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Polymeric spin transition compounds: EXAFS and thermal behaviour

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The structures of large thermal hysteresis Fe(II) polymeric spin transition compounds have been studied by EXAFS. The assumption that a peak at 7 Å can be assigned to a multiple scattering double metal-metal distance in an aligned polymeric structure is confirmed. For the first time, such an aligned structure was observed on High Spin (HS) compound of the family. A qualitative study of the thermal variation of this multiple scattering peak was performed. The correlation between this thermal behaviour, due to variations in the vibrational entropy, and the electronic structure of the metallic ions is discussed.

Keywords : inorganic polymers, spin transition, EXAFS structure, multiple scattering

1. Introduction

Polymeric Fe(II) triazole spin transition compounds are intensively studied for their strong cooperative behaviour with 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 and 1997). In these papers we have proved, either by FEFF modeling or by studying spectra of monomeric analogs, that multiple scattering paths involving light atoms from the cyclic ligands cannot interfere or are negligible at the distance of this multiple scattering Fe-Fe-Fe signal. More recently the L.S.M. team have succeeded in growing single crystals of a Cu(II) analog of the polymeric Fe(II) triazole family and solved the structure (Garcia, 1997) (figure I).

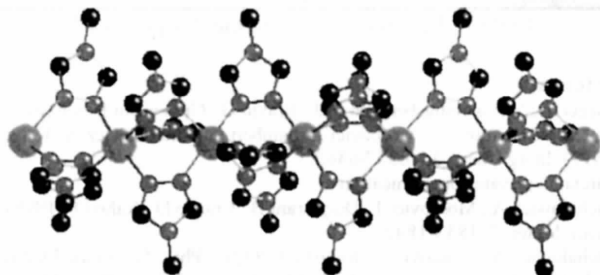


Figure I. Crystal structure of Catena[μ -Tris(4(2'-Hydroxy-Ethyl)-1,2,3,4-Triazole-N1,N2)Copper(II) bis (Perchlorate) trihydrate (ligand simplified for clarity)

Although the Cu(II) derivative does not show any spin transition, its crystal structure was very useful to realize a complete FEFF model which definitely proved the assignment of the so-called « 7 Å peak » as the multiple scattering signature of a metal chain alignment with a first metal-metal distance between 3 and 4 Å.

2. Structure of the Fe(II) polymeric species in the High Spin state.

In our earlier publications (Michalowicz, 1995 and 1997), the EXAFS spectra of the High Spin states of the polymers were only recorded on compounds with a transition temperature above 350 K. In these cases the metal alignment signature was never observed clearly. Such an absence of multiple scattering signal could be due to i) a drastic change in the molecular structure of the polymer, from an alignment to a « zig-zag » structure, as proposed for [Fe(Htrz)₂(trz)]BF₄ (noted 1A) (Verlest, 1998), ii) to an drastic increase of the thermal Debye-Waller factor, the average alignment remaining.

The EXAFS Fourier transform spectra of [Fe(hyprtz)₃](A)₂·2H₂O with hyprtz = 4-(3'-hydroxypropyl)-1,2,4-triazole and A = 4-chloro-3-nitrophenylsulfonate (noted POH) is shown in figure 2. The spin transition temperatures of this compound are T_c(up)=168K, T_c(down)=120K. It was possible to record the spectrum of the High Spin state of a compounds in this polymeric series at a quite low temperature (150 K). Moreover, the spectrum was recorded in the low-spin (LS) state at 130 K, inside the hysteresis loop.

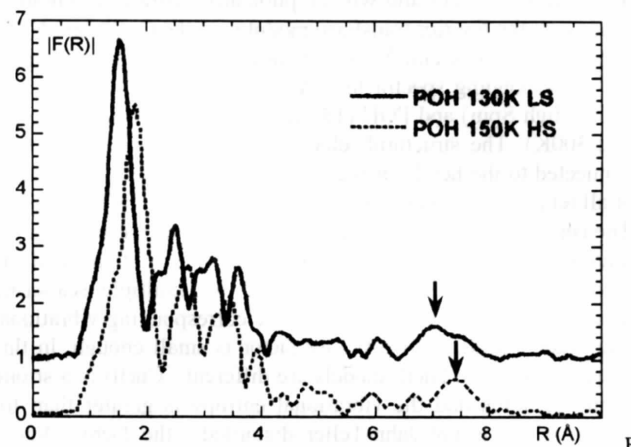


Figure 2 : FT of POH in the High Spin and Low Spin states

The fits of the Fourier filtered first shell (6 nitrogens) are given in table 1 for POH at 130K in Low Spin state and 150K in the High Spin state. The main results of these fits are :

i) In the Low Spin state there is a small amount of High Spin remaining since the best fit is obtained with two Fe-N distances, 1.98 Å characteristic of LS Fe(II), and 2.18 Å for the HS state. This mixing is confirmed by the magnetic susceptibility measurements (Garcia).

ii) In the High Spin state, we tried to fit with some short Fe-N distance and found that the LS→HS transition is almost complete. The site is composed of 6 N at 2.17 Å with a Debye Waller significantly greater than for the LS state, reflecting a measurable distortion of the octaedron. Such a rhombic local distortion is characteristic of the Jahn Teller effect expected for a High Spin d⁶ Fe(II) compound.

	N	s (Å)	R (Å)	DEo(eV)	χ^2_{ν}
POH LS 130K (one shell fit)	6 (fixed)	0.078(10)	1.97(1)	-9.0(3)	0.4

POH LS 130K (two shells fit)	5.2(1.2) 1.5(2.2)	0.068(12) 0.06(4)	1.98(2) 2.18(3)	-5.5(3.0) "	0.1
POH HS 150K (one shell fit)	6 (fixed)	0.076(1)	2.17(1)	0.0(7)	0.25

Table 1 : Fitting results for POH in Low Spin and High Spin states

Thus, the 7 Å peak observed for the High Spin state of **POH** is characteristic of a Fe-Fe-Fe alignment, observed for the first time in a HS polymeric Fe(II) triazole. Although the Fe(II) site behaves a local Jahn Teller distortion, the metal alignment is not drastically modified. This result obtained for **POH**, with a low T_c does not confirm the « zig-zag » model proposed for High Spin **1A** (Verlest, 1998). On the contrary we confirm what we have already observed by single crystal diffraction on the copper derivative (Garcia, 1997) : a local Jahn-Teller distortion may be present together with an aligned metallic long chain, and the corresponding EXAFS multiple scattering signal which is observed at low temperature, can vanish just by an increase of its Debye-Waller factor.

3. Thermal behaviour of the multiple scattering 7 Å peak.

In this section we compare the thermal behaviour of **1A**, **POH** and the Cu(II) or Ni(II) compounds EXAFS structures. For this short paper, we have reported only the properties of the 7 Å peak at a few temperatures.

The analysis is strictly qualitative : is the Fe-Fe-Fe multiple scattering signal clearly visible or not ? A complete thermodynamic study of the whole spectra with quantitative fits are in development and will be published elsewhere. Figure 3 represents the Fourier transform modulus of the Cu(II) and Ni(II) derivatives at 30K and 300K. On figure 4 we have represented the corresponding spectra for **1A** (300K, 380 K Low Spin and 380K High Spin) and **POH** (130 K Low Spin, 150 K High Spin and 300K). The structural, electronic and magnetic properties, connected to the height of the 7Å peak, for all these compounds at all temperatures and spin states are gathered in table 2.

The conclusion of this study is that all these polymeric inorganic materials have a metal alignment. This alignment is observable in the EXAFS spectra by the multiple scattering double metal-metal distance when the corresponding vibrational amplitude and the Debye-Waller factor is small enough. In this respect Cu(II) and Ni(II) models are different : Cu(II) is a strong Jahn-Teller ion and the vibrational entropy is greater than for Ni(II), which is not Jahn-Teller distorted : the Debye-Waller factor increases much more rapidly versus T for the Cu(II) compound than for the Ni(II) one. It is now possible to understand why the Fe-Fe-Fe alignment of the High Spin species was not observable for **1A** (380 K), and on the contrary visible for **POH** (150->300K) :

For Fe(II), it is well known that the Low Spin state is a regular octahedron, with no static and dynamic Jahn Teller effect. For the Low Spin state, the vibrations are the less sensitive to the temperature and the vibrational entropy is low, as in the Ni(II) model : the Fe-Fe-Fe peak is observed even at 380 K.

On the contrary, for the High Spin state of Fe(II), which is much similar to the Cu(II) model, the vibrational amplitudes are much sensitive to temperature variations and the Fe-Fe-Fe peak can be observed at low temperature, but not above room temperature.

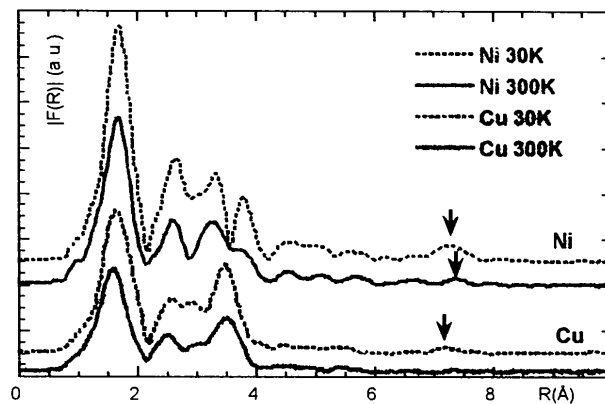


Figure 3 : FT of model polymers

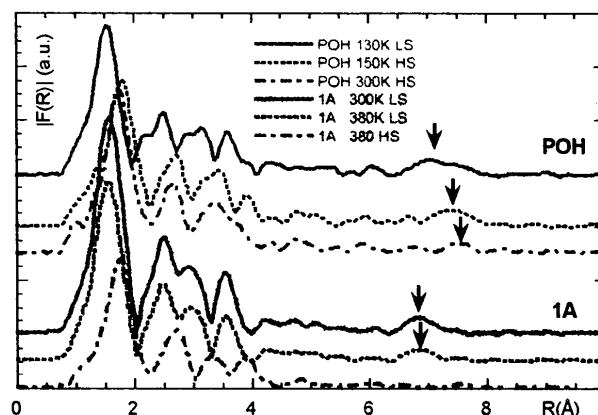


Figure 4 FT of POH and 1A

Compound	Properties	7 Å peak observed ?
Cu(II) 30 K model compound	3d ⁹ S=1/2 . No spin transition Jahn Teller distorted octahedron	Yes, medium
Cu(II) 300 K model compound	3d ⁹ S=1/2 . No spin transition Jahn Teller distorted octahedron	No
Ni(II) 30 K model compound	3d ⁸ S=1/2 . No spin transition Regular octahedron	Yes, strong
Ni(II) 300 K model compound	3d ⁸ S=1/2 . No spin transition Regular octahedron	Yes, low
Fe(II) 1A 300K S=0 Low Spin	3d ⁶ S=0 . spin transition Regular octahedron	Yes, strong
Fe(II) 1A 380K S=0 Low Spin	3d ⁶ S=0 . spin transition Regular octahedron	Yes, strong
Fe(II) 1A 380K S=0 High Spin	3d ⁶ S=2 . spin transition Jahn Teller distorted octahedron	very small
Fe(II) POH 130 K S=0 Low Spin	3d ⁶ S=0 . No spin transition Regular octahedron	Yes, strong
Fe(II) POH 150 K S=0 High Spin	3d ⁶ S=2 . spin transition Jahn Teller distorted octahedron	Yes, strong
Fe(II) POH 300 K S=0 High Spin	3d ⁶ S=2 . spin transition Jahn Teller distorted octahedron	Yes, low

Table 2 : Electronic state and the 7 Å peak vs T.

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