ESRF	**Experiment title:** L-edge XAS and XMCD investigation of molecular valence tautomers self-assembled on surface	**Experiment number**: HE-3523
Beamline:	**Date of experiment**: from: July 6th 2011 to: July 12th 2011	**Date of report**: August 24th 2011
Shifts:	**Local contact(s)**: Julio Criginski Cezar	*Received at ESRF:*

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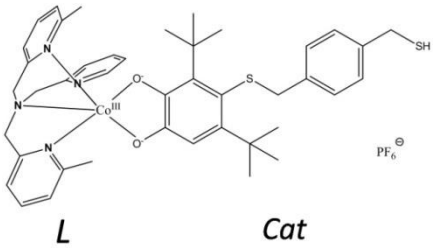
Report:

The 18 shifts beamtime has been successfully spent in the XAS and XMCD characterisation of the transition properties of molecular switchable materials in different structural environments: bulk phase and surface deposit. The high sensitivity and resolution afforded by the ID08 setup allowed to clarify the dependence of the VT behaviour on the chemical surroundings around the bistable molecules through the comparison of the conversion features of the bulk, crystalline phase, and the nanostructures on Au surface.

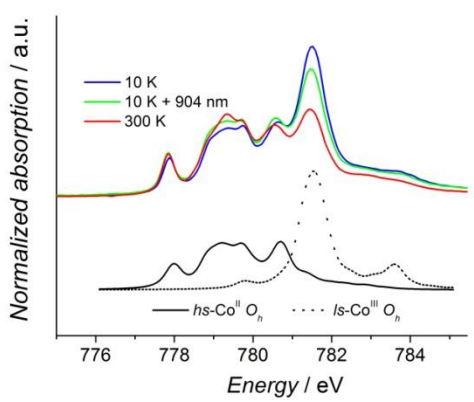
The first sample consisted in a metallo-organic Cobalt-dioxolene complex (**1**, reported on the right) showing Valence Tautomerism (VT), *i. e.* redox isomerism between the

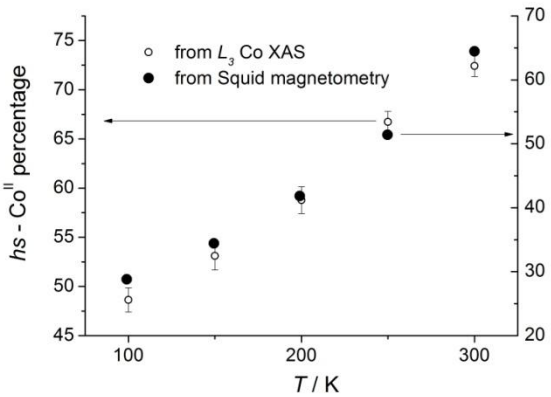
low spin $[Co^{III}(L)Cat]^+ \rightarrow$ high spin $[Co^{II}(L)(SQ)]^+$

forms, *Cat* and *SQ* being the bi and mononegative forms of the dioxolene ligand, respectively, and *L* an ancillary ligand.



The bulk material was analysed first in order to look out for the best experimental conditions, in particular to check for the presence of irreversible time evolution of the spectra under X-Ray irradiation, which was not detectable after 30 minutes beam on the same sample's spot. The temperature dependence of XAS and XMCD for **1** was then recorded at the $L_{2,3}$ edge of cobalt (*see left side of figure below for the L_3 edge*. By the analysis of the L_3 edge using calculated spectra, the quantification of the Co^{II}/Co^{III} ratio at each temperature can be carried out, making possible to extrapolate the

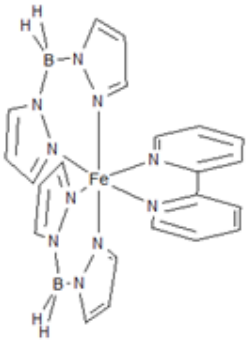




transition profile shown as empty circles in the right side of the figure above. The data confirm the occurrence of a VT transition from low spin Co^{III} to high spin Co^{II}, in agreement with magnetometry. The surface sensitive techniques used for the XAS acquisition give further insights into the conversion properties of **1**: the 25% higher high spin Co^{II} fraction, along with the reduced actually converting fraction of **1** found using XAS analysis suggests a dependence of the conversion profile of **1** to the lattice defects and grain boundaries, where the reduced crystal pressure favours the low temperature entrapment of the high temperature phase. This information is crucial for the reliability of the analysis of **1** when deposited in surface confined environments like Self Assembled Monolayers.

The behaviour of **1** when self- assembled as a monolayer from solution on a Au surface turned out to be reproducible and in line to what observed for the massive phase.

After completing the characterization of **1** a preliminary analysis of the conversion features of a Fe^{II} complex (**2**, *see left*) belonging to the Spin Crossover class of molecular switchable materials was performed. These species feature changes of the multiplicity of the spin of the ground state in function of temperature and light irradiation, and are known to tightly be sensitive to chemical surroundings. In particular, **2** looked promising because capable of being deposited on surface through clean processes carried out *in situ* (sublimation, leading to a 300 nm thick film evaporated on Au by thermal evaportion).



The results of the temperature dependence of the XAS spectra obtained before and after 658 nm laser irradiation are reported on the left hand side of the figure below. The conversion features of the thick deposit obtained from the analysis of the XAS spectra are in perfect agreement with the ones from magnetometry and point out a photoinduction of metastable high spin phase at low temperature due to soft X-Ray irradiation. We was not able observe an analogous SCO effect on a monolayer deposit obtained by thermal evaporation. A deeper investigation is required to understand if this due to a real effect of the surface interaction or to the disappearance of cooperative effects.