

(P,T,hv) phase diagram of spin crossover compounds

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The ultimate limit of miniaturization is that of molecules, which are the smallest composite entities with definite size, shape and controllable properties. Much effort has been devoted lately to the design at the molecular level of spin crossover systems to process and store information in binary form, due to the possibility of thermal and photoinduced switching between low-spin and high-spin state.

Understanding the properties of such systems is of interest for the design of improved systems. To do so it is most informative to cross data gathered from structural determinations under varied conditions (temperature, light irradiation or pressure) and properties determination under similar conditions (magnetism, spectroscopy,...). We will present two studies of spin crossover complexes. SCO compounds show a change of spin state under application of an external stimuli (pressure, temperature, photoexcitation) and therefore have been proposed for a number of potential applications, including piezochromism.[1-5] This change goes together with modification of the population of molecular orbitals, with anti-bonding orbitals corresponding to longer metal-ligand bond lengths being populated in the High Spin (HS) state. Pressure is one of the relevant thermodynamic constraints to consider: in SCO materials based on Fe²⁺ (d⁶) ions, it usually favors the diamagnetic low-spin (LS) state, which has a lower volume than the paramagnetic HS state.

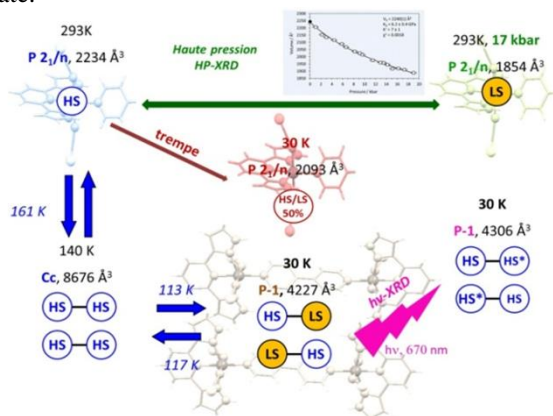


Figure 1. Phase diagram of dinuclear complex $[\{\text{Fe}(3\text{-bpp})(\text{NCS})_2\}_2(4,4'\text{-bipy})].2\text{MeOH}$
XRD = f(T, P, hv)

In the $[\{\text{Fe}(3\text{-bpp})(\text{NCS})_2\}_2(4,4'\text{-bipy})].2\text{MeOH}$ dinuclear complex, thermal spin crossover of only one iron is observed at ambient pressure, with full photoconversion in the metastable fully high-spin state by irradiation at low

temperature, as observed by both structural determination and magnetic measurements. The latter evidenced a strong magnetic anisotropy. We first undertook pressure studies using Raman spectroscopy and X-ray single diffraction at room temperature. Raman spectra evidenced a very gradual pressure-induced SCO, with markers of the LS state appearing above 7 kbar and complete SCO being observed above 25 kbar. X-ray structures evidenced that the RT centrosymmetric monoclinic structure is preserved, yielding a gradual pressure-induced SCO to a fully LS-LS state above 16 kbar.[6] Combining light irradiation, cryogenic temperature and high pressure is a difficult but interesting challenge since it allows to play with this 4-state system. Neutron diffraction data measured at the ILL using a new He gas pressure cell[7] at 10 K before and after light irradiation under 2 kbar of pressure showed that the pattern after light irradiation is consistent with conversion to the HS state. This experiment was possible since single crystals of this compound fully convert by light irradiation at low temperature, something usually difficult due to light depth penetration issues. Those preliminary results prompted us to undertake a more extensive study by X-ray absorption. Indeed the electronic and structural change in molecular SCO complexes can be thoroughly followed by XANES at the Fe K- and L_{2,3} edges,[8] the former being easily compatible with DAC environments. On SOLEIL synchrotron ODE beamline, we were able to evidence thus through their Fe K-edge spectra the HS-HS, HS-LS and LS-LS phases. At 1.8GPa conversion from the fully LS phase to apparently the mixed phase is observed, which should not be the case if indeed the LS-LS phase is the centrosymmetric phase IV. Furthermore, photoconversion by the beam to an undetermined metastable state of non negligible lifetime even at 2GPa was observed, showing that SCO compounds can be photoconverted under hydrostatic pressure. Those results were then completed by a X-ray diffraction study on single crystals on SOLEIL synchrotron CRISTAL beamline. Diffraction data collected at 200, 140, 15K and 15K after irradiation will be presented.

The second case deals with mononuclear complex showing a complete spin crossover with a rather large hysteresis. The presence of a hysteresis is the trademark of cooperative interactions between molecular complexes, and is the most interesting case for potential applications. Structural studies are often difficult due to the mechanical stresses induced by cooperative phase transitions. At ambient pressure, this compound shows a thermal SCO

with a hysteresis of 40 K centred at 143K.[9] The very abrupt spin transition is accompanied by an isostructural crystallographic phase transition.[10] We studied this compound under pressure by Raman spectroscopy and X-ray diffraction,[11] and evidenced that at room temperature no sign of the LS species is found before 25kbar, an unusually high pressure for SCO molecular compounds. A fully LS compound could be obtained at 29kbar, but the crystal amorphized. X-ray data evidenced that this compound shows both huge negative thermal expansion and negative linear compressibility below 5kbar, which was explained by a "scissor-like" geometric mechanism where SCO, thermal expansion and pressure effect act antagonistically.[11] We then completed this study with XANES at the Fe K-edge on the SOLEIL synchrotron ODE beamline, where we were able to evidence some photoconversion under a pressure of 1.2kbar at 10K. We also revisited the compressibility at room temperature with much more precise powder X-ray diffraction data collected at the SOLEIL synchrotron PSICHE beamline, which allowed us to evidence that actually NLC is present up to the range of pressures where pressure-induced SCO occurs (Figure 2).

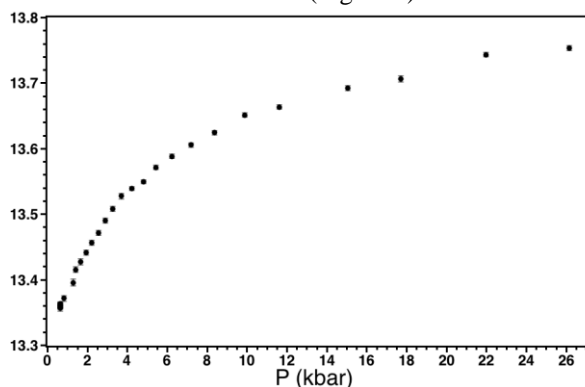


Figure 2. Evolution with pressure of the a cell parameter for complex $[\text{Fe}(\text{dpp})_2(\text{NCS})_2]$, evidencing a strong Negative Linear Compressibility

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