

**MS21-O3** Guest – induced polymorphism and quenching of disorder in the Hofmann spin-crossover compound  $\text{Fe}(\text{Pz})\text{Pt}(\text{CN})_4$  studied by *in-situ* powder diffraction.

Céline Besnard<sup>1</sup>, Delgado Pérez Maria Teresa<sup>2</sup>, Tissot Antoine<sup>3</sup>, Schouwink Pascal<sup>1</sup>

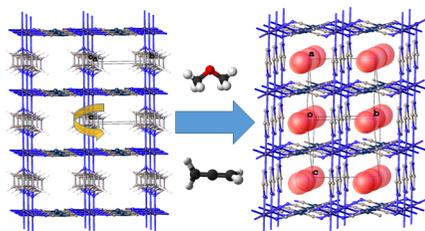
1. Laboratoire de cristallographie, University of Geneva, Switzerland
2. Département de Chimie Physique, University of Geneva, Switzerland
3. INSTITUT LAVOISIER CNRS : UMR8180, Université de Versailles Saint-Quentin-en-Yvelines, France

email: celine.besnard@unige.ch

The Hofmann-chlorate  $\text{Fe}(\text{Pz})\text{Pt}(\text{CN})_4$  has received significant attention due to its spin transition with a large hysteresis at room temperature and the possibility of bidirectional light switching. The spin-crossover behaviour, and hence colour change, can be modulated by means of absorbed gas species<sup>1</sup>, making this family of compounds very attractive materials for the design of gas sensors. The tetragonal crystal structure of both the HS and the LS state is formed by 2D layers of  $\text{Fe}(\text{Pt})(\text{CN})_4$  linked by the pyrazine ligands. In both guest-free HS and LS structure, disordered pyrazine molecules rotate around the Fe-Fe axis. As expected, most bulky guest molecules stabilize the HS state due to steric effects. Interestingly, the reverse was observed for  $\text{CS}_2$ -absorption, which was theoretically attributed to the molecule-specific sorption site, which in this case suppresses the rotational movement of the pyrazine rings<sup>2</sup>.

In order to get a better insight on the chemical sensitivity of the spin crossover properties, we have experimentally studied the effects of different gas molecules of various sizes (ethylene  $\text{C}_2\text{H}_4$ , propadiene  $\text{C}_3\text{H}_4$  and dimethylether  $\text{C}_2\text{H}_6\text{O}$ ) on the thermal spin-crossover transition. The samples were loaded in glass capillaries at a gas pressure of 1 bar, and synchrotron radiation X-ray powder diffraction data were recorded *in-situ* as a function of temperature and applied gas pressure. In agreement with the literature, the unloaded sample undergoes a phase transition with a small hysteresis ( $T_{\text{down}}^{\text{spin}}$  283 and  $T_{\text{up}}^{\text{spin}}$  309K). While the smallest guest molecule  $\text{C}_2\text{H}_4$  shifts this tetragonal – tetragonal transition by a small  $\Delta T$  ( $T_{\text{down}}^{\text{spin}}$  265K,  $T_{\text{up}}^{\text{spin}}$  278K), the absorption of the larger dimethyl ether and propanediene (loaded at 350K) causes a structural transformation to a monoclinic HS phase, whose structure was solved from the *in-situ* powder diffraction data. In this structure, pyrazine disorder is quenched. Additionally, the spin transition is significantly shifted to lower temperatures ( $T_{\text{down}}^{\text{spin}}$  207K,  $T_{\text{up}}^{\text{spin}}$  290K for propanediene and  $T_{\text{down}}^{\text{spin}}$  250K for DME)<sup>3</sup>. This exciting results illustrate that the geometry of gas molecules has a large impact on the guest-host interaction even in this very simple member of the Hofmann-family.

1 M. Ohba and others *Angew. Chem. Int. Ed.*, 2009, **48**, 4767–4771. 2 H. Ando and others *Chem. Phys. Lett.*, 2011, **511**, 399–404.



**Figure 1.** The absorption of dimethyl ether and propanediene causes a structural transformation to a monoclinic phase in which the pyrazine rotational disorder is quenched.

**Keywords:** spin crossover, *in situ* powder diffraction, gas sorption