Neutron powder diffraction studies of two spin transition Fe(II)-complexes under pressure

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The pressure dependences of the lattice parameters of two spin transition compounds have been derived from neutron powder diffraction measurements at ambient temperature. The study of Fe(PM–AzA)$_2$(NCS)$_2$ [PM is N-2′-pyridylmethylene and AzA is 4-(phenylazo)aniline] has been used to validate this new type of investigation of spin crossover compounds, and the study of Fe(PM–BiA)$_2$(NCS)$_2$ (BiA is 4-aminobiphenyl) has allowed the atypical spin crossover behaviour of this compound under pressure to be explained. In addition, this complex exhibits a pressure-induced structural transition with an associated symmetry change, inducing the transformation of Fe(PM–BiA)$_2$-(NCS)$_2$ into a different polymorph that avoids a first-order spin transition in favour of continuous transition.

1. Introduction

In the context of the development of new technology, efforts have increasingly been concentrated on the miniaturization of electronic devices and, therefore, on the production of nanosystems. A fascinating opportunity is given by molecular bistability based on spin crossover (Gütlich & Goodwin, 2004). Spin transition compounds can change their spin state by variation of an external constraint such as temperature, pressure, intense magnetic field or light irradiation. These materials have potential industrial applications as display devices or data storage elements (Kahn & Martinez, 1998; Létard *et al.*, 2004). In iron(II) complexes, the spin conversion is related to the electronic configuration of the ion changing from a high spin (HS, $S = 2$, $t_{2g}^4 e_g^2$) state to a low spin (LS, $S = 0$, $t_{2g}^6 e_g^0$) state. In addition to this electron redistribution, spin transition complexes show important structural variations, principally observed in the iron coordination environment. An increase in the octahedral deformation and a concomitant increase of the Fe–ligand bond length by 0.2 Å are typical for the LS → HS transition (Wiehl *et al.*, 1986, 1990; Guionneau *et al.*, 2004). Consequently, these modifications affect the molecular volume, which increases by several Å^3. It is well known that the LS → HS conversion is associated with an entropy change and that the thermodynamically stable spin state at high temperature is the HS phase (Sorai & Seki, 1974). When the temperature is decreased, the LS phase becomes thermodynamically stable and the thermal spin transition temperature $T_{1/2}$, where the LS and HS states are equally present in the material ($\gamma_{HS} = \gamma_{LS} = 0.5$; γ_{HS} and γ_{LS} are the HS and LS fractions, respectively), can be defined. Depending on the interaction strength between neighbouring molecules, the spin transition can be gradual (weakly cooperative), abrupt or abrupt with hysteresis (highly cooperative).

Most of the Fe^{II} spin transition compounds studied under pressure have been investigated by spectroscopic measurements or magnetic experiments (Jeftic *et al.*, 1996, 1997; Jeftic & Hauser, 1997; Ksenofontov *et al.*, 2004). Only four investigations have been performed by

X-ray diffraction measurements, on the compounds Fe(phen)$_2$(NCS)$_2$ and Fe(btz)$_2$(NCS)$_2$ (Granier *et al.*, 1993), Fe(PM–TeA)$_2$(NCS)$_2$·CH$_3$OH (Guionneau *et al.*, 2001), and Mn(pyrol)$_3$tren (Guionneau *et al.*, 2005) [phen is 1,10-phenanthroline, btz is 2,2′-bi-4,5-dihydro-thiazine, PM is N-2′-pyridylmethylene, TeA is 4-aminoterphenyl, pyrol is pyrrole-2-carboxaldehyde and tren is 2,2′,2″-tris(ethylamino)amine]. These studies showed that an increase of the applied pressure induces an increase of $T_{1/2}$, as expected because of the decrease in the volume of the iron(II) coordination sphere on going from the HS to the LS state. The consequence is a stabilization of the LS state under pressure.
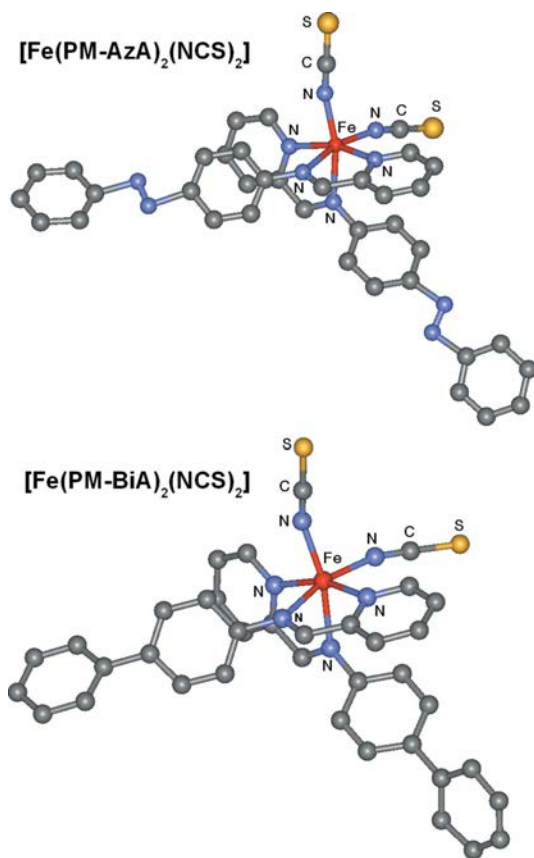
The complex Fe(PM–AzA)$_2$(NCS)$_2$ [AzA is 4-(phenylazo)aniline] is characterized by a gradual spin transition temperature $T_{1/2} = 189$ K (Guionneau *et al.*, 1999) and may be considered as an ideal compound with which to study the effect of temperature and pressure on the molecular structure of spin transition materials. Under applied pressure, it exhibits a more gradual transition with an increase of $T_{1/2}$, which induces a stabilization of the LS state (Ksenofontov *et al.*, 1998). However, Fe(PM–BiA)$_2$(NCS)$_2$ (BiA is 4-aminobiphenyl) shows contradictory behaviour. This complex is known to crystallize in two different polymorphs, denoted pI and pII, which exhibit very different spin crossover features (Marchivie *et al.*, 2003; Létard *et al.*, 2003). Fe(PM–BiA)$_2$(NCS)$_2$-pI undergoes a complete and abrupt transition under ambient-pressure conditions with a small hysteresis ($\Delta T = 5$ K), which is attributed to a regular and compact intermolecular interaction network. As the pressure is increased from 0.1 to 0.6 GPa, the compound exhibits a typical stabilization of the LS state with a reduction of the hysteresis (Ksenofontov *et al.*, 1998). Surprisingly, in the pressure range 0.6–0.8 GPa, the hysteresis increases strongly to reach 25 K, and above 0.8 GPa decreases again. In contrast, Fe(PM–BiA)$_2$(NCS)$_2$-pII exhibits a gradual thermal spin transition without hysteresis under ambient-pressure conditions; no magnetic high-pressure data are available for this polymorph.

Here, the structural properties of the spin transition compounds Fe(PM–AzA)$_2$(NCS)$_2$ and Fe(PM–BiA)$_2$(NCS)$_2$ (Fig. 1) are investi-

gated using neutron powder diffraction under pressures of up to 1.1 GPa. The goal is to relate the spin transition properties to the molecular variations while applying pressure in order to better understand the physical properties of these complexes and to explain the unexpected behaviour of Fe(PM–BiA)$_2$(NCS)$_2$-pI under applied pressure. To our knowledge, this is the first high-pressure neutron powder diffraction investigation performed on spin transition complexes.
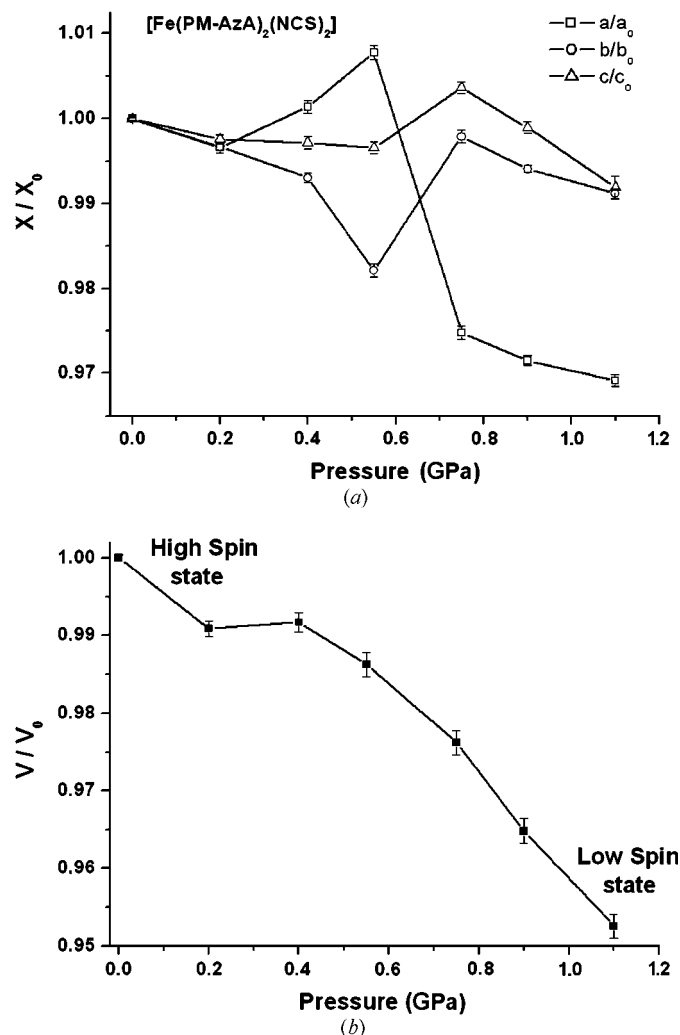
2. Experimental

Samples were synthesized following the usual method (Guionneau *et al.*, 1999; Marchivie *et al.*, 2003; Létard *et al.*, 2003). Neutron scattering measurements were performed at the Institut Laue–Langevin (Grenoble, France) using the high-resolution powder diffractometer D2B in high-flux configuration with a wavelength of 2.4 Å. The pressure cell was a TiZr clamped cell using Fluorinert liquid, *i.e.* hydrocarbon in which hydrogen is replaced by fluorine ('Fc75', 3 *M*, St Paul, MN, USA), as the pressure transmitter. It has been shown that Fluorinert 'Fc75' remains a hydrostatic pressure medium at room temperature up to the maximum applied pressure used in the present studies (Varga *et al.*, 2003; Sidorov & Sadykov, 2005). The experiments were performed at ambient temperature and, for both compounds, at seven pressure levels up to 1.1 GPa. Cell refinements were performed with the program *Fullprof* (Rodriguez-Carvajal, 1993).

3. Results and discussion

Neutron diffraction patterns of Fe(PM–AzA)$_2$(NCS)$_2$ demonstrated profound changes in both the Bragg peak intensity and its position as a function of pressure. These changes are also correlated with the modifications induced by the spin transition at high pressure. The pressure dependence of the lattice parameters (Fig. 2) confirmed that, as usually observed in high-pressure-dependence studies, the cell parameter evolution was anisotropic. A significant change of the lattice parameters can be clearly observed around 0.70 (5) GPa, particularly in the directions of the *a* and *b* crystallographic axes. These axes correspond to the highest interaction directions, as the structure can be thought of in terms of molecular sheets stacked through π–π interactions within the *ab* plane. The inter-sheet interactions are mainly formed through the S atoms in the *c*-axis direction. In the pressure range 0.4–0.6 GPa, where the HS phase is still dominant, the increase of the crystallographic *a* axis is accompanied by a decrease in the *b* axis. This is a result of both the pressure increase and the spin transition mechanism, which results in a global decrease of the cell volume due to the stabilization of the LS state. Above 0.75 GPa, the LS fraction dominates in the complex, thus inducing the important structural reorganizations shown in Fig. 2 by the large variations of the cell parameters. The pressure value of

Figure 1
Molecular structures of the spin transition complexes Fe(PM–BiA)$_2$(NCS)$_2$ and Fe(PM–AzA)$_2$(NCS)$_2$ in the HS state at ambient temperature and pressure (H atoms have been omitted for clarity).

Figure 2
Fe(PM–AzA)$_2$(NCS)$_2$: pressure dependence of (*a*) the relative lattice parameters and (*b*) the volume as a function of pressure at room temperature.
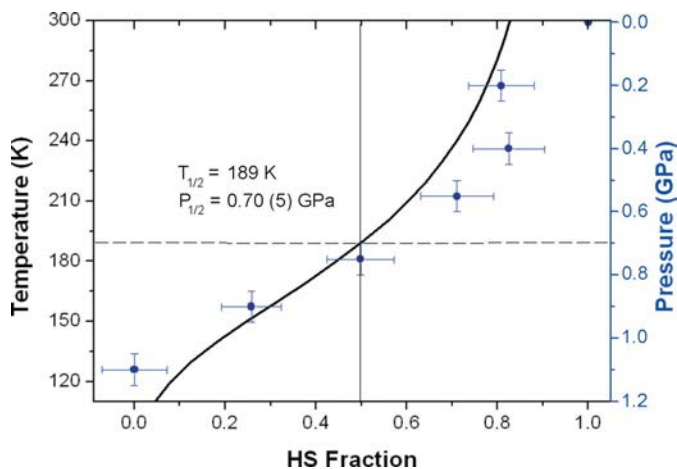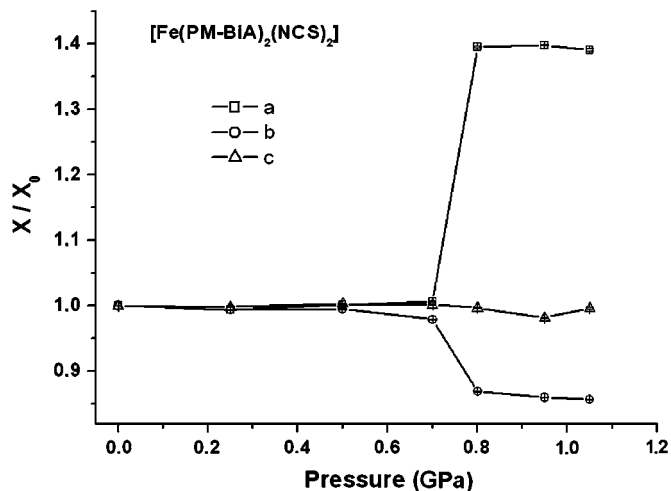
Figure 3
Fe(PM–AzA)$_2$(NCS)$_2$: neutron diffraction experimental pressure dependence (points) and calculated temperature dependence (continuous line) of the HS fraction (γ_{HS}). γ_{HS} = 0.5 defines $T_{1/2}$ and $P_{1/2}$.

0.70 (5) GPa characterizes the pressure $P_{1/2}(T = 298$ K), where the solid contains 50% of molecules in the HS state and 50% of molecules in the LS state, in perfect agreement with previous magnetic measurements (Ksenofontov et al., 1998). As expected, the lattice parameter evolution shows that the application of pressure induces a stabilization of the LS state for the complex Fe(PM–AzA)$_2$(NCS)$_2$, with a complete spin transition at 1.1 GPa. The cell volume curve displays a continuous and quasi-linear relationship with applied pressure, characteristic of weak cooperative spin transition compounds. In addition, the cell volume variation at ambient temperature between ambient pressure (HS state) and 1.1 GPa (LS state) is almost identical to that at ambient pressure between 298 K (HS state) and 110 K (LS state), e.g. ΔV_P = 174 Å^3 and ΔV_T = 172 Å^3, respectively. As shown in other spin transition investigations under constraint (Legrand et al., 2006, 2007), the cell volume of the HS and LS states correlates, to a first approximation, with the fraction γ_{HS} of the HS species, according to the formula $V(\gamma_{HS}) = \gamma_{HS}V_{HS} + (1 - \gamma_{HS})V_{LS}$. In Fig. 3, the pressure dependence of γ_{HS} deduced from the experimental data using this formula is compared with the temperature dependence of γ_{HS} calculated from the method given by Capes (2000).[1] The variation of γ_{HS} appears similar in both cases, showing that it is not influenced by the nature of the thermodynamic constraint for this compound.

Of the two modifications of the Fe(PM–BiA)$_2$(NCS)$_2$ complex, only the pI polymorph, which exhibits the abrupt spin transition (Marchivie et al., 2003; Létard et al., 2003), was investigated. The molecular structure remained in the HS state for all the measured pressures at 298 K, as reported by magnetic measurements (Ksenofontov et al., 1998). As for Fe(PM–AzA)$_2$(NCS)$_2$, the lattice parameters were refined as a function of pressure and demonstrated an anisotropic evolution (Fig. 4). There is a significant variation of the a and b lattice parameters, whereas the c lattice parameter stays almost constant. At pressures exceeding P = 0.75 (5) GPa, the a parameter expands by approximately 40% and the b parameter contracts by 15%. The refinement of the lattice parameters clearly illustrates that

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[1] The temperature as a function of γ_{HS} could be expressed by $T(\gamma_{HS}) = [\Delta H + \Gamma(1 - 2\gamma_{HS})]/\{R\ln[(1 - \gamma_{HS})/\gamma_{HS}] + \Delta S\}$, where ΔS and ΔH are the entropy and enthalpy variation, respectively, R is the molar gas constant, and $\Gamma = 2RCT_{1/2}$; C = 0.48, $T_{1/2}$ = 189 K, ΔH = 6.68 kJ mol^{-1} and ΔS = 35.3 J K^{-1} mol^{-1}.
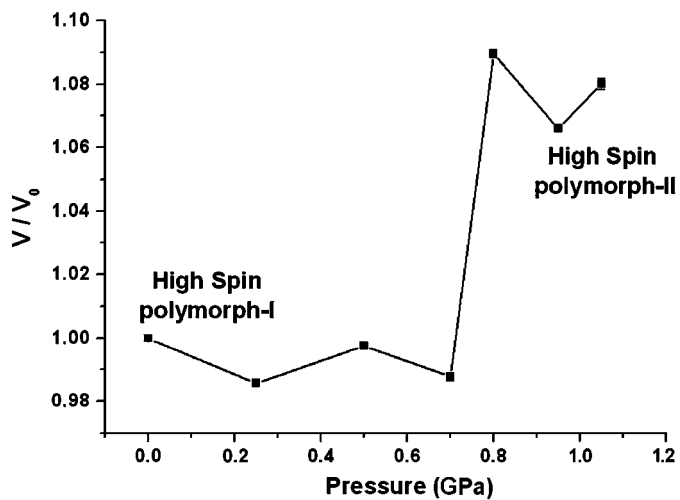
Figure 4
Fe(PM–BiA)$_2$(NCS)$_2$: pressure dependence of (a) the relative lattice parameters and (b) the volume as a function of pressure at room temperature.

below 0.75 (5) GPa the compound is orthorhombic (space group $Pccn$), which corresponds to polymorph I. Surprisingly, above 0.75 (5) GPa it becomes monoclinic (space group $P2_1/c$), which corresponds to polymorph II. Therefore, applying pressure to Fe(PM–BiA)$_2$(NCS)$_2$-pI induces a structural transition to a phase that adopts the features of Fe(PM–BiA)$_2$(NCS)$_2$-pII. The pI-to-pII transition pressure is estimated in this study to be 0.75 (5) GPa. Previous magnetic data yielded a decrease in the hysteresis for $P \geq$ 0.8 GPa and a more gradual spin crossover at higher pressures (Ksenofontov et al., 1998). The observed high-pressure structural transition from pI to pII here appears perfectly consistent with the magnetic data, since pII shows a gradual thermal spin crossover while pI shows hysteresis. In conclusion, the unusual observed high-pressure magnetic behaviour of Fe(PM–BiA)$_2$(NCS)$_2$-pI finds its origin in a pressure-induced structural transition between pI and pII.

The present study highlights very promising results in the field of spin crossover phenomena under constraint, where crystallographic studies under pressure are still very rare. Neutron and X-ray structural investigations are fundamental to the elucidation of the role of pressure on the occurrence of spin crossover properties. It has been demonstrated here that such an approach can be achieved with

success even if the experimental conditions are difficult and sometimes not favourable. Investigations of this type would also be applicable to the more general field of bistable materials with potential industrial applications under pressure, such as pressure sensors and piezochromic paints.

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