EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

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://wwws.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.

ESRF	**Experiment title:** Hydrogen ligands made visible with hard X-rays: HERFD-XANES and Valence emission spectroscopy on catalytic iron hydride complexes	**Experiment number**: CH 4958
Beamline: ID 26	**Date of experiment**: from: 16.11.2016 to: 22.11.2016	**Date of report**: 22.02.2017
Shifts: 18	**Local contact(s)**: Rafal Baran	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Copper complexes have gained increasing interest as photosensitizers for photocatalytic water splitting, as they would be a cheaper alternative to the primarily used noble metal complexes. The redox potential of Cu^+/Cu^{2+} is already small and can be tuned by varyiing the geometry around the copper center as well as the electronic structure by modifying the ligand system. In particular, the inner coordination sphere is dominating these parameters.

The so called entatic state is of great interest concerning this matter. With the copper complex already being closer to an excited state, the reorganisational barrier is lowered which could lead to enhanced electron transfer rates. This concept was subject to many studies already in bioinorganic and coordination chemistry.

Applying ligand field theory to these states leads to a tetrahedron being favorable for d^{10}Cu(I) and a square planar coordination for the d^9Cu(II) systems. This also means that any geometry deviation from the ligand field limit facilitates an interconversion between the two oxidation states.

It is thus important to experimentally access the electronic (d-electrons) as well as the geometrical (ligand coordination) structure around the copper site to gain insight into the working principle of such complexes.

In the experiment CH-4958 we therefore conducted measurements on the Copper K-edge in addition to the iron hydride measurements. These were preliminary measurements in preparation of future studies as proof of principle. Furthermore these results were obtained using analyzer crystals acquired by our group.

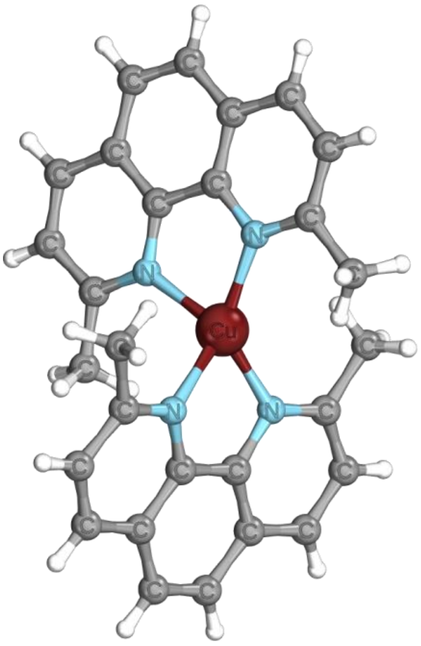

Figure 1: Crystal structure of the Cu(I) complex used for the measurements and calculations.

The complex used for this preliminary study is shown in Figure 1. The two most important facts about this system are the angle between the CuNN planes, which are important in hindsight of the entatic state, as well as the 4 CH_3 groups which can be substituted to change the electronic structure of the complex (e.g. with halides).

The spectra in Figure 2 clearly show a very nice agreement between experiment and theory. It can clearly be seen that at least one prominent feature is diminished or enhanced when changing the geometry (red arrow). This means that the ligand coordination around the central atom as well as the electronic structure (by looking at the orbitals from the calculations) can be extracted from the HERFD-XANES spectra. These are still preliminary results but they show that future studies with HERFD-XANES and vtc-XES can give tremendous insight into the structural change upon photooxidation and the influence of the ligands on this matter.

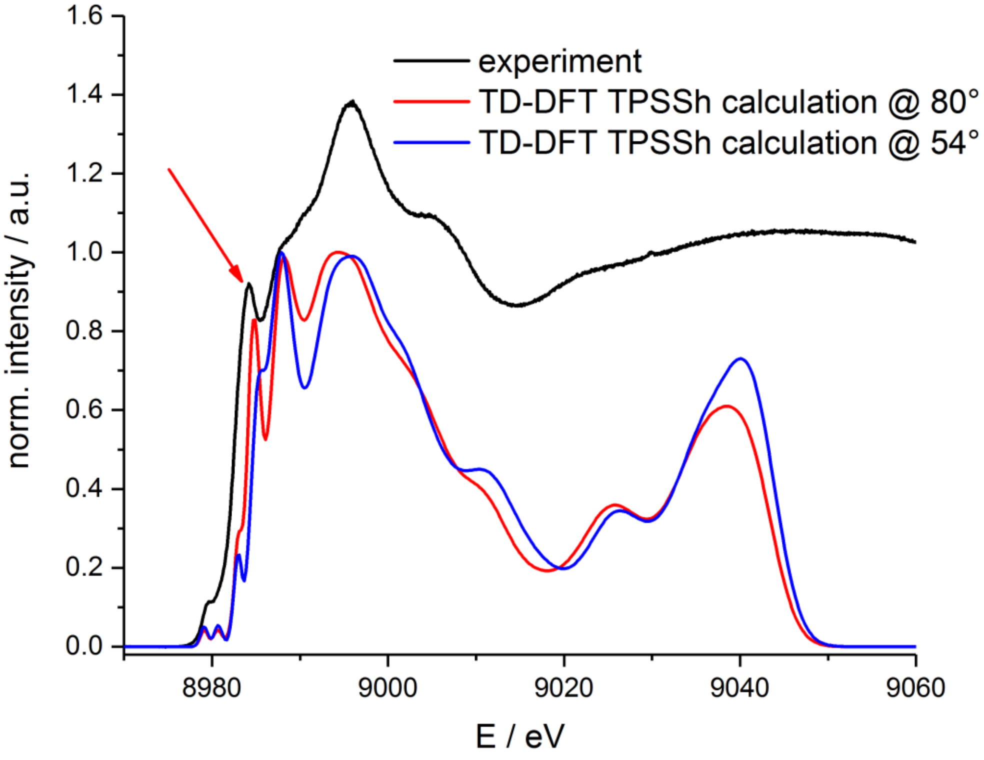

Figure 2: Experimental (black) and two theoretical HERFD-XANES spectra. The red spectrum was calculated using the crystal structure of the Cu(I) complex with an angle of 80° between the two CuNN planes. The blue spectrum was calculated using an angle of 54° to mimic the geometry of the Cu(II) (photooxidized) species.