

# Structural investigations of spin transition compounds under pressure.

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We aimed at determining the structural evolution of spin transition complexes under pressure. Further systems were investigated: (i) the two dimensional spin transition compound  $\text{Fe}(\text{btr})_2(\text{NCS})_2 \cdot \text{H}_2\text{O}$  presenting unusual and unexpected behaviour under pressure and (ii) compounds of the  $\text{Fe}(\text{PM-L})_2(\text{NCS})_2$  family to compare spin transition properties under pressure; moreover, some complexes in this family also present unusual properties under pressure which always remain unclear.

## Scientific background

Particular attention is paid to spin transition compounds since fifteen years [1]. These materials are especially interesting owing to their bistability properties which give them promising applications as data storage elements, thermal switches or display devices. As a matter of fact, these compounds can change their spin state (high spin -HS- or low spin -LS-) upon the variation of an external constraint as temperature, pressure, intense magnetic field or light irradiation [2-3]. Most of the spin transition compounds studied under pressure had been investigated by spectroscopic measurements or magnetic experiments. About structural investigations of spin transition complexes under pressure, studies are very rare and only three crystallographic measurements were established, always by X-ray diffraction. Spectroscopic and magnetic studies shown that an increase of the applied pressure induces an increase of the transition temperature  $T_{1/2}$ , which is the  $\text{LS} \leftrightarrow \text{HS}$  thermal spin transition temperature, as it could be expected due to decrease in the volume of iron(II) coordination sphere on going from the HS to the LS state. The consequence is a stabilization of the LS state under pressure.

## Experimental section

The measurements were performed at  $\lambda = 0.41 \text{ \AA}$  on the high pressure beamline ID09A. Data were collected using the MAR345 image plate at a distance of 260 mm with  $\phi$ -scan over  $30^\circ$  ( $\Delta\phi = 2^\circ$  and  $\Delta t = 0.8, 1$  or  $2 \text{ s}$  per image depending the complex). Crystals of very good quality were introduced in the center of a diamond anvil cell; silicon oil was used as pressure transmitter. The pressure was controlled *in situ* thanks to ruby fluorescence initially calibrated. All the experiments were performed at ambient temperature and particular attention was paid during pressure increase to not damage the crystal and well stabilize the pressure.

## Preliminary results

The spin transition compounds family  $\text{Fe}(\text{PM-L})_2(\text{NCS})_2$  is particularly interesting because it regroups several complexes with very different behaviours under pressure. The aim of the present experiment was to investigate the structural properties of the spin transition compounds  $\text{Fe}(\text{PM-PeA})_2(\text{NCS})_2$  and  $\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2$  (PM = N-2'-pyridylmethylene; PeA = 4-(phenylethynyl)aniline; BiA = 4-aminobiphenyle) under pressure up to 17 kbar, to rely the spin transition properties and the molecular variations when applying a pressure.

**The complex  $\text{Fe}(\text{PM-PeA})_2(\text{NCS})_2$**  is characterized by a thermal hysteresis loop of 37 K. Under applied pressure, the spin transition shifts to lower temperature and the hysteresis becomes larger ( $\Delta T = 57 \text{ K}$ ) than at atmospheric pressure. When the pressure reaches 3 kbar, the spin transition in the warming mode presents an unusual hump around 160 K, and magnetic data clearly

shows that the complex is not completely in the HS state even at ambient temperature [4]. Finally, coming back to ambient pressure induces irreversible change of the magnetic properties. This behaviour is not clarified yet and lets presumed the formation of a new stable crystallographic phase at elevated pressure.

The complex was measured on ID09A at 7 pressures up to 11.35 kbar. The refinement of the lattice parameters clearly showed that the pressure change is accompanied by a structural phase transition from monoclinic, at low pressure, to orthorhombic, at high pressure. It was showed that decreasing temperature has the same effect. This symmetry change occurs at  $P = 4.15$  kbar and is particularly visible on the  $a$  crystallographic parameter which decreases by 12%, the  $b$  and  $c$  parameters increasing by about 2%. Moreover, the volume variation is extremely large, about 12%, which is in good agreement with the magnetic data and the observed wide hysteresis width ( $\Delta T > 100$  K).

**The complex  $\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2$**  shows a complete and abrupt transition under normal pressure condition, with a small hysteresis ( $\Delta T = 5$  K). The spin transition has been found not to be accompanied by a space group change (Pccn). When the pressure increases from 1 to 6 kbar, it exhibits a typical stabilization of the LS state with a reduction of the hysteresis width [4]. Surprisingly, in the pressure range 6-8 kbar, the hysteresis width strongly increases to reach 25 K. For  $P > 8$  kbar, the hysteresis width decreases again. As for  $\text{Fe}(\text{PM-PeA})_2(\text{NCS})_2$ , this behaviour is not clarified yet and lets presumed the formation of a new crystallographic phase at elevated pressure.

A single crystal of  $\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2$  was measured on ID09A at 293 K up to 17 kbar (in increase then decrease pressure modes). For this complex, the molecular structure remains in the HS state for all the measured pressure. The refinements of the lattice parameters showed a decrease of all the crystallographic parameters induces a volume change of 8%. The structural refinement of this complex at high pressure is very delicate due to a supposed symmetry change. Structural refinement work is always in progress on that spin transition compound.

The application of hydrostatic pressure ( $< 10.5$  kbar) on **the two-dimensional spin transition compound  $\text{Fe}(\text{btr})_2(\text{NCS})_2 \cdot \text{H}_2\text{O}$**  (btr = 4,4'-bis-1,2,4-triazole) results in an unexpected stabilization of the HS state [5]. For this spin transition compound, it is noted a stabilization of the HS state under pressure with an increase of thermal spin transition. Coming back to  $P = 1$  bar, the complex exhibits a new magnetic behaviour with an observed HS state residue in the ground LS state. It is presumed that a structural phase transition probably governs the spin transition under pressure.

To clarify the behaviour of this compound under pressure, we measured single crystals of  $\text{Fe}(\text{btr})_2(\text{NCS})_2 \cdot \text{H}_2\text{O}$  up to 10 kbar at ambient temperature. Structural refinements did not show symmetry change from the monoclinic common space group of this complex. All the lattice parameters decrease when applying pressure with the largest change for the  $a$  parameter. The volume change was calculated to be of the order of 8%. The structural changes were studied in increasing and decreasing pressure modes pointing out a reversible variation of all the parameter, excepted for the beta angle which significantly increase during the  $8 \rightarrow 10 \rightarrow 4$  kbar way ( $\Delta\beta = +1^\circ$ ). Structural refinement work is always in progress on that spin transition compound to rely the magnetic behaviour changes to the structural properties.

## **References**

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