

**Experiment title:**

“EXAFS investigation of light induced valence tautomeric transition in Co-dioxolene molecular complexes”

Experiment number:

HE-3087

Beamline: BM29	Date of experiment: from: 06/05/2009 to: 12/05/2009	Date of report: 28/07/2009
Shifts: 21	Local contact(s): Olivier Mathon	<i>Received at ESRF:</i>

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Report:

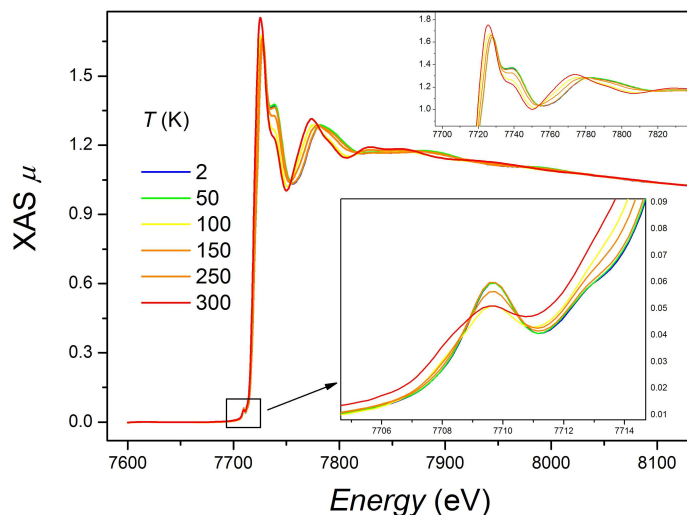
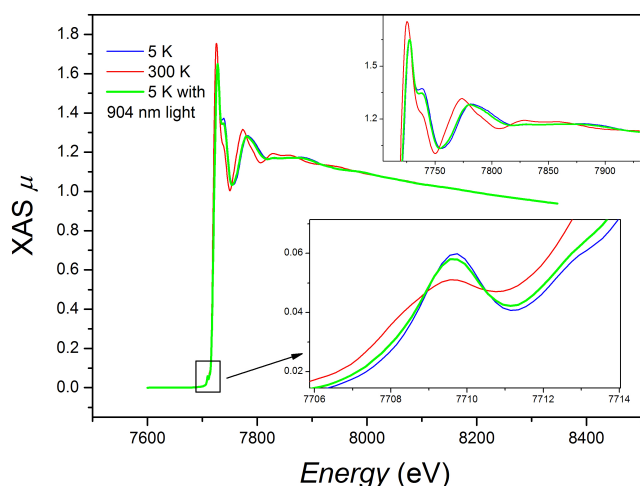
The 21 shifts beamtime has been spent in the characterisation of valence tautomeric behaviour (VT) of different Co-dioxolene molecular complexes by means of EXAFS spectroscopy, allowing to clarify the structural features of the photoinduced metastable phase for the first time for 1:1 Co/dioxolene complexes.

Co-dioxolene compounds are known to undergo an intramolecular electron transfer, induced by temperature or by light irradiation on the metal to ligand charge transfer absorption band, along with a change of spin state of the metal atom, thus yielding two species featuring different charge molecular distributions, namely **low spin** $[\text{Co}^{\text{III}}(\text{L})\text{Cat}]^+$ \rightarrow **high spin** $[\text{Co}^{\text{II}}(\text{L})(\text{SQ})]^+$, being Cat and SQ the binegative and mononegative forms of the dioxolene ligand, respectively, and L an ancillary ligand. We chose three different classes of valence tautomers to be investigated: a 1:1 Co:dioxolene valence tautomer (**1**), a 1:2 Co:dioxolene one (**2**), and a Co:polyoxolene one (**3**).

We investigated the valence tautomeric transition in function of temperature and light irradiation for each of these compounds, mixed with boron nitride and pelletized, in order to gain structural information on the photoinduced metastable state at cryogenic temperature. First of all we have measured the temperature dependence of the XAS spectrum at the K edge of cobalt, working at 300 K and 5 K and paying particular attention to the reproducibility of the signal without damaging the samples in function of the time of exposure to the X-ray beam. The obtained spectra, shown in the figure on the right just for **1** for brevity purposes, clearly let us address the contribution of the Co ion in the valence tautomeric process, showing an increase of the edge energy lowering the temperature, confirming the Co^{II} to Co^{III} transition, in line with what previously seen with magnetometric and XAS analysis on pure sample carried out at ID12 beamline at ESRF. In

particular have been taken as fingerprints of the VT process the increasing of the edge energy and the enhancing of the intensity of the pre-edge features.

Thanks to the capabilities of BM29 beamline we successfully installed a laser holder to shine on the sample the excitation light (class IIIb CW laser diode, working at 904 nm with a radiant power on the sample of about 5 mWcm^{-2}) with the aim of measuring the irradiated species: it is in fact known that exciting VT molecules on their LMCT band at cryogenic temperatures is possible to trap the high spin $[\text{Co}^{\text{II}}(\text{L})(\text{SQ})]^+$ metastable state for a long period of time.



It has been possible to measure the absorption spectra of the photoinduced metastable phase of these compounds while irradiating them with the excitation wavelength. The results obtained for **1** are shown in the graph on the left. The sample showed a 18% of photoconverted molar fraction, value that can be explained taking into account a non complete penetration of the IR light into the whole pellet's thickness and confirming XAS as a powerful tool for the characterization of metastable electronic states of these classes of molecular materials.

Thanks to the high sensitivity setup afforded by the BM29 beamline we were able to characterize the structural modifications of the first coordination sphere of the Co ion during the VT conversion following the EXAFS oscillations in function of temperature and light irradiation. During the VT process, in fact, the average distances between Co and neighboring atoms increase, acting as a fingerprint of the conversion. Preliminary data treatment taking into account a double scattering path mechanism (the first coordination sphere of Co in these molecules is made of two oxygen and four nitrogen atoms, each featuring a typical coordination length) lead to follow the transition by means of structural changes of the coordination bonds around the Co ion. The diagram, shown on the right for **1**, for the first time for this class of compounds gives evidence of the structural features of the photoinduced metastable state at low temperature, pointing out the structural changes in the first coordination sphere of the Co ion during the thermal and light induced processes. A detailed and complete analysis of the obtained data is in progress and it foresees the use of the X-ray ESRF source to investigate such molecular materials in non crystalline environments from magnetic and structural point of view.

