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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.

	Experiment title: Ex-situ and in-situ X-ray absorption spectroscopy on bimetallic nano-particular iron-copper catalysts for CO oxidation as alternative to noble metals	**Experiment number**: CH-4086
Beamline: BM 25A	**Date of experiment**: from: 09 Jul 2014 to: 14 Jul 2014	**Date of report**: 10.12.2014
Shifts: 15	**Local contact(s):** Eduardo Salas	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

During the preparation of bimetallic iron-copper-nanoparticles used in this project, it was discovered that the iron precursors, which were used for the CO oxidation catalyst synthesis, show also notable magnetic properties as single molecule magnets (SMMs). In frame of the beamtime, these iron complexes were examined. The analysis of the properties and the synthesis of single-molecule magnets (SMMs) attracted a high degree of attention since their discovery in 1980[1]. Magnets are widely used in various applications but information storage is certainly one of the most important uses of magnets. In this field the size for each storage unit is of high importance with regard of storage density. By using single-molecule magnets the storage density could be increased dramatically. A further application of SMMs could be as processing elements in quantum computation[1b]. Beside manganese, whose d-orbitals are half filled with electrons, which generates a maximal spin (d^5), iron (d^6) is one of the most prominent elements, which were used for synthesis. Through varaition of the coordinating ligands the electronic structure and spin states can be influenced and with this the energy required for the change between high- and low-spin state. Iron complexes show a very high reactivity and variability to enable the synthesis of potential SMMs.

The use of cyclopetadienyl ligands represent an easy way to control the number of other coordinating ligands. The application of very bulky cyclopentadienyl ligands like penta-isopropyle cyclopentdienyl (^{5}Cp) avoids formation of sandwich complexes and allows the realisation of dimeric iron complexes. In a formation with these low valent iron complexes even triple carbon bonds like in tolane (diphenylethine) can be splitted. In the resulting carbon bridged iron dimers the iron centers show high- or low-spin properties dependend on the

Scheme: Presumed dimeric structures of the iron precursor complexes.
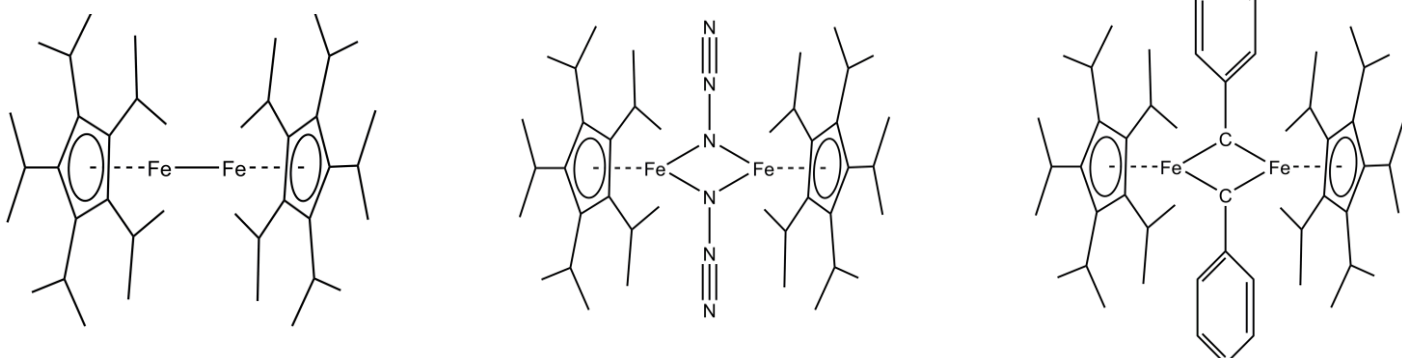
magnetic communication through the bridging atoms. Through X-ray absorption spectroscopy the oxidation state of the iron centers and their structural environment could be determined. Since no single crystal structure could be obtained for the shown complexes and due to their paramagnetic nature, no other method was available to clarify the geometric coordination. Here three complexes are shown exemplarily for an iron-iron single bond (1), a carbon bridged (2) and a nitrogen bridged (3) species.

Table: EXAFS analysis fitting parameters and results of the spectrum of $[^5CpFe]_2$, $[^5CpFeCPh]_2$ and $[^5CpFeN_3]_2$					
Sample	Abs-Bs[a]	N(Bs)[b]	R(Abs-Bs)/Å[c]	σ/Å^{-1} [d]	R/%[e] χ^2_{red} [f] E_f/eV[g] Afac[h]
1 $[^5CpFe]_2$	Fe-C	4.9±0.4	2.092±0.020	0.059±0.005	34.05
	Fe-Fe	1.2±0.1	2.256±0.022	0.087±0.008	26.4558E-6
	Fe-C	8.1±0.8	3.313±0.033	0.112±0.011	5.006
	Fe-C	2.2±0.2	3.582±0.035	0.032±0.003	0.4846
	Fe-C	2.6±0.2	4.318±0.043	0.045±0.004	
2 $[^5CpFeCPh]_2$	Fe-C	1.7±0.1	1.926±0.019	0.045±0.005	26.97
	Fe-C	8.4±0.8	2.094±0.020	0.102±0.010	13.3699E-6
	Fe-C	2.1±0.2	2.382±0.023	0.110±0.011	1.575
	Fe-Fe	1.2±0.1	3.024±0.030	0.112±0.011	0.800
3 $[^5CpFeN_3]_2$	Fe-C	3.6±0.3	2.080±0.020	0.097±0.009	31.68
	Fe-C	1.3±0.1	2.730±0.027	0.032±0.003	6.1128E-6
	Fe-N	2.2±0.2	3.179±0.031	0.112±0.011	7.407
	Fe-N	3.4±0.3	3.653±0.036	0.095±0.009	0.800

a) Abs=X-ray absorbing atom, BS=backscattering atom, b) number of backscattering atoms, c) distance between absorbing and backscattering atom, d) Debye-Waller-like factor, e) fit index, f) reduced χ^2 error (considers beside error to experiment the number of independent points and number of varied parameters), g) Fermi energy, that account for the shift between theory and experiment, h) amplitude reducing factor

For all species the presumed dimeric structures (see Scheme) could be confirmed through XAS analysis, which represents an important step for the understanding of the magnetic properties of these complexes. With knowledge about the synthesis and the siutability of XAS as spectroscopic method for verification of the structure of the complexes modifications of the complexes can be made to increase their magnetic properties.
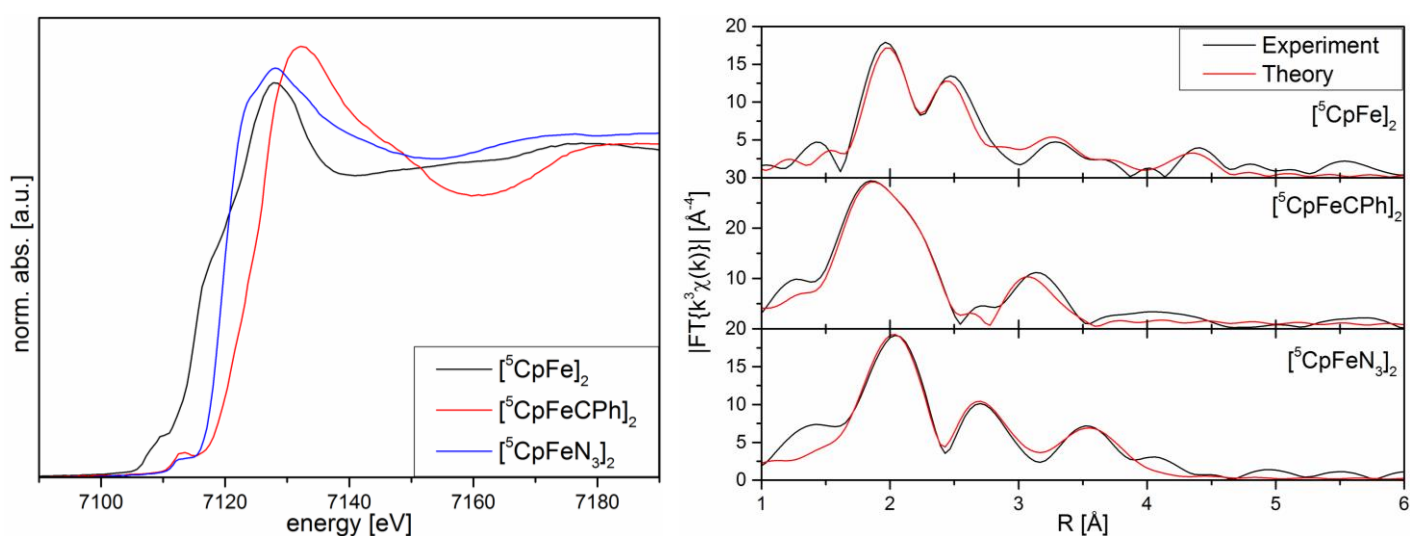

Figure: X-ray absorption spectra (left) and the Fourier-transformed spectra (right) of $[^5CpFe]_2$, $[^5CpFeCPh]_2$ and $[^5CpFeN_3]_2$.

[1] a) G. Christou, D. Gatteschi, D. N. Hendrickson and R. Sessoli, *MRS Bulletin* 2000, *25*, 66-71; b) J. R. Friedmann and M. P. Sarachik, *Annu. Rev. Condens. Matter Phys.* 2010, *1*, 109-128.