EXAFS and thermodynamics of Fe(II) spin transition polymeric compounds

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We have studied the temperature variations of the EXAFS spectra of three Fe(II)/triazole-based spin transition polymeric compounds compared to a monomer belonging to the same family. These compounds have various temperatures of transition and hysteresis loop widths. In the three polymers, the Fe-Fe-Fe alignment, detected by a multiple scattering signal at the double Fe-Fe distance, is preserved through the spin transition. For the four compounds, we have studied the variations versus temperature of the Debye-Waller factors for both FeN_6 (first shell) and Fe-Fe-Fe (multiple scattering path, only for the polymers). We report a strong increase of $\sigma^2(FeN_6)$ through the spin transition for the monomer and two of the polymeric species. For the polymers an increase of σ^2(Fe-Fe-Fe) is also observed. These observations confirm the results available in the literature, and we confirm the interpretation as an increase of the vibrational part of the DW. For one particular polymer, we observe an unexpected behaviour: no significant increase of the Debye-Waller factor from low spin to high spin states. The EXAFS study of these non mono-crystalline species is the only way to discuss the local structure-thermodynamics properties relationships, and particularly the so-called cooperative effect in the spin transition process.

Keywords: spin transition, polymeric triazoles, EXAFS Debye-Waller factors, multiple scattering focusing effect

1. Introduction

Polymeric Fe(II) triazole spin transition (ST) compounds are intensively studied for their strong cooperative behaviour with an abrupt ST and a large thermal hysteresis loop across their thermal and optical transition leading to promising industrial applications for imaging and memory devices. It has been impossible to grow any single crystal of this series of compounds and we have used an exceptionally intense multiple scattering EXAFS signal as the signature of an alignment of the Fe(II) ions in the polymeric chain (Michalowicz, 1995, 1997, 1999), (Garcia, 1997), (Van Koningsbruggen, 2000), as described on figure 1.
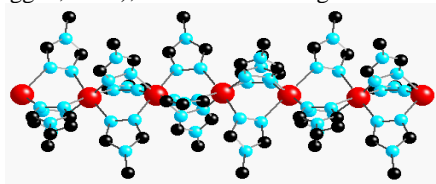

Figure 1
Linear structure of Fe(II)-triazole polymeric spin transition compounds.

The general formula of this family is $[Fe(\alpha trz)_3](cti)_x.nH_2O$ where αtrz is a triazole (or a tetrazole) ligand, and cti a counter ion. The thermodynamic properties of the related compound depend strongly on the residues attached to the ligand, the nature of the counter ions, and the number of water molecules. The spin transition temperature $T_{1/2}$ can vary from less than 100 to 400 K and the hysteresis loop width ΔT from less than 5 K to more than 50 K. In general the hysteresis loop is larger for polymers than for monomers. This property is attributed to the better connectivity between Fe(II) centres in polymers which enhances the cooperativity of the ST. For most compounds of this family, the lowest $T_{1/2}$ corresponds to the smallest ΔT. This applies for example to $[Fe(Htrz)_2(trz)]BF_4$ ($T_{1/2}\uparrow = 375K$, $T_{1/2}\downarrow = 335K$, $\Delta T = 40K$) (named **1A**) or $[Fe(hyptrz)_3](4Cl-ps)_2.H_2O$ (Garcia, 1999) ($T_{1/2}\uparrow = 174K$, $T_{1/2}\downarrow = 172K$, $\Delta T = 2K$) (Garcia, 1999) (named **POH.1H$_2$O**). $[Fe(hyptrz)_3](4Cl-3NO_2ps)_2.2H_2O$ (named **POH.2H$_2$O**) (Garcia, 1999) is exceptional since its hysteresis loop is the largest ever found ($\Delta T = 48K$) for such a low temperature ST ($T_{1/2}\uparrow = 168K$, $T_{1/2}\downarrow = 120K$). The strong cooperativity of these spin transitions and its relationship with the structural behaviour of these derivatives are still a subject of intense discussions. For $[Fe(ptz)_6]$ $(BF_4)_2$, a monomeric derivative ($T_{1/2} \sim 130K$, $\Delta T = 7K$) (called **ptz6**), the cooperativity is explained by a significant structural change of the crystal lattice detected by X-Ray diffraction (Wiehl, 1996). It has been suggested that strong cooperative ST cannot occur without crystal lattice changes. In polymeric derivatives, such a change should imply a significant modification of the Fe-Fe-Fe alignment, as suggested by an X-Ray scattering study on **1A** (Verelst, 1998). This point is the first goal of this work. The thermodynamics of these compounds is now well established (Kahn, 1993). The most commonly driving force invoked to explain the cooperative behaviour is the vibrational entropy. EXAFS Debye-Waller factors are suitable parameters to study partial vibrational entropy terms. DW variation versus temperature and across the spin transitions is the second important goal of this study.

2. Materials and Methods

EXAFS spectra of the three polymers (**1A**, **POH1.1H$_2$O** and **POH.2H$_2$O**) and the monomer **ptz6** were recorded at LURE-DCI on the EXAFS13 port, in transmission mode. The samples were prepared as homogeneous compressed pellets of about 50mg of pure product. The spin states of the compounds were checked optically before EXAFS measurement since compression of the pellets can alter the thermodynamic properties. EXAFS data reduction and modelling was performed with the standard package "EXAFS pour le Mac" (Michalowicz, 1997). Fourier transforms of $k^3\chi(k)$ are calculated in the range 2-13 Å^{-1}. Fourier filtered FeN_6 and Fe-Fe-Fe shells were fitted either with FEFF or experimentally extracted phases and amplitudes, from **1A** spectrum at the lowest temperature (40K). Fitting Fourier filtered spectra is not the most accurate method to get absolute numbers, but in this work our purpose is to follow the *relative* variations of the Debye-Waller versus temperature. For the FeN_6 shell, σ^2 represents the actual Fe-N bond vibrational Debye-Waller factor, whereas the vibrational study of the Fe-Fe-Fe signal is more complicated, including longitudinal and transversal vibrations. Consequently, the effective Fe-Fe-Fe Debye-Waller study reported in this work is only qualitative and deserves to be re-examined in a future study of the vibrational modes of such systems. In most cases fits could be done on single shells. When the transition is not complete, a mixing of two Fe-N or Fe-Fe distances is necessary. In this case the ratio of coordination numbers for the two states is deduced from Mossbauer

measurements (Garcia, 1999) and fixed in the EXAFS fit in order to avoid correlation between number of neighbours and Debye-Waller, which dramatically alter the accuracy of two shells fittings (Van Koningsbruggen, 2000). Error bars were evaluated following the Standard and Criteria committee recommendations.

3. Results and Discussion

EXAFS spectra and Fourier Transforms of typical octahedral Fe(II)-triazole and tetrazole complexes in both Low Spin (LS) and High Spin (HS) states has been already published (Erenburg, 1999), including FEFF multiple scattering calculation for the triazole rings (Yokoyama, 1998) and even for the Fe-Fe-Fe alignment (Michalowicz, 1995, 1997, 1999), (Garcia, 1997), (Van Koningsbruggen, 2000). They concluded that the multiple scattering peak at 7 Å is a suitable signature of the Fe-Fe-Fe alignment in the polymeric series. They also concluded that the single scattering path Fe-Fe cannot be directly extracted since it is largely overlapping with strong multiple scattering signals from C and N belonging to the triazole rings. Figure 2 represents the FT modulus of **1A**, **POH.1H$_2$O, POH.2H$_2$O and ptz6**, in both LS and HS states. The temperatures of these spectra are chosen as close as possible in the two spin states. For compounds having a very abrupt transition and a large hysteresis loop (**1A, POH.2H$_2$O**) it was possible to present both states at the same temperature. For **1A, and ptz6** the transition is complete for both temperatures. On the contrary, the two **POH** compounds are not completely Low Spin, even at 40K. However, it has been shown by Mossbauer spectroscopy that the LS/HS ration is greater than 75 % in the worse case (Garcia 1999).
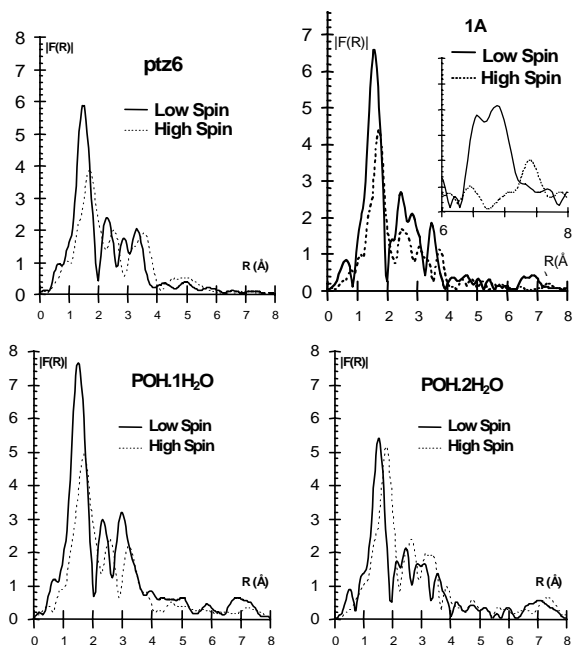

Figure 2
Fourier transform modulus of **ptz6, 1A, POH.1H$_2$O and POH.2H$_2$O** in both Low Spin and High Spin states

The LS->HS spin transition is detected for the four compounds by the shift of all the structures. The dilatation is about 0.19 Å for the first Fe-N distance. This shift is standard for Fe(II)-nitrogen ligands spin transition. In all the fits, the first Fe-N distance was found to be 1.99(2) Å (LS state) and 2.17(2) Å in the HS state. The multiple scattering peak at 7 Å, characteristic of the double Fe-Fe distance and assigned to the signature of the metallic centres alignment is totally absent in the spectrum of the

monomer **ptz6**, as expected. On the contrary it is observable on all the polymer spectra, for both spin states. In the case of **1A** the presence of this alignment signature for HS state was considered as doubtful in previous publications (Michalowicz, 1995, 1997, 1999). The zoom of the 7Å region in this spectrum (figure 2) shows that the peak is there, although its amplitude has significantly decreased. On this new measurement, recorded especially to improve the signal/noise ratio, the Fe-Fe-Fe multiple scattering signal appears definitely above the noise level. The FT modulus of **ptz6** in figure 2 illustrate the overlap between Fe-Fe single scattering signal and triazole ring multiple scattering contributions, which are present around 3-4 Å even for a monomer. For the two POH samples, which undergo their spin transition at low temperature, the Fe-Fe-Fe alignment is clearly established, even in high spin state. This result was already published for **POH.2H$_2$O** (Michalowicz, 1999) and by other groups (Yokoyama, 1998). For **1A** the important decrease of the Fe-Fe-Fe peak in the HS state as been attributed either to an increase of its thermal vibration Debye-Waller factor or to a drastic change of the structure from alignment in the LS state to a twisted linear chain for HS. A FEFF simulation of the Fe-Fe-Fe multiple scattering signal versus the bending angle is presented in figure 3. For θ=5° the FT amplitude reduction is greater than the experimentally observed one.
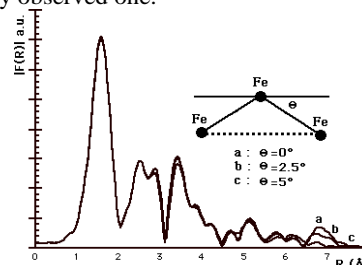

Figure3
FEFF calculation of the amplitude reduction for the Fe-Fe-Fe multiple scattering path versus the bending angle θ.

We can say now that, even for **1A** the amplitude reduction of the Fe-Fe-Fe signal is due essentially to an increase of the thermal vibration rather than a change in the structural alignment, which remains for the high spin state. It is normal to observe a greater reduction for **1A**: its spin transition occurs near 360K whereas the ST occurs near 130 K for the other samples.

We must underline that this result is in contradiction with the assumption of a necessary change of the metallic centres lattice for cooperative spin transitions. Apparently such structural changes are necessary only on monomeric compounds, because their metal-metal interactions are weak. In the case of strongly interacting metallic centres, like the polymers of the present study, cooperative transitions can occur without a significant change of the metal-metal alignment.

The spin transition cannot lead to any change in coordination numbers. In all the presented samples the Fe(II) site is a nitrogen octahedron in the two spin states. Moreover, in polymeric samples each Fe(II) ion is always surrounded by two neighbouring Fe(II) complexes. Thus, amplitude variations are related to a change in the corresponding Debye-Waller factors. Figure 2 gives a qualitative analysis of the amplitude reduction corresponding to a Debye-Waller increase from Low Spin to High Spin state: there is a significant increase of σ^2 for **ptz6, 1A, POH.1H$_2$O**, whereas the Debye-Waller of **POH.2H$_2$O** do not seem to undergo any detectable change through the transition. We have chosen to focus our study to the first FeN$_6$ shell for the four samples, and the Fe-Fe-Fe multiple scattering signal for the polymers. FeN$_6$ first shell Debye-Waller versus temperature

curves through spin crossover transitions have been already published by other authors on similar compounds, either monomeric (Lübbers, 1997) or polymeric (Yokoyama, 1998). Figure 4a represent these DW variations for **1A** and **POH.2H$_2$O**. In addition the Debye-Waller thermal behaviour of the Fe-Fe-Fe signal is also displayed (figure 4b). Several temperatures have been measured in both spin states within the bistable domains in order to follow the hysteresis loops.
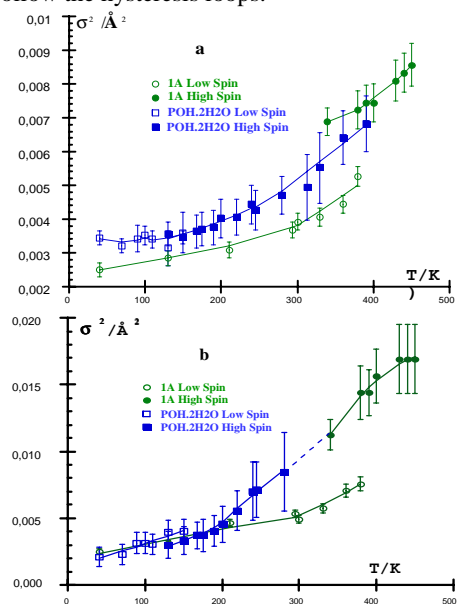

Figure 4
Debye-Waller factors vs T for **1A** and **POH.2H$_2$O** a)FeN$_6$ b)Fe-Fe-Fe

Our results for the polymers **1A** confirm the earlier studies: the Debye-Waller factors undergo a strong and abrupt increase in the ST. This applies for both the FeN$_6$ and the Fe-Fe-Fe signals. The result obtained for **POH.2H$_2$O** is unexpected: for both EXAFS signals **there is no change of σ^2** although this spin transition is abrupt and the hysteresis loop exceptionally large. We remark on figure 4a that the FeN$_6$ Debye-Waller of **POH.2H$_2$O** is larger than for **1A** in the low spin state. The slope of its variation versus T is also larger. This is a quantitative confirmation of the FT amplitude observation on figure 2 : **POH.2H$_2$O** FT amplitude does not vary through the transition but it is significantly weaker than for the three other compounds in the low spin state.

The thermal behaviour of the Fe-Fe-Fe Debye-Waller is similar, except that before the LS->HS transition all the σ^2 values are identical, within the error bars. As proposed by Yokoyama (1998), we tried to fit these $\sigma^2(T)$ curves with the thermal vibration Einstein model :

$$\sigma^2 = \frac{A}{\theta} \coth\left(\frac{\theta}{2T}\right) + \sigma_0^2 \text{ with } \theta = \frac{h\omega}{2\pi k_B}$$

The results are displayed in table 1.

	Θ Low Spin /K	Θ High Spin /K
FeN$_6$ **1A**	439	331
FeN$_6$ **POH.2H$_2$O**	373	373
Fe-Fe-Fe **1A**	260	170
Fe-Fe-Fe **POH.2H$_2$O**	200	200

Table 1
Einstein temperatures for the FeN$_6$ and Fe-Fe-Fe vibrations modes of **1A** and **POH**.**2H$_2$O.**

Theses values are similar to those previously published (Yokoyama, 1998) and coherent with the curves of figure 4

smaller Θ value means weaker bound, greater σ^2 and larger variation slope. These Θ values were obtained assuming that σ_0^2 variation (representing the static distortion of the Fe site, induced by the static Jahn-teller effect in the High Spin state of Fe^{2+}) is negligible. We were unable to estimate Θ error bars since this parameter is highly correlated with parameters A and σ_0^2. This is why such an EXAFS Debye-Waller study must be compared to vibrational spectroscopy (IR and Raman) results previous to any definite interpretation (in progress for the compounds presented in this work).

The statistical thermodynamic theory of spin transition in polymeric Fe(II) compounds invoke the volume dilatation and the rigidity of the lattice (Spiering, 1998). The lattice volume is related to Fe-N and Fe-Fe distances and the rigidity to the corresponding Debye-Waller factors. The volume dilatation seems to be identical for the four compounds presented here. Their difference lies in the rigidity: **1A** is more rigid than **POH.2H$_2$O** and keeps its rigidity up to the spin transition at 380 K, where it undergoes an abrupt decrease (figure 4a). On the contrary the rigidity of **POH.2H$_2$O** decreases more rapidly, but without any change in the spin transition region (130K) although it's exceptional cooperative character.

4. Conclusion

The linear structure and the rigidity of the polymeric lattice of three different Fe(II)-triazole spin transition polymers were respectively characterised by the EXAFS Fe-Fe-Fe multiple scattering signal and the variations of the FeN$_6$ and Fe-Fe-Fe Debye-Waller factors versus T. It has been shown that the three polymers undergo their spin transitions without any measurable loss of the linearity of the chain. The Debye-Waller factors of almost all the spin transition compounds increase significantly in the transition, except in the case of **POH.2H$_2$O** whose thermodynamic and structural properties revealed exceptional behaviour. These results disagree with previous assumptions, based on an analogy with monomeric species.

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This work is dedicated to the memory of Professor Olivier Kahn