Structural Study by Wide-Angle X-ray Scattering of the Spin Transition Molecular Materials [Fe(Htrz)$_2$(trz)](BF$_4$) and [Fe(NH$_2$trz)$_3$](NO$_3$)$_2$ (Htrz = 1,2,4-4H-Triazole, trz = 1,2,4-Triazolato)

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A precise structural study by wide-angle X-ray scattering (WAXS) has been carried out on two spin transition materials: [Fe(Htrz)$_2$(trz)](BF$_4$) (**1**) and [Fe(NH$_2$trz)$_3$](NO$_3$)$_2$ (**2**), with Htrz = 1,2,4-4H-triazole, trz = 1,2,4-triazolato, and NH$_2$trz = 4-amino-1,2,4-triazole, both at room temperature in the low-spin state (LS) and at higher temperature in the high-spin state (HS). These compounds exhibit cooperative spin transitions between LS and HS state above room temperature with a large thermal hysteresis and a pronounced thermochromic effect. Both compounds have a polymeric chain structure where each Fe^{2+} metal ion is triply bridged to their neighbors through nitrogen atoms of the triazole or triazolato groups. In the LS state the polymeric chain is linear, whereas at higher temperature, in the HS state, the magnetic transition causes an elongation and a deformation of the chain. The chain loses its linear character. We explain this behavior by a rhombic-type distortion of the iron octahedral environment associated with the spin transition. Compound **1** presents an important interchain order in the LS state, probably due to a hydrogen-bond network connecting together linear chains through N−H···BF$_4$···H−N linkages, where the nitrogen atoms occupy the 4-position of the triazole ligands. When the spin transition occurs, the interchain long-range order vanishes. For compound **2** each polymeric chain seems to be independent from its neighbors.

Introduction

Cooperative magnetic phenomena in molecular compounds such as spin transition, or ferro- and ferrimagnetic long-range ordering have increasingly attracted the attention of chemists.[1] Indeed, it has been realized that the phenomena in the meantime raised some fundamental scientific questions and could lead to some important applications. A crucial concept associated with cooperativity is that of bistability. Molecular bistability may be defined as the property for a molecular system to exhibit two electronic states in a given range of external perturbation. Usually, one of the states is the ground state, and the other one is a metastable state. Bistability leads to the hysteresis effect, which confers a memory effect on the system. Usually, cooperative behaviors are observed for supramolecular assemblies with one-, two-, or three-dimensional polymeric structures.[2] Because the polymerization procedure is an uncontrollable fast growing mechanism, molecular polymers are very often amorphous or at least badly crystallized. Getting structural

information of such disordered materials is therefore difficult, and classical structural study by X-ray diffraction on single crystal is impossible. The EXAFS technique, which gives valuable structural information, is now widely used; however EXAFS information is restricted to the first or second coordination sphere around a central atom. Another possible technique for obtaining significant information on the structural architecture of amorphous or poorly crystallized materials is WAXS (wide-angle X-ray scattering). For more than 20 years, this technique has been used to investigate quite different materials such as silica glasses, amorphous semiconductors, or metallic oxides.[3] Provided careful data collection and reduction procedures are performed, WAXS can be used as an almost routine technique providing useful structural information on short and medium range order up to 20 Å. However, WAXS studies on molecular materials including large units[4] were rarely performed because of modeling difficulties of such compounds. But recent progresses on molecular

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⊗ Abstract published in *Advance ACS Abstracts,* November 15, 1997.
(1) Kahn, O.; Launay, J. P. *Chemtronics* **1988**, *3*, 140.
(2) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993.

(3) See for example: (a) Mosset, A.; Lecante, P.; Galy, *Phil. Mag. B* **1982**, *46*, 137. (b) Burian, A.; Lecante, P.; Mosset A.; Galy, J. *J. Non-Cryst. Solids* **1987**, *90*, 633. (c) Laberty, C.; Verelst, M.; Lecante, P.; Mosset, A.; Alphonse, P.; Rousset, A. *J. Solid-State Chem.* **1997**, *129*, 271−276.
(4) Vogt, T.; Faulmann, C.; Soules, R.; Lecante, P.; Mosset, A.; Castan, P.; Cassoux, P.; Galy, J. *J. Am. Chem. Soc.* **1988**, *110*, 1833.

modeling programs have allowed us to start WAXS investigations on such molecular compounds.

Recently, one of us[5] has revived the interest for the spin crossover phenomenon and emphasized that the spin crossover materials could be used as active elements of memory devices. For the first time he synthesized a molecular material showing a spin transition between the singlet diamagnetic $^1A_1$ ($S = 0$) low-spin state (LS) and the quintet paramagnetic $^5T_2$ ($S = 2$) high-spin state (HS) around room temperature with a very large thermal hysteresis and a well-pronounced thermochromic effect. This material was a Fe^{2+}−1,2,4-triazole polymer. Ever since, several studies have been carried out on compounds of that kind;[6] in particular Michalowicz et al.[7] performed EXAFS and X-ray powder diffraction studies on $[Fe(Htrz)_2(trz)](BF_4)$ and $[Fe(Htrz)_2(trz)](BF_4) \cdot H_2O$ compounds, with Htrz = 1,2,4-4H-triazole and trz = triazolato anion. The aim of our investigation is to confirm and complete Michalowicz[7] conclusions. Moreover, we would like to show how a WAXS investigation combined to an EXAFS study can bring very precise structural information on inorganic polymers even when those are poorly crystallized or totally amorphous.

Experimental Section

Synthesis. The compounds $[Fe(Htrz)_2(trz)](BF_4)$ (**1**) and $[Fe(NH_2trz)_3](NO_3)_2$ (**2**), with NH_2trz = 4-amino-1,2,4-triazole, were synthesized as previously described for **1**[6] and following a similar procedure for **2**. Complete magnetic characterization for compound **1** has been published in ref 6 and will be published soon for compound **2**. Let us just remind that both compounds exhibit abrupt spin transitions with a wide thermal hysteresis. The transition temperatures have been found at $T_c^\uparrow = 383$ K and $T_c^\downarrow = 345$ K for **1**, and $T_c^\uparrow = 348$ K and $T_c^\downarrow = 313$ K for **2**. For both compounds, the spin transitions are accompanied by a violet − white change of color.

WAXS Study. Powder sample of compound **1** (or **2**) was sealed in a Lindeman capillary. The diffusion pattern scattered by the sample irradiated with graphite-monochromatized silver Kα radiation ($\lambda = 0.560\,83$ Å) was obtained using a LASIP diffractometer.[8] 580 intensities corresponding to equidistant s points ($s = 4\pi(\sin\theta/\lambda); \Delta s = 0.035$ Å^{-1}) were collected in the range $0 < \theta < 65°$ at different temperatures. Measurements of air and Lindeman capillary diffusion were also performed exactly in the same conditions. The raw sample scattered intensity (sample + air + capillary) was corrected for air and capillary contribution by spectra subtraction, and then corrected for polarization and absorption effects. Normalization was performed using Norman and Krogh-Moe's method.[9] The atomic scattering factors were taken from Cromer and Waber.[10] The reduced experimental radial distribution function (RDF), which shows the distribution of the interatomic distances, was calculated as explained in ref 4.

Measurements at high temperature were performed using a homemade heater system. A hot air laminar flux was

carefully sent on the capillary. High-temperature measurements in the HS state were done at 105 °C for **1** and 75 °C for **2**. The accuracy on the temperature is around ±5 °C, but the temperature stability is around ±2 °C.

Molecular Modeling. Theoretical structural models were built up using CERIUS2 program.[11] Energy minimization was done by molecular mechanics technique using the universal force field (UFF).[12] The theoretical RDF was computed from the structural models by Fourier transform of the theoretical intensities calculated using the Debye formula.[13] Most parameters of the UFF were used without any change. Only the free distance relative to the Fe−N coordination bond was modified. In a first step it was set up according to a classical Fe−N distance encountered in spin crossover compounds (2.00 Å in LS state and 2.18 Å in HS state[14]) and then finally adjusted, step by step, until a good agreement was reached between the theoretical and experimental RDF's.

Results

Study at Room Temperature in the Low-Spin State. *Compound 1.* Figure 1a shows the reduced experimental RDF for $[Fe^{II}(Htrz)_2(trz)](BF_4)$ (**1**). This RDF is typical of a long-range ordered material since significant order contributions are present up to 20 Å (20 Å is the maximum sensibility limit for our WAXS facility). According to the previous EXAFS work from Michalowicz et al.,[7] we have built a first molecular model consisting of iron centers connected together via triazole or triazolato bridges as shown on Figure 2. An 11 iron atom model is large enough to simulate correctly the long-range interaction up to 20 Å and sufficiently small to be easily tractable. Energy minimization was performed considering that the free length for a bond between a nitrogen atom and a low-spin iron(II) center is 1.99 Å. Figure 1b shows that the theoretical RDF fits perfectly the experimental one up to 6 Å and beyond 8 Å up to 12 Å. In the 6−8 Å range, on the other hand, the fitting is not so good. Beyond 12 Å, the theoretical model does not follow the experimental data in any way. At this stage, we can conclude that the core of the model is right. This material is undoubtedly constituted of polymeric chains. The Fe−Fe first distance is very close to 3.63 Å (compared to 3.65 Å found by Michalowicz[7]). The chain is linear with all 11 iron atoms along a straight line. Indeed, since the coordination sphere of every iron core is very symmetric, energy minimization leads to N−Fe−N angles very close to 180° and 90°, characteristic of a perfect octahedron (difference less than 0.2°). We can be very confident with our structural model. As a matter of fact, a light distortion of coordination octahedron would result in some damage on the fitting agreement (see below the high-temperature study).

In a second step we tried to interpret the fitting discrepancy in the 6−8 Å range and for this we incorporated the BF_4^- counterions in the model. If the tetrafluoroborate anions are not disordered, they must present a nonnegligible contribution to pair interactions. Because fitting discrepancy occurs in the 6−8 Å

(5) Kröber, J.; Codjovi, E.; Kahn, O.; Golière, F.; Jay, C. *J. J. Am. Chem. Soc.* **1993**, *115*, 9810.

(6) Kröber, J.; Audiere, J.; Codjovi, E.; Kahn, O.; Haasnoot, J.; Grolière, F.; Jay, C; Bousseksou, A.; Linares, J.; Varret, F.; Gonthier-Vassal, A. *Chem. Mater.* **1994**, *6*, 1404.

(7) Michalowicz, A.; Moscovici, J.; Ducourant, B.; Cracco, D.; Kahn, O. *Chem. Mater.* **1995**, *7*, 1833.

(8) The LASIP diffractometer has a geometry specially set up for diffusion measurements. It minimizes every external parasite diffusion phenomenon.

(9) (a) Norman, N. *Acta Crystallogr.* **1957**, *10*, 370. (b) Krogh-Moe, J. *Acta Crystallogr.* **1956**, *9*, 951.

(10) Cromer, D.; Waber, J. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. 4.

(11) CERIUS2 molecular simulation program is supplied by BIO-SYM technologies and runs on an Indy Silicon Graphics workstation.

(12) See for example: Rappe, A.; Colwell, K.; Casewit, C. *Inorg. Chem.* **1993**, *32*, 3438.

(13) Debye, P. *Ann. Phys. (Leipzig)*, **1915**, *46*, 809.

(14) (a) König, E. *Prog. Inorg. Chem.* **1987**, *35*, 527. (b) Gallois, B.; Real, J. A.; Hauw, C.; Zarembowitch, *J. Inorg. Chem.* **1990**, 29, 1152.
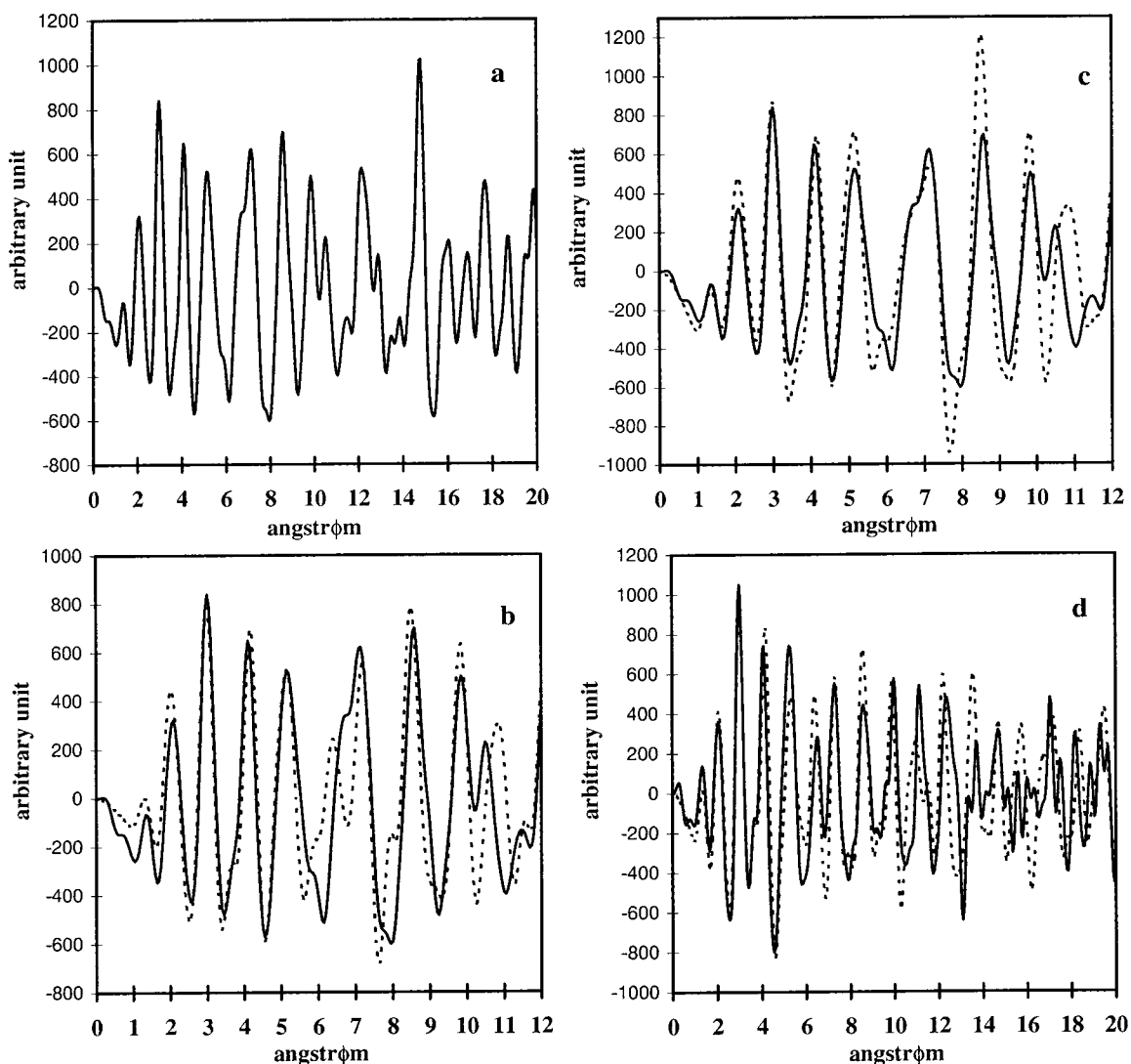
Figure 1. (a) Experimental reduced RDF for [Fe^{II}(Htrz)$_2$(trz)](BF$_4$) (**1**) in the LS state. (b) Experimental RDF (plain line) and theoretical 11-Fe^{II} model RDF (dotted line) for [Fe^{II}(Htrz)$_2$(trz)](BF$_4$) (**1**, LS state) from the model of Figure 2. (c) Experimental RDF (plain line) and theoretical extended model RDF (dotted line) for [Fe^{II}(Htrz)$_2$(trz)](BF$_4$) (**1**, LS state) from the model of Figure 3. (d) Experimental RDF (plain line) and theoretical model RDF (dotted line) for [Fe^{II}(NH$_2$trz)$_3$](NO$_3$)$_2$ (**2**, LS state) from the model of Figure 4.
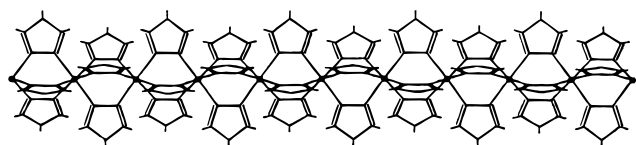
Figure 2. Eleven-Fe^{II} polymeric model for [Fe^{II}(Htrz)$_2$(trz)]-(BF$_4$) (**1**) (without BF$_4^-$ ions).

range, we can assume that the BF$_4^-$ anions are located anywhere between 6 and 8 Å from the iron metallic centers. In fact, this agrees perfectly with a hypothesis where each nitrogen atom occupying the 4-position of the nondeprotonated triazole ligand is hydrogen bonded to a tetrafluoroborate anion as shown on Figure 3. With this new model the fitting procedure is now quite perfect up to 10 Å as shown in Figure 1c.[15]

What happens beyond 10 Å? Long-range interaction cannot be modeled anymore by a single-chain model. Interchain interactions become preponderant. To determine the relative positions of the chains within the lattice is not an easy task because the experimental RDF is very complex, and the molecular modeling

program does not provide us much help. Moreover, the problem is now to build a 3D packing model which includes several hundreds of atoms. Computing procedure and model handling become very heavy and less conclusive. Anyway, some remarks can be made. The most intense peak of the experimental RDF is located at 14.8 Å (see Figure 1a). Undoubtedly this peak corresponds to a "pseudo cell parameter"; i.e., to a translation distance between two polymeric chains. Considering this hypothesis, it should be possible to build a chemically acceptable model in which two chains are interconnected through a hydrogen-bond network

(15) In fact, on Figure 1c the fit is almost perfect between 6 and 8 Å but the theoretical peak centred at 8.6 Å is now too strong as compared to Figure 1b. This increase is due to Fe−F distances with non-hydrogen-bonded fluoride atoms. It is possible to cancel this defect by introducing high thermal parameters for these atoms. Even if it is chemically acceptable to consider that these atoms are not well localized, we prefer to follow a fitting procedure using fixed thermal parameters for each atom. Indeed in WAXS we have not enough experimental parameters to allow us to use a refinement procedure including many fitting parameters. Working with such a large number of parameters would result in very well-fitted curves but in an artificial way.

WAXS of Spin Transition Molecular Materials

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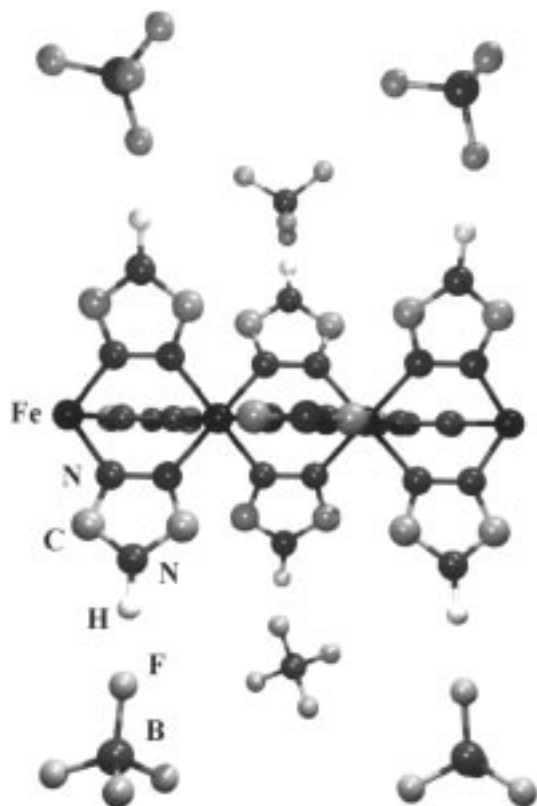
Figure 3. Extended model for $[Fe^{II}(Htrz)_2(trz)](BF_4)$ (**1**) with hydrogen-bonded BF_4^- anions. For clarity only four iron atoms are represented but the complete model deals with 11 ferrous centers. Only H-bonded hydrogen atoms are shown. d (Fe−N) = 1.99 Å; d(Fe−Fe) = 3.63 Å; perfect octahedron iron core; $d(NH−FBF_3)$ = 1.8 Å; **N−H−F**−BF$_3$ angle = 180°; **NH−F−B**−F$_3$ angle = 160° d(Fe−F) = 6.8 and 8.7 Å.

via BF_4^- anions. However, the location of the second chain at 14.8 Å from the first one remains an open question. Indeed, we were unable to improve significantly the fitting quality of the RDF of Figure 1c. We reached here the limit of a WAXS study coupled with a molecular modeling simulation.

Compound 2. The same investigation procedure was carried out for $[Fe^{II}(NH_2trz)_3](NO_3)_2$ (**2**). This case seems to be more simple due to the fact that the compound is more amorphous. It seems that no interchain interaction takes place. Indeed, no intense peak is present in the experimental R.D.F after 12 Å, and a single 11-iron chain model (Figure 4; without taking into account the NO_3^- anions) fits quite well the experimental RDF up to 20 Å (Figure 1d). Compared to the preceding case, the Fe−N distance seems to be a little bit longer (2.01 Å, Fe−Fe 3.65 Å). Up to 10 Å the fit is almost perfect, and beyond this value the experimental RDF becomes noisy and the fitting quality decreases sensibly. The noisy character of the experimental RDF is not due to a data collection problem (in fact the data collection time was 3 times as long for compound **2** as for compound **1**) but to a shorter coherence length in the material. Perhaps this chain presents some degree of flexibility that causes a progressive collapsing of long-range interaction. Moreover, even if the nitrate anions are not as well localized as the BF_4^- ones, their contribution probably causes some minor perturbations after 10 Å, which are not taken into account by the model.
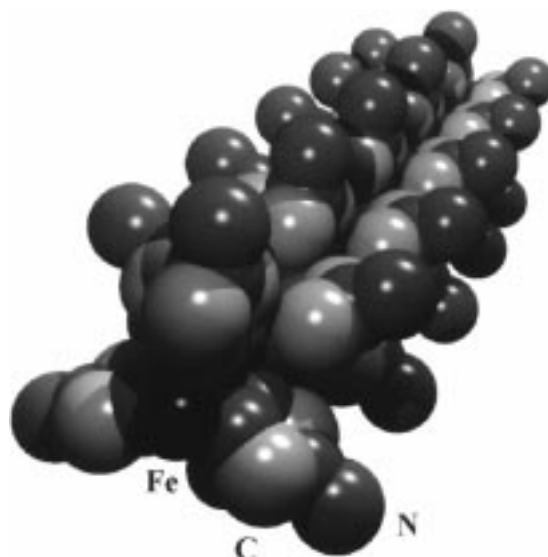
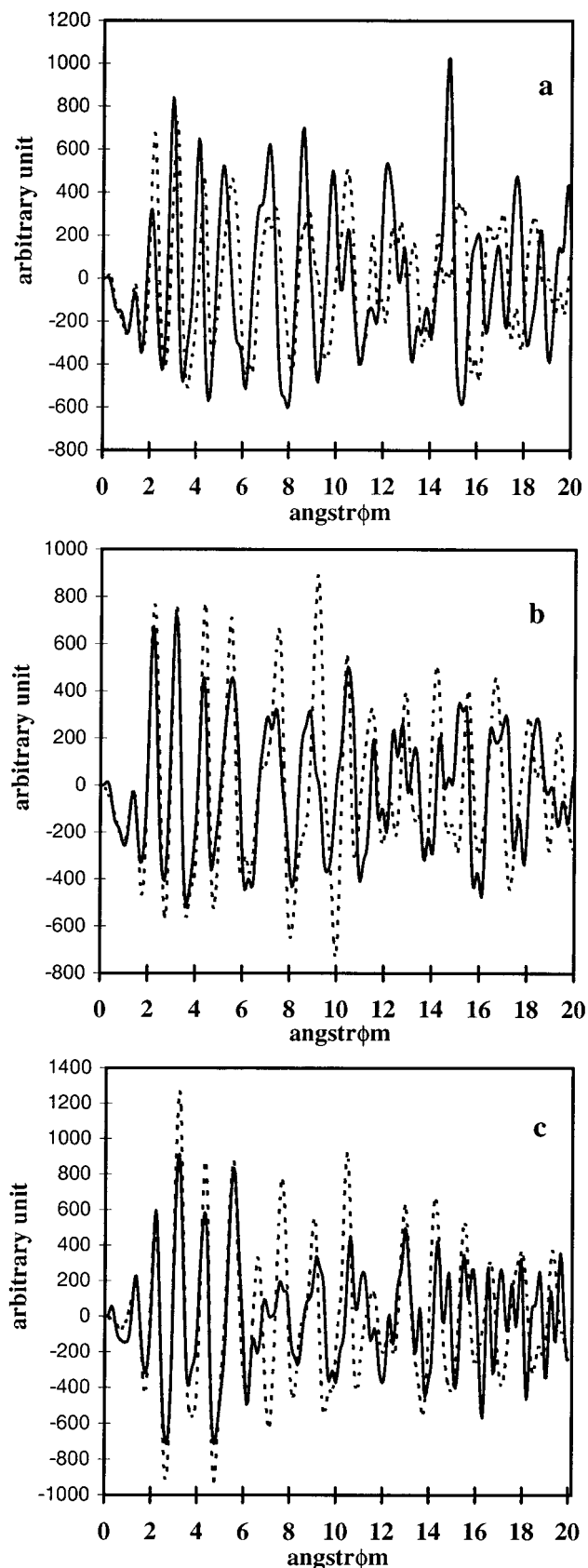**Figure 4.** Eleven-Fe^{II} polymeric model of $[Fe^{II}(NH_2trz)_3]$-$(NO_3)_2$ (**2**) (without NO_3^- counterions). d(Fe−N) = 2.01 Å; d(Fe−Fe) = 3.65 Å; perfect octahedron iron core. No interaction between NO_3^- anions and the polymeric chain has been detected. Hydrogen atoms have been omitted for clarity.
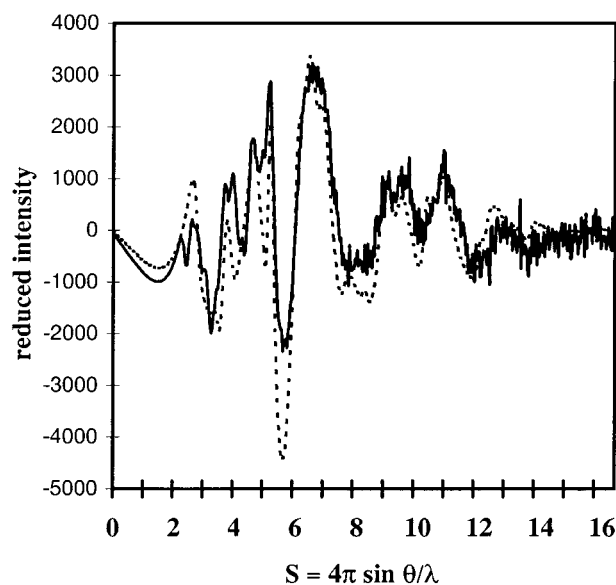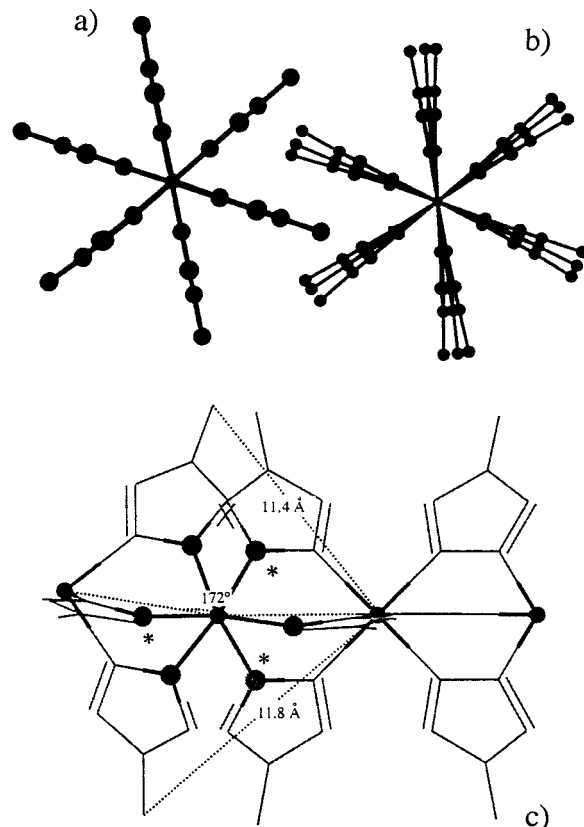

Figure 5. Experimental reduced intensity (plain line) and theoretical one (dotted line) for $[Fe^{II}(NH_2trz)_3](NO_3)_2$ (**2**) in the LS state, from the model of Figure 4.

Figure 5 shows the fitting quality between the theoretical model and experimental data for compound **2**, not in the real space after a Fourier transform as for the previous figures but directly in the reciprocal space. Working in the reciprocal space is not convenient, but the fitting quality may be better appreciated because it compares more directly experimental data to models. In this case we can see a rather perfect agreement of the fitting procedure in the high-angle area ($S > 4$) which mostly corresponds to short distances in the real space. In the small-angle area, fast oscillations of experimental data are not very well reproduced by the model. That means that long-range order interactions are not very well modeled and probably also that our model is too small. This double-fitting procedure was performed in every case, but only in this case is the result shown.

Figure 7. (a) View of the $[Fe^{II}(NH_2trz)_3](NO_3)_2$ (**2**) model along the $\lambda 3$ growth axis in the LS state (seven-iron atom model). (b) The same view in the HS state with a pure rhombic distortion of $8°$ around the $\lambda 3$ growth axis; the iron atoms remain aligned. (c) Nitrogen atoms in gray (with *) have rotated of $8°$ around the $\lambda 3$ axis defined by the barycenter of nitrogen atoms in black and gray. The chain has lost its linearity. The example of 11.4 Å and 11.8 Å Fe−N distances (initially symmetric in a linear chain) explains why long-range RDF peaks adopt now a splitted nature.

Study at High Temperature in the High-Spin State (HS). *Compound 1.* Figure 6a compares the experimental RDF's for compound **1** in both the LS (20 °C) and HS (75 °C) state. Up to 6 Å the main difference is a general shift of RDF peaks toward longer distances in the HS state. This is due to the well-documented lengthening of the Fe−N coordination bond associated with the LS → HS transition.[16] More interesting is the drastic change of long-range interaction beyond this value. For example the very intense peak centered at 14.8 Å in the LS state completely vanishes in the HS state. In this HS state the experimental RDF becomes very noisy, and probably long-range order interaction is totally destroyed. Figure 6b shows that an 11-iron chain model including BF_4^- anions with Fe−N distances equal to 2.17 Å (Fe−Fe = 3.83 Å) fits perfectly the experimental RDF up to 6 Å. Beyond this value the noisy and splitted character of the experimental RDF is not perfectly reproduced by the model; however, it corresponds roughly to the periodic oscillations of the experimental RDF.

Compound 2. The case of compound **2** is very similar. The model fits perfectly the experimental data up to 6

Figure 6. (a) Experimental RDF for $[Fe^{II}(Htrz)_2(trz)](BF_4)$ (**1**) in the LS state (room temperature, plain line) and in the HS state (75 °C, dotted line). (b) Experimental RDF (plain line) and theoretical model RDF (dotted line) for $[Fe^{II}(Htrz)_2(trz)]$-(BF_4) (**1**, HS state). d(Fe−N) = 2.17 Å; d(Fe−Fe) = 3.83 Å. (c) Experimental RDF (105 °C, plain line) and theoretical model RDF (dotted line) for $[Fe^{II}(NH_2trz)_3](NO_3)_2$ (**2**, HS state). d(Fe−N) = 2.18 Å; d(Fe−Fe) = 3.84 Å.

(16) See for example: (a) Gütlich, P. *Struct. Bonding (Berlin)* **1981**, *44*, 83. (b) König, E.; Ritter, G.; Kulshreshtha, S. *Chem. Rev.* **1985**, *85*, 219.

Å, and beyond this value the goodness of fit decreases noticeably even if the general shape of the experimental RDF remains valid (see Figure 6c). Clearly, as in the LS state, no interchain interaction gives rise to a noticeable contribution to the experimental RDF. For both compounds **1** and **2**, a linear chain model is not well adapted in the high-spin state. It is well-known that Fe^{2+} LS spin complexes show usually an almost regular octahedral core due to the $(t_{2g})^6$ electronic configuration.[16] On the contrary, in the HS state, the antibonding e_g orbitals are doubly occupied, resulting in a distortion of the octahedral core. Usually, this distortion in the HS state is more or less rhombic.[17] This distortion is not taken into account in our models because the UFF is not at all adapted to incorporate such a distortion. Moreover, supposing that the distortion is purely rhombic, four twist axes are possible.[18] The first axis is simply the growth axis of the chain. A rhombic distortion along this axis retains the iron atoms aligned (see Figure 7b); the chain becomes only twisted as a screw, and such a distortion will not disturb much the RDF. A twist of a few degrees along other $\lambda 3$ axes will create undulations, and probably the chain will take a waving shape. Such undulations would explain why the long-range order becomes noisy with a splitted

feature (see Figure 7c). In other words this high-temperature investigation strongly suggests that the chain in the HS state loses its linear character, as well as its periodicity. This may be attributed to a rhombic distortion of the iron core.

Conclusion

This wide-angle X-ray scattering study on compounds **1** and **2** confirms unambiguously the chain structure of these spin transition materials. At room temperature, in the low-spin state, the chain is linear, and in the case of $[Fe^{II}(Htrz)_2(trz)](BF_4)$ (**1**) each chain is probably hydrogen bonded to neighboring chains through BF_4^- anions. For $[Fe^{II}(NH_2trz)_3](NO_3)_2$ (**2**) no interchain interaction was detected. At higher temperature, in the HS state, the Fe–N coordination bond lengths increase as usually observed for such spin crossover compounds, and the chains lose their linear character. They very probably adopt a zigzag shape due to a rhombic distortion of the Fe^{2+} coordination octahedron. These chain undulations destroy interchain long-range order for compound **1**. This does not mean that the hydrogen-bond network is also destroyed but simply that it has lost its regular and periodic character.

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(17) For interesting studies of the correlation between the spin crossover phenomenon and the rhombic distortion see for example: (a) Real, J. A.; Muñoz, M. C.; Andreas, E.; Granier, T.; Gallois, B. *Inorg. Chem.* **1994**, *33*, 3587. (b) Chang, H.-R.; McCuster, J. K.; Toflund, H.; Wilson, S. R.; Trautwein, A. X.; Winkler, H.; Hendrikson D. N. *J. J. Am. Chem. Soc.* **1990**, *112*, 6814. (c) Purcell, K. F. *J. J. Am. Chem. Soc.* **1979**, *101*, 5147.

(18) The definition of the rhombic distortion has been clearly presented by: Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748.