



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



Experiment title: Valence-to-core XES as a Probe of Oxygen-Oxygen Bond Cleavage

Experiment number:
CH-3666

Beamline: ID-26	Date of experiment: from: 30-01-2013 to: 05-02-2013	Date of report: 26-08-2013
Shifts: 18	Local contact(s): Pieter Glatzel	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Nature has selected manganese-containing enzymes as catalysts for a number of fundamental biochemical transformations involving O-O bond formation and cleavage. For example, a tetra-nuclear manganese cluster present in the active site of the Oxygen Evolving Complex of PSII is responsible for photosynthetic H₂O splitting and O-O bond formation enabling aerobic life to utilize the energy stored in the O-O bond for growth and repair. On the other hand O-O bond cleavage is involved in DNA repair, a reaction carried out by class Ib Ribonucleotide reductases. In both processes, Mn-peroxo species (Mn-μ-(O₂²⁻)-Mn) are invoked as key intermediates.¹⁻³ However, such peroxo intermediates have yet to be isolated in enzyme systems and small molecule analogues are few. Yet an understanding of such species should provide key mechanistic insights into transition metal dioxygen chemistry.

Herein, in collaboration with the Kovacs group,^{2,3} we initiated an X-ray absorption and emission study for a series of reactants, products and intermediates involved in the activation and cleavage of an O-O bond by Mn (Figure 1). These include the Mn(II) starting compound (1), the Mn(III)-peroxo dimer intermediate (2) that in turn converts into a Mn(III)-bis-u-oxo species (3) upon O-O bond cleavage. In addition we have started investigating a series of Mn-alkyl peroxo monomers with O-O bond lengths that vary over ~0.1 Å, in principle allowing us to quantitatively assess the degree of O-O activation. Extensive radiation studies were carried out for all compounds, and data was

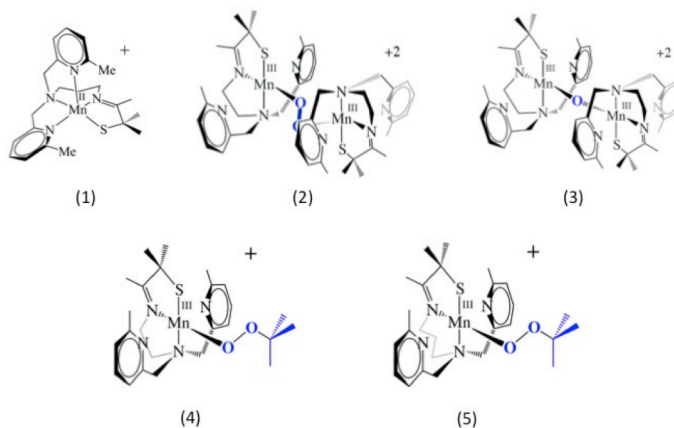


Figure 1: List of Mn compounds

acquired using multiple sample spots with a collection time per spot optimized to give the best signal to noise ratio with minimal or no radiation damage. Clear differences are seen in both the XAS and XES-V2C spectra of the starting compound (1) and the final product (3). The XAS spectra are consistent with a Mn(II) and Mn(III) species, respectively, while comparison of the XES-V2C data with theoretical calculations, are consistent with a Mn-oxo species in the final product. Unfortunately, the XES-V2C spectra of the Mn(III)-peroxo intermediate (2), resembles the Mn(III)-bis-u-oxo final product (3) and is inconsistent with its respective calculated XES spectrum, both in terms of the K $\beta_{2,5}$ relative intensities and the K β'' , suggesting a mixture of intermediate and final product, with the latter being dominant. Similarly, the rising edges of the XAS spectra of the Mn-alkyl peroxo compounds (4,5) reveal that these are mixed samples containing both Mn(III) alkyl peroxo as well as starting material, which has Mn(II) centers. As such these samples did not merit further detailed study by RIXS as initially planned. These results highlight the difficulty in synthesizing and isolating Mn-oxo and Mn-peroxo intermediates in yields and purities that are optimal for XAS/XES. We are currently working with our collaborators to better optimize the conditions for these measurements.

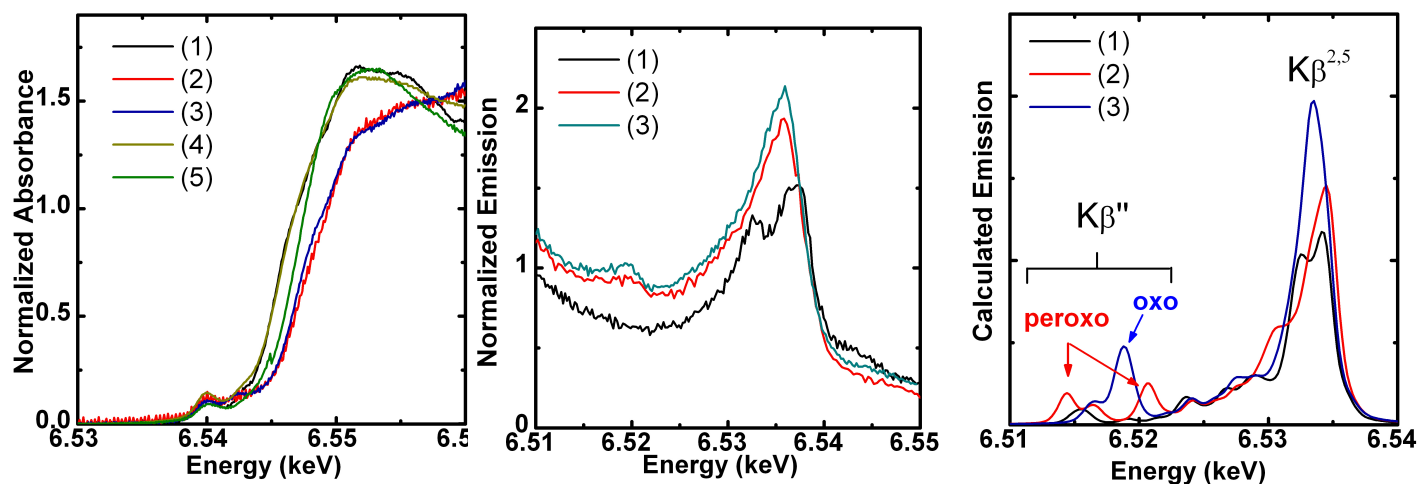


Figure 2: (left) XAS of compounds (1)-(5); (center) XES-V2C spectra of (1)-(3); (right) Calculated XES-V2C spectra of (1)-(3).

As our measurements on the Mn-oxo/peroxo systems did not yield good initial results the remainder of our beamtime was utilized to obtain initial VtC XES data, which has formed the basis for a new proposal. The preliminary experiments were aimed at understanding the information content of high energy resolution fluorescence detected x-ray absorption spectra (HERFD XAS). It has been proposed that chemically-selective XAS spectra may be obtained by detecting from valence-to-core x-ray emission (VtC XES) features known to correspond to a given ligand, though these experiments do not seem to have yet been reported. Thus, we have investigated a series of well-characterized manganese model compounds in order to develop VtC HERFD as a ligand-selective spectroscopic probe.

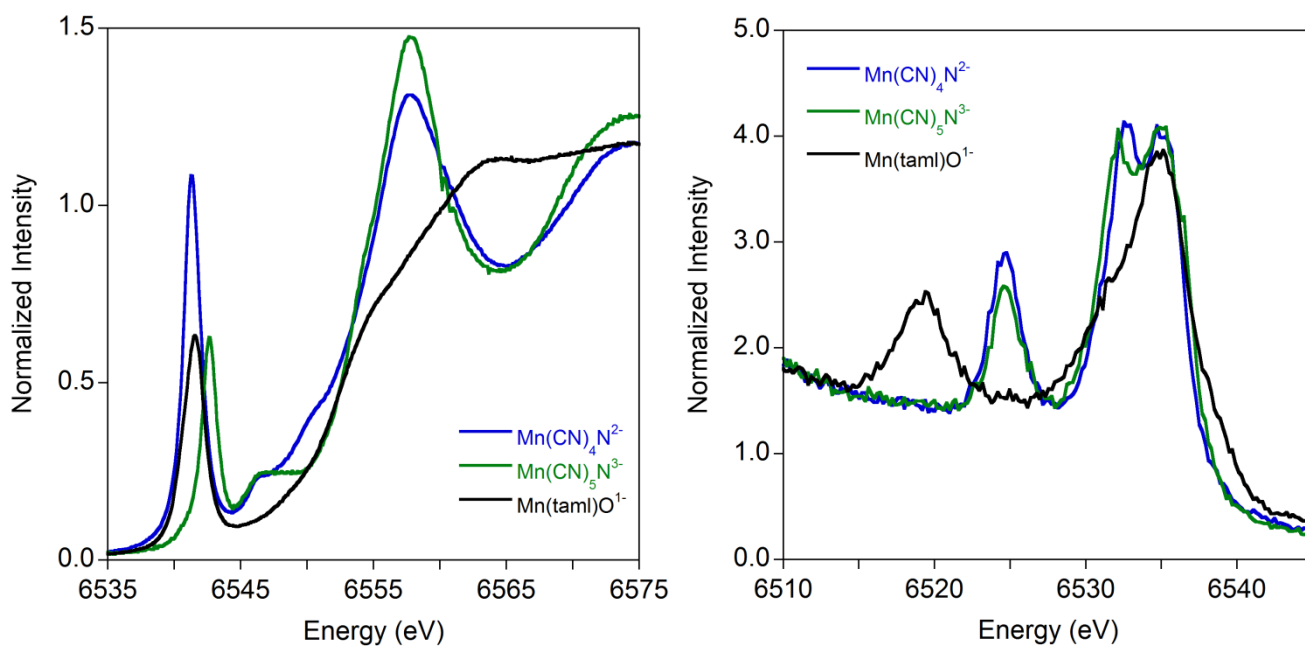


Figure 3: The standard TFY XAS (left) and non-resonant XES (right) spectra of the compounds under investigation.

We began by collecting standard total fluorescence yield (TFY) XAS and non-resonant XES spectra of our compounds (Figure 3). These spectra clearly demonstrate the respective sensitivities of these techniques: XAS to compound symmetry and ligand field strength and XES to ligand identity and metal-ligand bond length. From established methods of interpretation, we can assign the intense pre-edge XAS features as being dominated by the oxo or nitrido ligands interacting with the Mn 3d orbitals that, due to the low symmetries and short bond lengths seen in these compounds, also have significant 4p mixing. For the XES spectra, the $K\beta''$ peak may be assigned as originating from the oxo / nitrido 2s orbitals that possess a small amount of Mn np character. For the nitrido compounds, the $K\beta_{2,5}$ feature is composed of contributions from the cyanide 2s2s σ^* orbital (lower energy peak) and a mix of cyanide 2p2p σ and nitride 2p orbitals (higher energy peak) while the same feature in the oxo compound corresponds to a mixture of taml and oxygen 2p orbitals.

From these assignments it was clear that the $K\beta''$ XES features were an ideal spectroscopic handle for collecting ligand-selective XAS since they derived almost exclusively from the oxo / nitrido ligands. Further, because the pre-edges are also dominated by contributions from these same ligands, intensity modulations were expected to be pronounced and easily discernable.

HERFD spectra were thus collected by detection from these VtC features. Because energetic shifts of the peaks were possible during resonant excitation, full resonant x-ray emission (RXES) planes were collected so as to allow accurate determination of appropriate detection energies. An example of this procedure is shown in Figure 4 for $(NMe_4)_2Na[Mn(CN)_5N]$.

The VtC HERFD spectra for $(PPh_4)_2[Mn(CN)_4N]$ and $(NMe_4)_2Na[Mn(CN)_5N]$ are shown in Figure 5 and are overlaid with the respective TFY spectra. Dramatic modulations of pre-edge intensity are observed that range from slight decreases to large increases and that depend strongly on the VtC feature used for detection. Interestingly, a decrease in intensity is seen when detecting from the $K\beta''$ while detection from either of the $K\beta_{2,5}$ peaks yields large increases. This is perhaps counterintuitive as, from an analogy to resonance Raman spectroscopy, it might be expected that detecting from the oxo / nitrido-dominated $K\beta''$ would enhance the oxo / nitrido-dominated pre-edge; similarly, the low energy $K\beta_{2,5}$ feature almost exclusively derives from the cyanide ligands, so detection from this peak might be expected to result in a decrease in pre-edge intensity. Neither of these predictions, however, is supported by the experimental results.

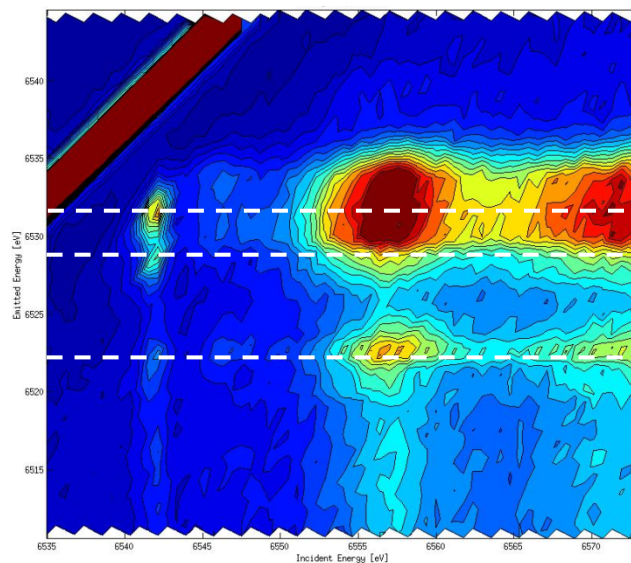


Figure 3: RXES plane for $(NMe_4)_2Na[Mn(CN)_5N]$ with the detection energies indicated by dashed lines.

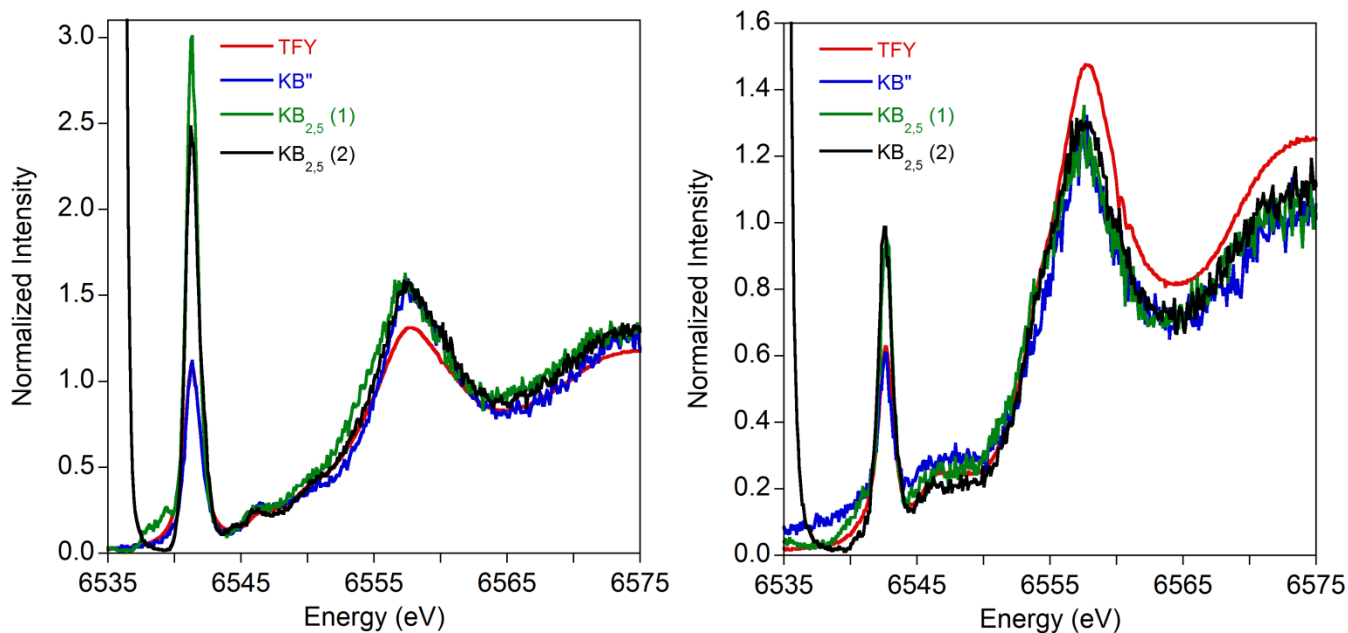


Figure 5: *VtC HERFD spectra for $(PPh_4)_2[Mn(CN)_4N]$ (left) and $(NMe_4)_2Na[Mn(CN)_5N]$ (right) shown overlaid with standard TFY XAS.*

These data demonstrate that the simple picture of being able to use VtC features for ligand-selective XAS is not entirely accurate. They do, however, indicate that additional information may be obtained by detecting XAS from VtC features. While an in-depth understanding of the physical mechanisms governing the intensity modulations observed is currently elusive, it is clear that additional factors must be considered to rationalize these observations and predict how VtC-detection will affect XAS spectra. Further study is merited.

References:

- [1] J. Yano, V. Yachandra, *Inorg. Chem.* 2008, 47, 1711.
- [2] Coggins, M. K.; Martin-Diaconescu, V., et al., *J. Amer. Chem. Soc.*, 135, 4260 (2013).
- [3] Coggins, M. K.; Toledo, S., et al., *Inorg. Chem.*, **51**, 6633 (2012).