

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:

Sustainable chemistry at the synchrotron: Water oxidation

Experiment number:

CH-4078

Beamline: BM23	Date of experiment: from: 12.6.14 to: 17.6.14	Date of report: 14.12.14 <i>Received at ESRF:</i>
Shifts: 15	Local contact(s): Suresh Gatla	

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Oxoiron(IV) species are key intermediates in the catalytic cycles of numerous heme and non-heme iron enzymes that insert an O atom from dioxygen into unactivated C–H bonds [1]. Because of the enormous importance of such oxygenase reactions in biology as well as in synthetic chemistry, over the last decade much effort has been devoted to the isolation and characterization of those reactive oxoiron(IV) intermediates and to the understanding of their reactivity patterns [2,3,4]. Macrocyclic tetracarbene framework [5] efficiently stabilizes the oxoiron(IV) unit.

In this investigation the oxidation state and the exact geometric environment of the central iron atom in different tetracarbene complexes containing iron in various formal oxidation states were subject to X-ray

absorption measurements. The complexes are depicted in scheme 1.

As can be seen in figure 1, all of the four measured samples show prepeak structures, which can be ascribed to transitions between 1s and higher unoccupied orbitals, like 3d or 4s [6] and are caused from a strong covalent iron-ligand bond [7]. Based on the edge and the prepeak energies, which was extracted using an exponential function as baseline-correction followed by a fitting with Gaussian curves, the formal oxidation states of all four complexes could be confirmed. Additionally these results can be used in DFT calculations to obtain more information about the electronic structure of iron.

Scheme 1: Structures and formal oxidation states of the examined tetracarbene iron complexes.

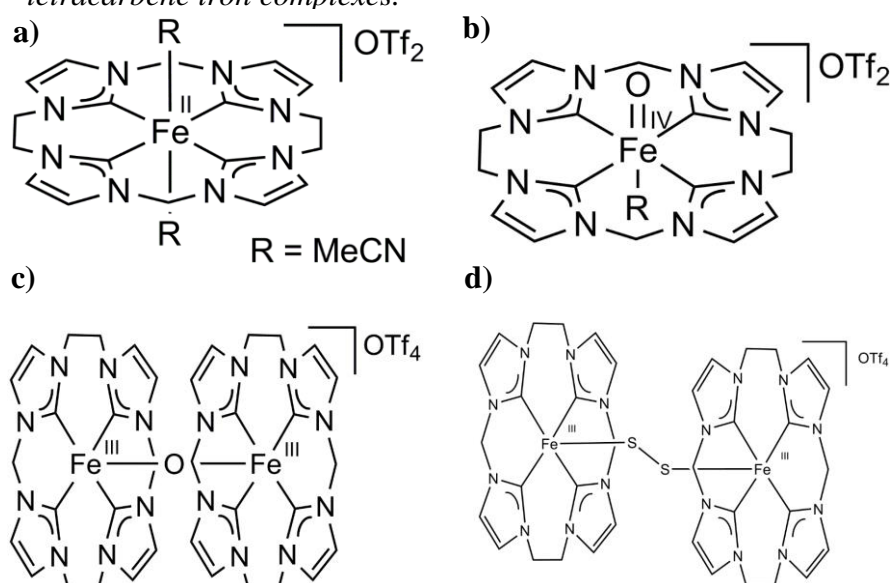
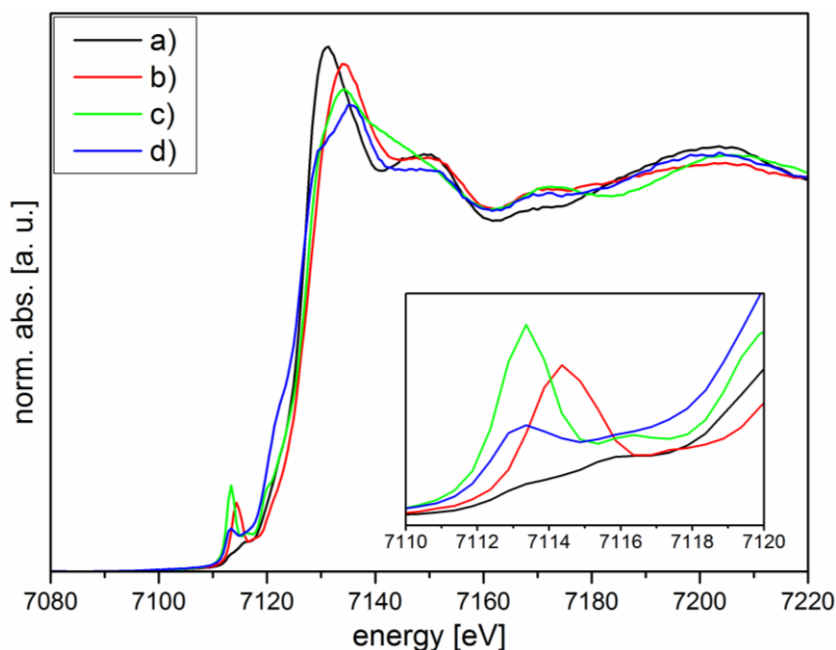
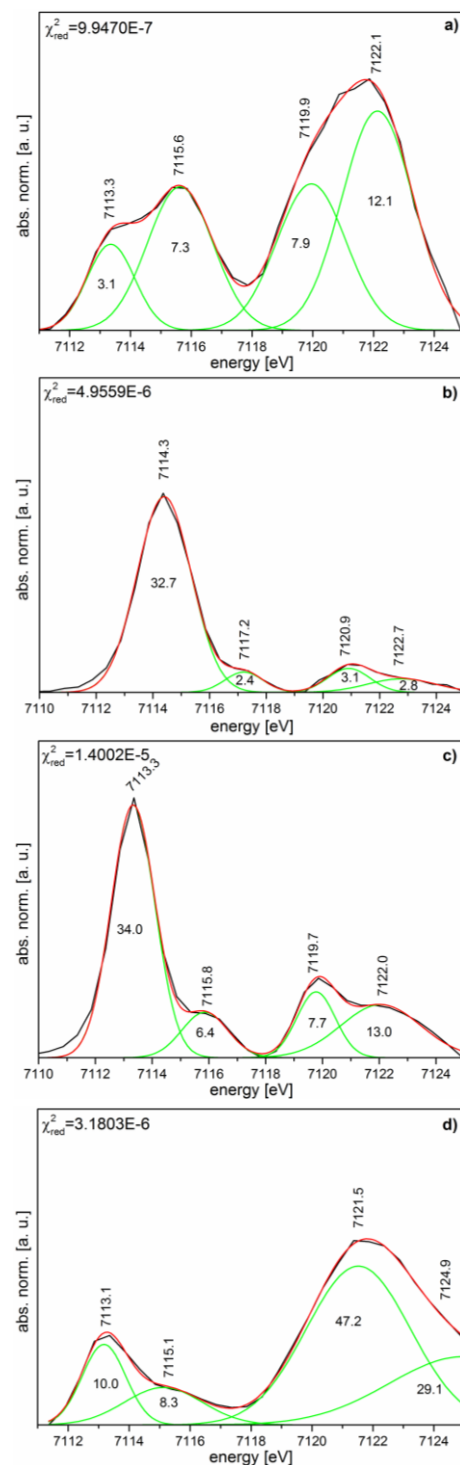


Figure 1: Left: X-ray absorption spectra of the four tetracarbene iron complexes with enlarged prepeak range. Right: background-corrected prepeak-structures fitted with Gaussian curves.



Until now, there are no tetracarbene iron EXAFS spectra known in literature, which could be used as reference for the carbon coordination shell. But there are many data for oxoiron species with tetra N-donor ligands and comparable $\text{Fe}^{\text{IV}}=\text{O}$ and Fe-O bond lengths [8]. Together with single crystal structures that were available for some of the examined complexes, a thorough EXAFS analysis was possible. There are only small differences between the distances of the available single crystal structure and the values obtained by EXAFS analysis. In general the results fit very well with the expected structures, but there are multiple scattering effects visible, which are currently analyzed.



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