ESRF	**Experiment title:** "K-edge XANES and XMCD investigation of the Valence Tautomeric conversion of a Cobalt – Dioxolene complex induced by temperature and light irradiation"	**Experiment number**: HE-2544
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Shifts: 18	**Local contact(s)**: Andrei Rogalev, Fabrice Wilhelm, Alevtina Smekhova	*Received at ESRF:*

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Report:

The allocated time has been successfully spent in characterising the thermal and light induced valence tautomeric transition in a Cobalt – monodioxolene adduct,

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

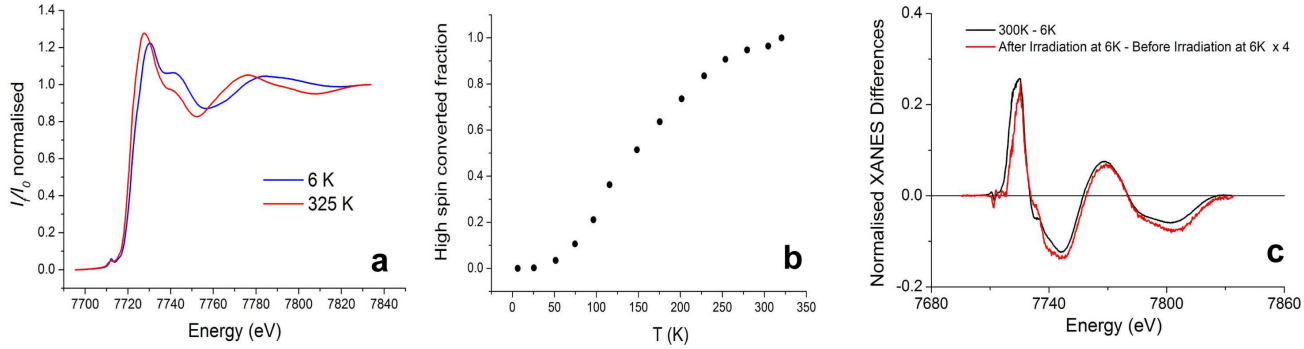
Cat and SQ being the bi and mononegative forms of the dioxolene ligand, respectively, and L an ancillary ligand. The element-sensitiveness afforded by the X-ray absorption spectroscopy assured by the ID12 beamline helped to clarify for the first time the role of the metal ion in the light-induced process for this kind of systems.

In close connection with ID12 technical staff, we developed a set-up allowing us to enlight the sample inside the experimental chamber with a laser diode of the IIIb class, paying particular attention to the personal security during the irradiation experiment. The laser has been focused on the sample keeping it almost orthogonal (incoming angle close to 80°) to the X-ray beam, affording an effective irradiation power on the sample of about 5 mW/cm^2. We want to stress that this innovative setup was arranged thanks to the powerful support of the technical staff of ID12 and in particular to the workshop team of ID12 that supported us during the whole experiment and permitted the success of the experiment. The technical development is likely to be adapted to the scheduled beamtime allocated on ID8 (July 2008).

The radiation damage of the samples under the X-rays beam has been checked at room temperature, revealing an evolution in time when full power of the beam was shining the sample. However, thanks to the means of ID12, it has been possible to adjust the photon density on the samples without degrading the optical path of the X-rays. With this adapted set-up, we could prevent degradation on time scales larger than 100 hours, and still obtain very nice SNR and reproducibility of the signal.

In order to carry out a complete and coherent investigation of the tautomeric transition we chose as first sample the mononuclear complex [Co Me_2TPA DBCat] PF_6 (1), because of its peculiar very high conversion under temperature and light stimulation and its intrinsic simpler chemical nature with respect of the dinuclear ones.

The temperature dependence of the XANES spectrum of 1 is reported in **figure a**. Following the evolution of the XANES, it has been possible to record a transition curve, shown in **figure b**, in perfect agreement with the magnetic and structural data, already ascertained. The process has been found to be completely reversible. We remark that this is the first time that this kind of reversibility is proven by XANES investigation. Since reversibility is at the core of such temperature induced or light induced transformations, we cycled several times the same sample and found that the original structure of the sample was fully preserved.



The light-induced conversion has been followed measuring the sample at 6 K in the dark, irradiating for two hours, switching off the laser source and measuring X-ray absorption again. The results, reported in **figure c**, show a percentage of conversion of about 30 %. For the first time such phenomenon has been studied with XANES, checking its reversibility and hence ruling out the possibility of instrumental artefacts. Fundamental result is the confirmation that irradiated species and high temperature species are exactly the same. To settle our findings on a firm ground, we redid the experiment on another preparation of the same sample. We found again the same temperature and light transformations, thus confirming all the experiments.

At low temperature, for a sample in the high-spin Co(II) state after irradiation, we performed an XMCD investigation. We have recorded a small XMCD signal (below 10^{-4}) that reverses with photon helicity. Further instrumental development of the sample irradiation are needed to increase the conversion rate in order to increase the XMCD signal. We are working on that in collaboration with ID12 staff to ask for more beamtime by the end of 2008. These exciting new measurements are needed to confirm the important evidence of Co(II) magnetization.

Future developments of this project are: i) a more exhaustive XMCD study of the sample, in order to obtain more detailed magnetic information on the Co centre; ii) the recording of the EXAFS spectrum with a similar laser irradiation apparatus in the 6 – 300 K temperature range, for which an apposite setup is needed to avoid x-ray diffraction peaks; iii) an analysis of the matrix dependent properties of the valence tautomeric transition also in function of the dilution, focused to evidence the eventual cooperative effect; iv) study of more complexes, dinuclear systems, to understand the role of electronic delocalisation in the process.