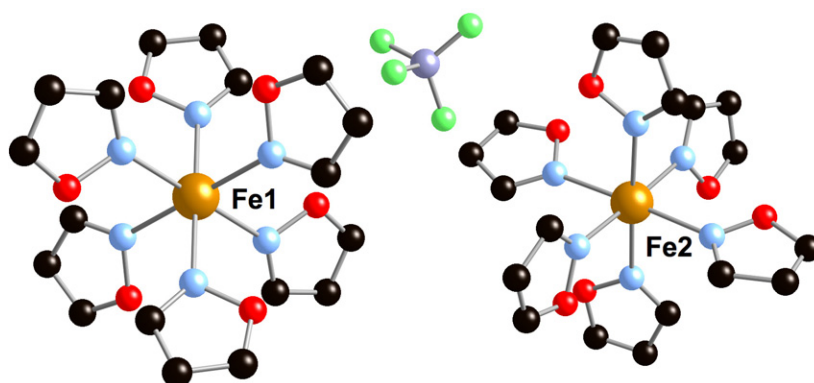


Figure 1. Structure of $[\text{Fe}(\text{II})(\text{isoxazole})_6](\text{BF}_4)_2$ (red is oxygen, blue is nitrogen, black is carbon, gray is boron, and green is fluorine).

scale in molecular electronics [1, 2]. In this context hexa-coordinated Fe(II) spin crossover materials have been widely studied, which has been motivated by their favorable response towards a change in temperature or pressure, as well as upon light irradiation as they undergo interconversion from a low-spin ($S = 0$) diamagnetic state to a high-spin ($S = 2$) paramagnetic state under the influence of these external perturbations [1]. For instance, upon increasing temperature the mononuclear compound $[\text{Fe}(\text{II})(\text{isoxazole})_6](\text{BF}_4)_2$ [3–5] exhibits an interconversion from the low-spin (LS) to the high-spin (HS) state. Moreover, this magnetic response is associated with a drastic thermochromic effect: at room temperature this compound appears as colorless crystals, whereas upon cooling the color changes to an intense pink. It became evident that $[\text{Fe}(\text{II})(\text{isoxazole})_6](\text{BF}_4)_2$ displays a rather complicated Fe(II) spin crossover behavior [4, 5].

Recently, the magnetic behavior of $[\text{Fe}(\text{II})(\text{isoxazole})_6](\text{BF}_4)_2$ could be analysed in relation to the structural features (figure 1) [4, 5]. This compound undergoes two reversible spin transitions at 91 and 192 K. The crystal structure determinations carried out at 130 and 260 K [5] revealed the space group to be $P\bar{1}$ and $P\bar{3}$, respectively. The unit cell consists of three high-spin Fe(II) containing $[\text{Fe}(\text{isoxazole})_6]^{2+}$ entities together with six non-coordinated tetrafluoroborate anions. In the crystal structure determined at 260 K, Fe1 lies on the inversion center and on the C_3 axis; therefore, the coordination geometry about this Fe(II) ion is entirely symmetric, i.e. all six coordinated isoxazole ligands are crystallographically identical. Fe2 lacks the inversion center; however, the symmetry-related Fe2' is generated using the inversion center located on Fe1. This implies that the Fe1:Fe2 ratio is 1:2, and this prevails down to 130 K, although the crystallographic symmetry is lowered to $P\bar{1}$ at this temperature, implying that the threefold axis about Fe1 has disappeared. Moreover, the geometric features (i.e. Fe–N bond distances) at 130 K indicate that Fe1 remains in the HS state, whereas Fe2 in the LS state.

Although the crystallographic studies have considerably contributed to the assignment of the spin state for each Fe(II) ion at various temperatures, a complete analysis of the Fe(II) spin-crossover behavior is only possible when direct information on the temperature-dependent evolution of the various Fe(II) sites becomes available. On the basis of the isomer shift and quadrupole splitting values, different spin states of iron(II) are readily and unambiguously assigned. The temperature dependence of these parameter values is a further characteristic feature. Even iron sites of like spin and oxidation states, as occurring in the present system with up to three iron(II) HS sites, should be detectable by Mössbauer spectroscopy, as the

slightest molecular distortion causes a change in the quadrupole splitting. This has indeed been observed in the present study.

This paper reports a detailed and extended ^{57}Fe Mössbauer spectroscopy study on the $[\text{Fe}(\text{II})(\text{isoxazole})_6](\text{BF}_4)_2$ spin crossover system.

2. Experimental details

The polycrystalline $[\text{Fe}(\text{II})(\text{isoxazole})_6](\text{BF}_4)_2$ material used for the present study was synthesized as reported earlier [5]. ^{57}Fe Mössbauer spectra were measured at various temperatures in the 60–240 K range using a conventional constant-acceleration spectrometer with a liquid helium cryostat. The hyperfine parameters were obtained by least-square fitting to the Lorentzian lines using the Recoil (1.03a) Mössbauer software analysis program [6].

3. Results and discussion

Mössbauer spectra of $[\text{Fe}(\text{II})(\text{isoxazole})_6](\text{BF}_4)_2$ were recorded at different temperatures in the range of 60–240 K, first during cooling and then while heating. In figure 2 some representative Mössbauer spectra at different temperatures obtained in the cooling as well as the heating direction are shown. The unit cell of this compound contains two unique iron sites [5]; the analysis of the Mössbauer spectra was initiated considering two high-spin Fe(II) sites and one low-spin Fe(II) site at the highest temperature of study. In this way all the spectra recorded above 90 K can be well resolved into three doublets. The main doublet of the 220 K spectrum (displayed in gray), for example, can be characterized by the quadrupole splitting, $\Delta E_Q = 1.61 \text{ mm s}^{-1}$, and isomer shift, $\delta = 0.97 \text{ mm s}^{-1}$ (relative to α -iron), which correspond to the high-spin ground state of Fe(II) ($S = 2$). Another doublet (deep gray) appears with $\Delta E_Q = 3.27 \text{ mm s}^{-1}$ and $\delta = 1.06 \text{ mm s}^{-1}$ and also corresponds to the Fe(II) ($S = 2$) state. A contribution from a third doublet (light gray) is also evident in this spectrum. The parameters for this poorly resolved doublet, $\Delta E_Q = 0.04 \text{ mm s}^{-1}$ and $\delta = 0.34 \text{ mm s}^{-1}$, are indicative of low-spin Fe(II) ($S = 0$). With decreasing temperature below 220 K, the intensity of the main high-spin doublet (HS-A) starts to decrease, while the intensity of the low-spin (LS) doublet increases until around 160 K. In the 160–100 K region the intensity of the HS-A doublet does not change. While cooling further, the intensity of the HS-A doublet gradually decreases to its minimum value, while the intensity of the LS doublet acquires its highest value at around 70 K. In contrast, the other high-spin Fe(II) doublet (HS-B) shows a very small change in its intensity throughout this cooling process.

While heating, the HS-A doublet intensity gradually re-appears at the expense of the low-spin doublet intensity, that follows exactly the behavior observed while cooling. Finally, at 240 K, the feature emerges as the prominent doublet along with the small LS doublet already seen in the spectrum at the beginning of the cycle. During heating the intensity of the HS-B doublet has a similar response as in the cooling process.

The quantitative determination of the spin transition (ST) curve from a series of Mössbauer spectra recorded over a certain temperature range is based on the evolution of the area fractions n_{HS} and n_{LS} of the resonance lines. The area fractions are proportional to the products $f_{\text{HS}} \cdot \gamma_{\text{HS}}$ and $f_{\text{LS}} \cdot \gamma_{\text{LS}}$, respectively, where γ and f are the molar fraction and Lamb–Mössbauer factor of the corresponding spin states. The area fractions of the resonance signal in the Mössbauer spectra do not necessarily reflect the actual concentrations of the different iron spin states, as different bond strengths of the Mössbauer nuclide in its lattice position lead to different Lamb–Mössbauer factors, which in turn give rise to different intensities of the corresponding Mössbauer resonance signals [7, 8]. However, the present procedure presumes identical Lamb–Mössbauer factors f_{HS} for high-spin 5T_2 and f_{LS} for low-spin 1A_1 states,

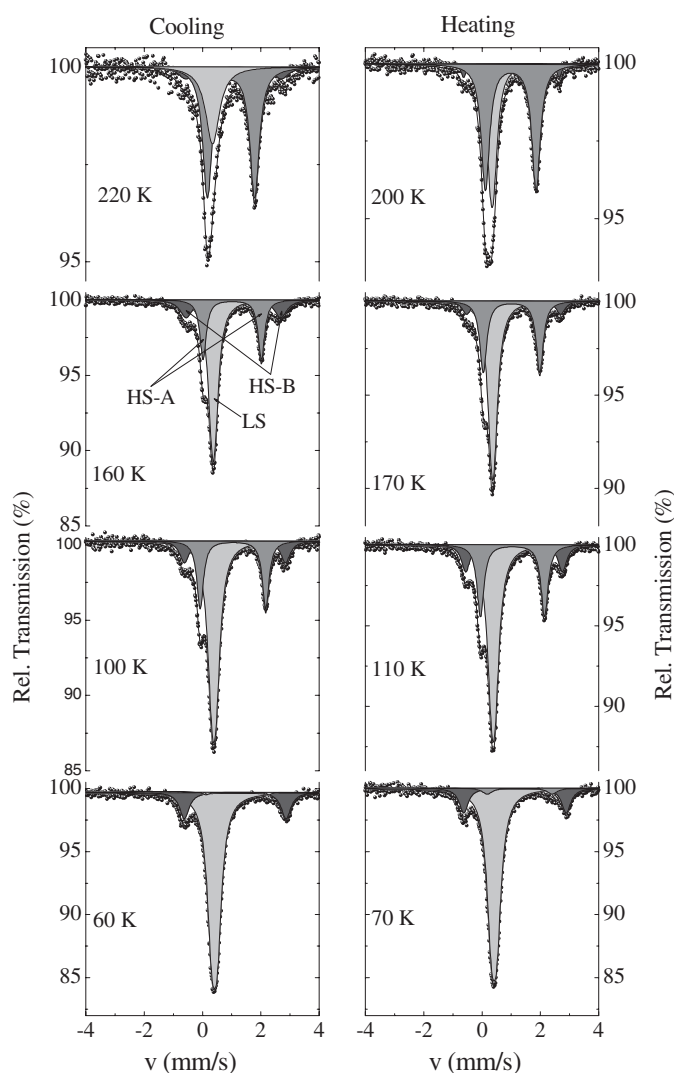


Figure 2. Mössbauer spectra of $[\text{Fe}(\text{II})(\text{isoxazole})_6](\text{BF}_4)_2$ at selected temperatures.

where the high-spin and low-spin fractions just correspond to their area fractions n_{HS} and n_{LS} , respectively. Although it is frequently found that $f_{\text{HS}} < f_{\text{LS}}$ [7], the error involved in the assumption of $f_{\text{HS}} = f_{\text{LS}}$ in the present case is unlikely to be high ($\sim 5\%$). Figure 3(a) represents the temperature variation of the area fraction of the individual Fe(II) spin sites at different temperatures during cooling and heating. The spin transition curve $\gamma_{\text{HS}}(T)$ (where $\gamma_{\text{HS}} = n_{\text{HS}}/(n_{\text{HS}} + n_{\text{LS}})$) was constructed from the Mössbauer data by directly relating the high-spin (HS) fraction to the area fraction of the doublets due to the HS species, and is shown in figure 3(b). This plot clearly shows that the title compound undergoes a two-step spin transition, in accord with the magnetic measurements [5].

From figure 3(a) it is interesting to note that only the HS-A Fe(II) site undergoes the two-step spin transition process, which reflects the predictions from crystal structure analysis [5]. The temperature variations of the area fractions of the HS-A and LS quadrupole doublets

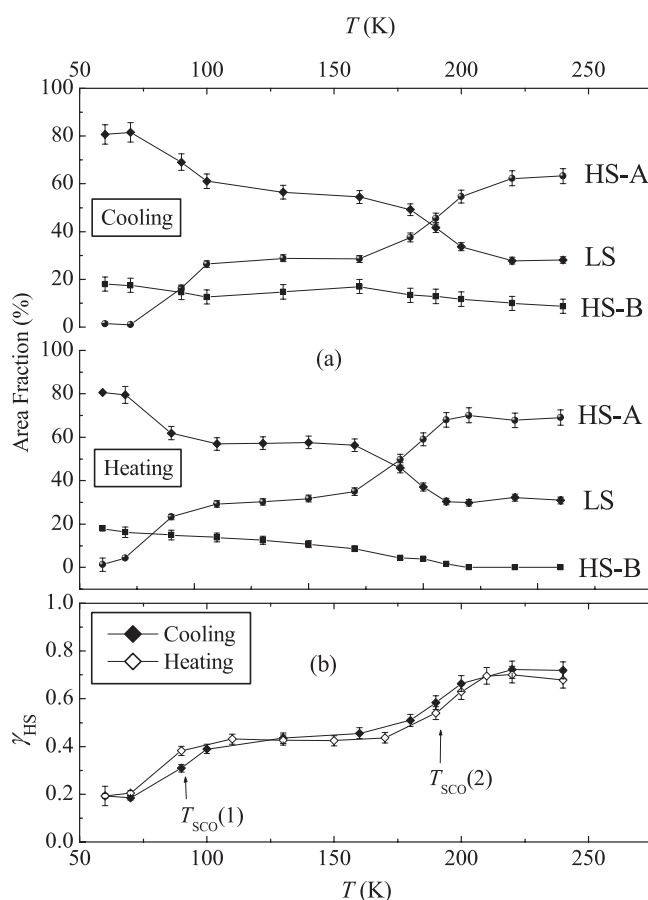


Figure 3. (a) Thermal variation of the area fraction of the quadrupole doublets in the Mössbauer spectra for different Fe(II) spin sites in $[\text{Fe}(\text{II})(\text{isoxazole})_6](\text{BF}_4)_2$ during cooling and heating. (b) Thermal variation of total high-spin fraction (γ_{HS}) estimated from the area fraction of quadrupole doublets during cooling and heating for $[\text{Fe}(\text{II})(\text{isoxazole})_6](\text{BF}_4)_2$.

are almost the same in the cooling and heating directions, reflecting practically no or small ($\Delta T \approx 1$ K) hysteresis associated with each transition step. The thermal spin transition temperatures evaluated from the present study are 92 K ($T_{SCO}(1)$) and 191 K ($T_{SCO}(2)$) for steps 1 and 2, respectively, which exactly correspond to those obtained (91 and 191 K) from the previous magnetic measurements [5]. The intermediate plateau in $\gamma_{HS}(T)$ consists of 44% HS Fe(II) sites at 130 K, which is close to that estimated from magnetic data (43%) [5]. The HS Fe(II) fraction at low temperatures (e.g. 60 K) is found to be $\sim 19\%$, which is higher than the 13% deduced from magnetic measurements. This is likely to be a consequence of the two experiments being carried out using two different batches of sample, which may lead to some differences in the grain size and hence affect the spin transition at low temperatures [9]. It may also result from the intrinsic differences between the two experimental techniques. For instance, the evaluation of the magnetic data may involve uncertainties in the applied correction terms (diamagnetic correction, TIP), which may particularly affect the low-temperature data. Interestingly, the compound retains $\sim 30\%$ of its LS state even at 240 K and above, where the transition curves have merged into a plateau.

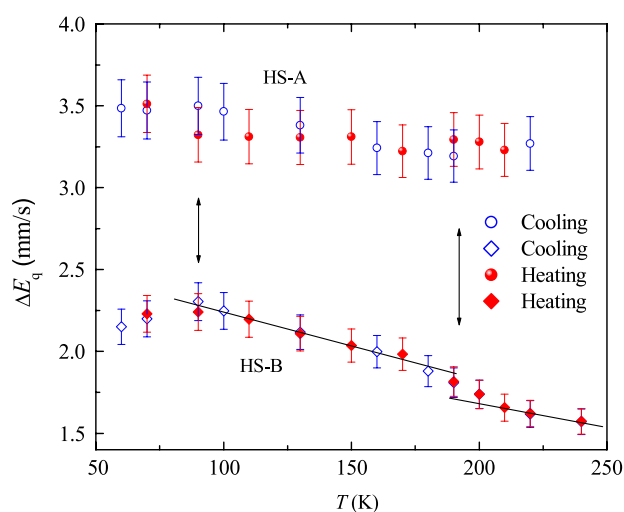


Figure 4. Thermal variation of the quadrupole splitting of the high-spin doublets obtained from Mössbauer measurements of $[\text{Fe}(\text{II})(\text{isoxazole})_6](\text{BF}_4)_2$.

The least-square fitted quadrupole splitting (ΔE_Q) and isomer shift (δ) values (relative to α -iron) were obtained at all the measuring temperatures. Figure 4 shows the temperature variation of ΔE_Q values for the two high-spin Fe(II) sites. The $\Delta E_Q(T)$ plot for HS-A deviates from linearity around two temperatures in the vicinity of the spin transition temperatures detected in figure 3. On the other hand, the $\Delta E_Q(T)$ plot for HS-B shows a very gradual variation with change of temperature. From figure 3 it is interesting to note that only the HS-A site of Fe(II) undergoes the spin transition, whereas the HS-B remains unaffected in the whole temperature region, which is also reflected in the $\Delta E_Q(T)$ variation (figure 4). No significant anomaly in the $\Delta E_Q(T)$ plot for LS has been detected in the whole temperature range. The ΔE_Q and δ values are strikingly different from those reported in an earlier communication on Mössbauer spectroscopic study of this compound at 188 and 233 K [3]. One quadrupole doublet for HS Fe(II) and one singlet due to LS Fe(II) were resolved both at 233 and 188 K. (At 233 K, ΔE_Q (HS) = 1.36(6), δ (HS) = 1.30(4), δ (LS) = 0.66(4); at 188 K, ΔE_Q (HS) = 1.75(6), δ (HS) = 1.35(4), δ (LS) = 0.70(3)). Presumably these differences might have originated from the differences in synthesis of the title compound.

Recalling the x-ray crystal structure of $[\text{Fe}(\text{II})(\text{isoxazole})_6](\text{BF}_4)_2$, the unit cell contains three $[\text{Fe}(\text{isoxazole})_6]^{2+}$ entities comprising two unique iron sites, Fe1 and Fe2 (equivalent to HS-B and HS-A, respectively in the present case) at 240 K is indeed 32:65 \approx 1:2 along with \sim 30% LS Fe(II) sites. The crystal structure at 130 K could be elucidated in the lower-symmetry space group $P\bar{1}$, albeit still revealing the presence of two crystallographically independent Fe(II) sites, Fe1 and Fe2, in a 1:2 ratio. In this instance, the Fe1–N distances average 2.169 Å, whereas the average Fe2–N distances are 1.977 Å. The corresponding Mössbauer data recorded at 130 K in the intermediate plateau reveal that the site population ratio of HS-A, HS-B and LS Fe(II) is found to be 2:1:4, whereas at 60 K this becomes 0.11:2:9, indicating an almost complete conversion of HS-A Fe(II) to the LS state. The present Mössbauer spectroscopic study successfully detects the two-step spin transition phenomenon occurring in this compound, where only the HS-A Fe(II) site takes part in the spin transition process and not the HS-B Fe(II) site. Now the question arises—how does the same HS-A Fe(II) site undergo two spin transitions at two different temperatures separated by \sim 100 K? Either 50% of the Fe(II) at

HS-A site undergoes spin transition at each step of the spin transition curve, or there may be two slightly different HS Fe(II) sites instead of a uniquely defined HS-A site, favoring a two-step spin transition at two different temperatures. To discuss this problem we next consider some distinctive cases of one- or two-step spin transitions occurring in Fe(II) spin transition compounds.

The mono-nuclear $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$ (2-pic = 2-aminomethylpyridine = 2-picolylamine) undergoes two first-order phase transitions on cooling from an HS phase via an intermediate phase to an LS phase, where the HS and LS phases are isostructural [10]. This reveals that the intermediate plateau observed in the two-step spin transition of this mononuclear compound is due to two crystallographically different iron sites. However, $\{\text{Fe}[\text{HC}(\text{3,5-Me}_2\text{pz})_3]_2\}(\text{BF}_4)_2$ with tris(pyrazoly) methane ligands has one crystallographically unique Fe(II) site at 220 K; 50% of Fe(II) undergoes LS \leftrightarrow HS transition at 206 K and 50% of the Fe(II) sites remain in the HS state down to 10 K [11]. In this case, the crystal system changes from monoclinic to primitive triclinic with $Z = 2$ (i.e. yielding two crystallographically independent Fe(II) sites) along with a shortening of Fe–N bond distances for 50% of the molecules. The mononuclear $[\text{Fe}(\text{5-NO}_2\text{-sal-N}(1,4,7,10))](\text{5NO}_2\text{-sal-N}(1,4,7,10)\text{H}_2 = \text{bis}(5\text{-nitrosalicylidene})\text{triethylenetetramine})$ compound exhibits a 1:1 two-step LS \leftrightarrow HS transition associated with two structural phase transitions [12].

Magnetic studies of the dinuclear compound $[\text{Fe}(\text{bpym})(\text{NCSe})_2]_2\text{bpym}$ (bpym = 2,2'-bipyrimidine) report that at 300 K two Fe(II) ions are in the high-spin state and $\sim 60\%$ of them undergo a smooth spin transition around 235 K [13]. The remaining dinuclear units do not take part in spin transition in the whole temperature range. However, no structural information on this compound is available. On the other hand, $[\text{Fe}(\text{btr})_3](\text{ClO}_4)_2$ (btr = 4'-bis-1,2,4-triazole) having two identical Fe(II) sites exhibits a complete exactly 1:1 two-step LS \leftrightarrow HS transition, though the crystal system remains the same throughout the spin transition process [14], whereas the compound $[\text{Fe}(\text{btzb})_3](\text{PF}_6)_2$, (btzb = 1,4-bis(tetrazol-1-yl)butane) with one crystallographically independent Fe(II) site exhibits a sharp two-step spin transition behavior between 164 and 182 K with $T_{1/2} = 174$ K [15]. The occurrence of two slightly different Fe(II) sites is believed to be the reason for the spin transition, as Mössbauer spectroscopy could detect two different HS Fe(II) sites in the former [14], whereas in contrast two distinguishable HS Fe(II) sites could not be observed in the latter [15]. The thermodynamic stabilization of an alternating ordering of the HS and the LS Fe(II) sites around T_{SCO} has been held responsible for this two-step spin transition in the $[\text{Fe}(\text{btzb})_3](\text{PF}_6)_2$ system. The dinuclear iron(II) complex $[\text{Fe}(\text{bt})(\text{NCS})_2]_2\text{bpym}$ (bt = 2,2'-bithiazoline; bpym = 2,2'-bipyrimidine) [9] exhibits a two-step LS \leftrightarrow HS transition, although the sample contained a single structural phase; and intra- and intermolecular processes were held responsible for the spin transition taking place in two steps, (LS, LS) \leftrightarrow (LS, HS) and (LS, HS) \leftrightarrow (HS, HS). Here the two-step transition by the isostructural Fe(II) site is considered to be due to the synergistic effect of intramolecular interactions favoring (LS, HS) pairs and intermolecular interactions favoring (HS, HS) and (LS, LS) pairs. In the trinuclear triazole compound $[\text{Fe}(\text{4-Etr})_2(\text{H}_2\text{O})_2]_3(\text{CF}_3\text{SO}_3)_6$ (4-Etr = 4-ethyl-1,2,4-triazole), only the central Fe(II) atom undergoes an LS \leftrightarrow HS transition near 203 K, which corresponds to a change to the LS state for one-third of the iron ions [16]. Mössbauer spectroscopy of this compound has detected two doublets in the ratio 1:2, corresponding to two HS Fe(II) sites at 300 K, where the comparatively low-intensity doublet changes into a singlet corresponding to low-spin Fe(II) at 150 K, though the structure at this temperature is essentially similar to that at 300 K. In comparison to these one- or two-step spin transitions in Fe(II) compounds having one, two, or three crystallographically inequivalent HS Fe(II) sites at high temperatures, the present mononuclear compound having two Fe(II) sites exhibits an LS \leftrightarrow HS transition in two steps (at 92 and at 191 K) that is only due to

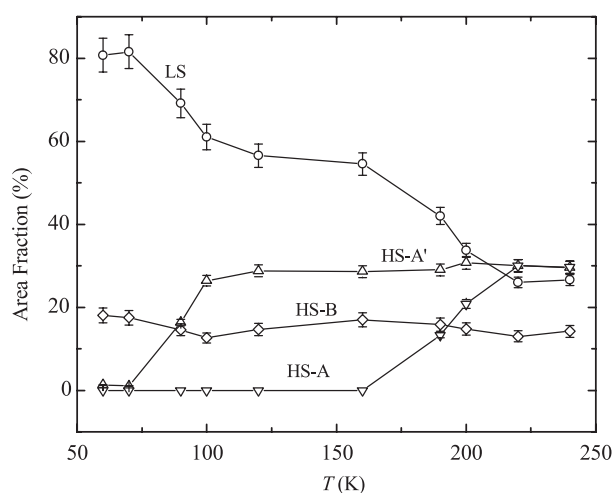


Figure 5. Thermal variation of the area fraction of the quadrupole doublets in the Mössbauer spectra for different Fe(II) spin sites in $[\text{Fe}(\text{II})(\text{isoxazole})_6](\text{BF}_4)_2$ during cooling after modified analysis.

one HS Fe(II) site, while interestingly the other HS Fe(II) site does not take part in the spin transition.

Thus, in view of the above spin transition phenomena, the following two possibilities can be considered for the two-step $\text{LS} \leftrightarrow \text{HS}$ transition occurring in the present compound. Firstly, the title compound may be crystallographically isostructural in the high- and low-temperature phases, giving rise to an intermediate phase corresponding to the plateau at intermediate temperatures. Secondly, there exist three Fe(II) HS sites in this compound at the highest temperatures, among which two are in a nearly equal coordination environment. An XRD study also predicts such a possibility [5]. Any discussion according to case (i) will require the crystal structure information at the lowest temperatures. It should be noted that the temperatures at which the structures of the present compound were solved correspond to two different phases (high temperature and intermediate) of the spin transition curve, but the nature of the structure at the lowest phase of the spin transition curve is unknown. The lack of structural information of the present compound at low temperatures does not allow us to give any further explanation along this direction. Thus, an analysis of the observed Mössbauer spectra is used to explain the results in view of the second possibility, presuming the title compound has three different Fe(II) HS sites—HS-A, HS-A' and HS-B, with HS-A and HS-A' being in nearly equal coordination environment at the highest temperatures of study.

The observed Mössbauer spectra at 240 K are now resolved into three HS quadrupole doublets and one LS quadrupole doublet with isomer shift values (with respect to α -iron) 0.99, 0.93, 0.96 and 0.39 mm s^{-1} and quadrupole splitting values 2.70, 1.29, 1.66 and 0.24 mm s^{-1} for HS-A, HS-A', HS-B and LS Fe(II), respectively. As the population ratio of HS-B and combined HS-A and HS-A' sites in the unit cell is 1:2 from the x-ray study [5], we tentatively assign equal population to HS-A and HS-A' sites at this temperature. Under this scheme we find the area ratio of HS-A, HS-A', HS-B, LS Fe(II) at 240 K to be 15:15:7:13. We have adopted the same reasoning for resolving the Mössbauer spectra obtained at all other temperatures. Figure 5 shows the temperature variation of the area fractions corresponding to different doublets thus obtained in the cooling direction. This figure clearly shows that HS-A undergoes the complete $\text{LS} \leftrightarrow \text{HS}$ transition at ~ 191 K, while HS-A' remains in the HS state till ~ 92 K, beyond

which it starts to undergo a complete transition to the LS state, giving rise to a two-step spin transition process. However, it is not possible to distinguish the two different LS doublets. In the whole temperature range of study (240–60 K) the area fraction of the HS-B doublet varies only by 5%. Similar temperature variations of the area fractions for HS-A, HS-A', HS-B and LS Fe(II) were observed during heating. The spin transition curve obtained under this new analysis is essentially the same as shown in figure 3(b). This new analysis successfully explains the temperature-dependent evolution of different Fe(II) sites giving rise to two steps in the spin transition process. A small difference in the coordination sphere of HS-A and HS-A' can give rise to this two-step spin transition process, although the XRD at 260 and 130 K was not able to detect this. Perhaps these two Fe(II) sites are structurally very similar. Similar observations are made for $[\text{Fe}(\text{btr})_3](\text{ClO}_4)_2$, that has two identical Fe(II) sites in the unit cell [14]. However, a slight difference between the Fe(II) sites due to the interactions between these sites and the non-coordinated perchlorate anions through the weak Fe–N–C–H \cdots ClO $_4^-$ and Fe–N–N–H \cdots ClO $_4^-$ hydrogen bonding contacts is ascribed to the origin of the two-step spin transition process. The two-step spin transition in the present case may be of a similar origin.

4. Conclusion

The present variable-temperature Mössbauer spectroscopic study of the mononuclear spin crossover compound $[\text{Fe}(\text{II})(\text{isoxazole})_6](\text{BF}_4)_2$ exhibits a temperature-dependent two-step spin crossover transition phenomenon. Analysis of the Mössbauer spectra and the crystallographic information reveals that one Fe(II) site undergoes spin transition in two steps separated by ~ 100 K, while the other Fe(II) site remains non-active in the whole temperature range. To understand the origin of the two steps, the spectra were reanalyzed on the basis of three different Fe(II) sites. This analysis satisfactorily describes the spin transition curve and holds the two slightly different spin sites responsible for the origin of the two steps. The possibility of existence of similar structures in the high- and low-temperature phases along with an intermediate structure in the intermediate-temperature range has been discussed as another viable origin of the two-step spin transition. However, this possibility can only be verified with temperature-dependent crystal structure determination down to the region of complete spin transition. The present Mössbauer spectroscopic study has certainly shed new light on the mechanism of thermal spin crossover in a system with complex interplay of temperature-dependent spin transition and structural rearrangements.

Acknowledgments

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