ESRF	**Experiment title:** "L-edge XMCD investigation of the valence tautomeric interconversion in dinuclear cobalt tetraoxolene bridged complexes"	**Experiment number**: HE-2667
Beamline: ID08	**Date of experiment**: from: 02/07/2008 to: 08/07/2008	**Date of report**: 23/07/2008
Shifts: 18	**Local contact(s)**: Julio C. Cezar, Nick Brookes	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Andrea DEI, University of Florence; Matteo MANNINI*, University of Florence; Lorenzo SORACE, University of Florence; Marie-Anne ARRIO, IMPMC – CNRS.

Added experimentalists: Giordano PONETI*, University of Florence; Philippe SAINCTAVIT*, IMPMC – CNRS; Edwige OTERO*, Synchrotron SOLEIL.

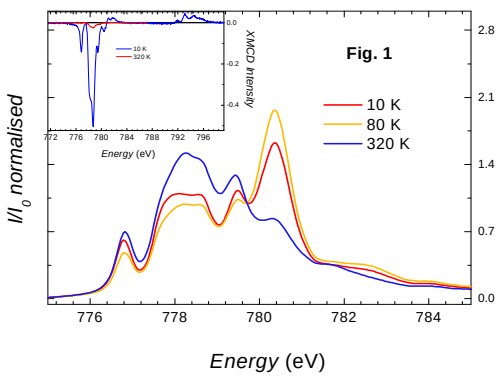
Report:

The allocated time has been successfully spent in the XAS and XMCD characterisation of two metallo-organic Cobalt-dioxolene complexes showing Valence Tautomerism (VT), i. e. redox isomerism between the

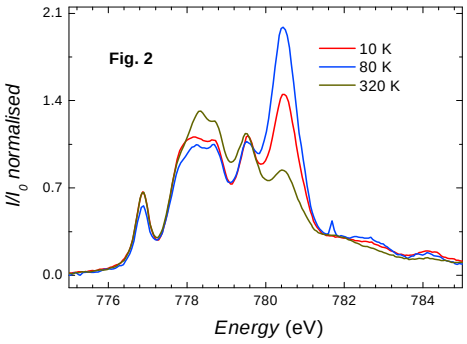
low spin $[Co^{III}(L)Cat]^+ \rightarrow$ high spin $[Co^{II}(L)(SQ)]^+$

forms, Cat and SQ being the bi- and mono-negative forms of the dioxolene ligand, respectively, and L an ancillary ligand. Thanks to the high sensitivity and resolution afforded by the ID08 setup, the VT behaviour has been investigated in function of temperature and light irradiation, allowing to unambiguously address the Co^{II}/Co^{III} ion contributions to the molecular magnetism and to directly follow its change of oxidation state during the VT transition.

Our investigation started from a mononuclear Co-dioxolene complex, previously characterised with standard magnetometry and structural analysis[1] and with Co K-edge XANES spectra in function of temperature and light irradiation (*cfr.* HE-2544 experiment). This species has been chosen as first sample because of its high percentage of photoinduced



molar fraction of the metastabile Co^{II} at cryogenic temperatures. Thanks to ID08 capabilities, it has been possible to find the appropriate experimental conditions to follow the temperature dependence of XAS and XMCD at the Co $L_{2,3}$ edges between 10 and 325 K, revealing a thermally induced transition, in accordance with the standard characterization for structural and magnetic properties (fig. 1). Moreover, a reversible x-ray induced VT conversion at low temperatures seems to occur. Data analysis (currently in progress, with Ligand Field Multiplets) aims to understand this process. All the data have been checked for reversibility and reproducibility in order to safely avoid instrumental artefacts and sample degradation.



In close connection with ID08 technical staff, we developed a set-up letting us irradiate the sample mounted in the cryostat with *III-B* class laser diodes in complete security, allowing us to pump our system to the metastabile high spin state at cryogenic temperature. Also in this case the temperature dependence of the XAS and XMCD has been recorded, showing a similar behaviour of the previous, X-rays induced, one (fig. 2).

Then we focused our attention to a more complex system: a dinuclear Co-dioxolene molecule, already characterised in function of temperature and light irradiation by standard magnetometry and electronic spectroscopy techniques[2] and by XANES investigation, recorded at the ID12 beamline (*cfr.* HE-2544 experiment). XAS at Co L_3 and L_2 edges have been recorded in function of temperature as well as under visible laser irradiation, while XMCD studies have been performed at low temperature to check the nature of the photoinduced phase. Fully oxidised (Co^{3+}) and fully reduced (Co^{2+}) analogues, for which no VT exists, have been used as standard samples The complete analysis of the acquired data will provide fundamental information concerning these VT compounds enabling the full understanding of the phenomena occurring during the laser irradiation process.

References

1 – P. Dapporto *et al*, Chem. Eur. J., submitted.

2 – C. Carbonera *et al*, Angew. Chem. Int. Ed., 43 (2004) 3136.