



Beam line: BM23	Experiment title: Iron XAS Investigations Relevant to Base Metal Catalysis	Experiment number: CH-4356
	Shifts: 18	Date of experiment: from: 29/04/2015 to: 04/05/2015 Local contact(s): Dr. Sakura Pascarelli
Names and affiliations of applicants (* indicates experimentalists): Prof. Dr. Serena DeBeer - Max Planck Institute for Chemical Energy Conversion Julian A. Rees*- Max Planck Institute for Chemical Energy Conversion Rebeca Gomez Castillo* - Max Planck Institute for Chemical Energy Conversion Stefan Hugenbruch* - Max Planck Institute for Chemical Energy Conversion Jessica Barilone* - Max Planck Institute for Chemical Energy Conversion		

Many important chemical processes carried out on the industrial scale involve oxidative or reductive transformations of more than one electron. The transition metal catalysts used for these processes are often costly second- and third-row metals that prefer multi-electron redox cycling, because the less expensive base metals such as iron and cobalt typically undergo one-electron redox events. The development of affordable base metal catalysts with redox-active ligand scaffolds is a promising area of research for enabling two-electron chemistry with first-row metals. The electronic structures of these complexes are complicated, and require investigation by a range of techniques to fully characterize and understand the interplay of ligand and metal-based redox events.

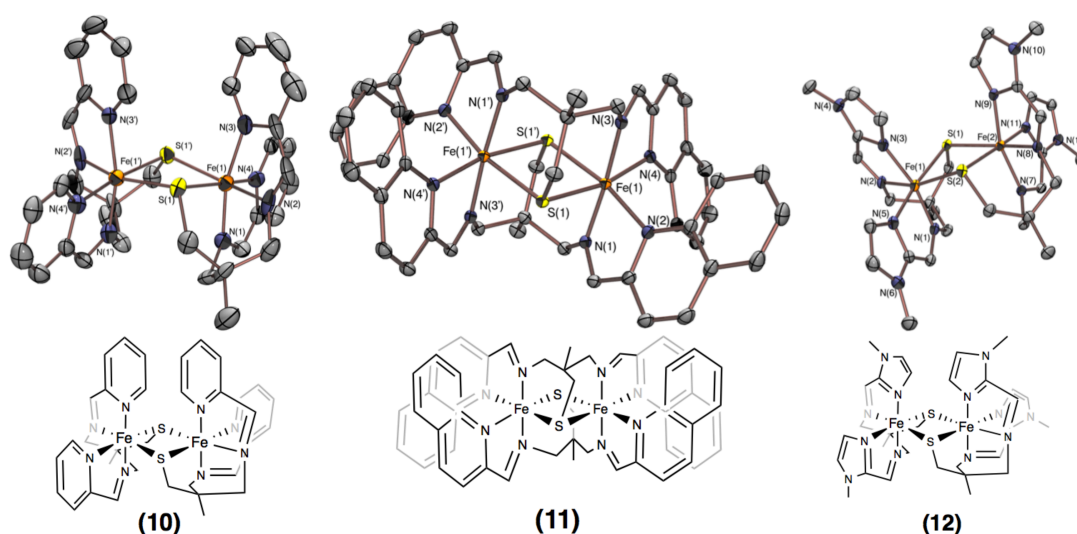


Figure 1. X-ray crystal structures and ChemDraw representations of Fe complexes **10-12** investigated in this work.

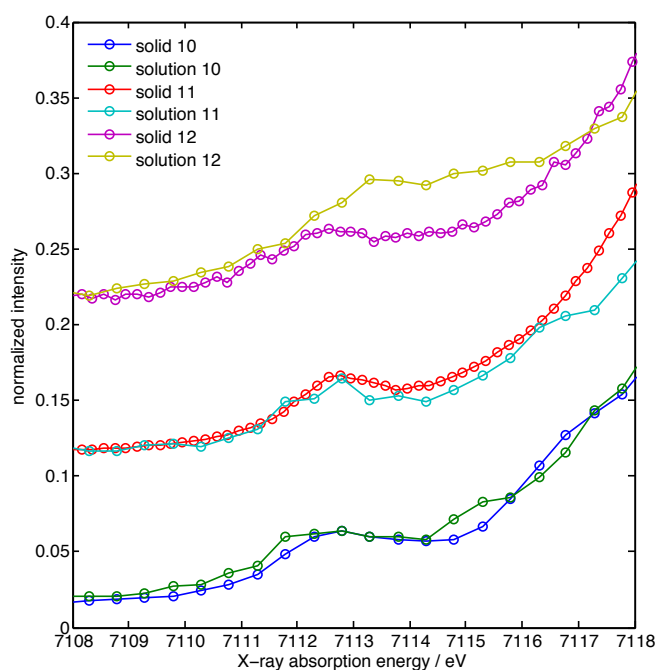


Figure 2. Pre-edge region of XAS spectra of **10-12** measured as solids and in solution.

K-edge X-ray absorption spectroscopy (XAS) can provide element-selective information on the oxidation state, spin state, and geometry of metal ions. We have investigated these properties for a series of novel Fe complexes with redox-active ligands, as well as Fe complexes of the prototypical redox-active ligand tetraphenylporphyrin (TPP) to understand the electronic structure and differences in solution and solid-state speciation.

One of the goals of this study was to identify the solid-state vs. solution-state structures of **10-**

12, as our magnetic data and reactivity studies suggest that the dimeric μ -S₂ core of **12** cleaves in solution to provide two monomeric Fe complexes. The pre-edge regions of solid and solution samples of **10-12** are shown in Figure 2. The region from ~7113-7116 is markedly different only in the case of **12**, indicating that the structure in the solution state is different from that shown in Figure 1.

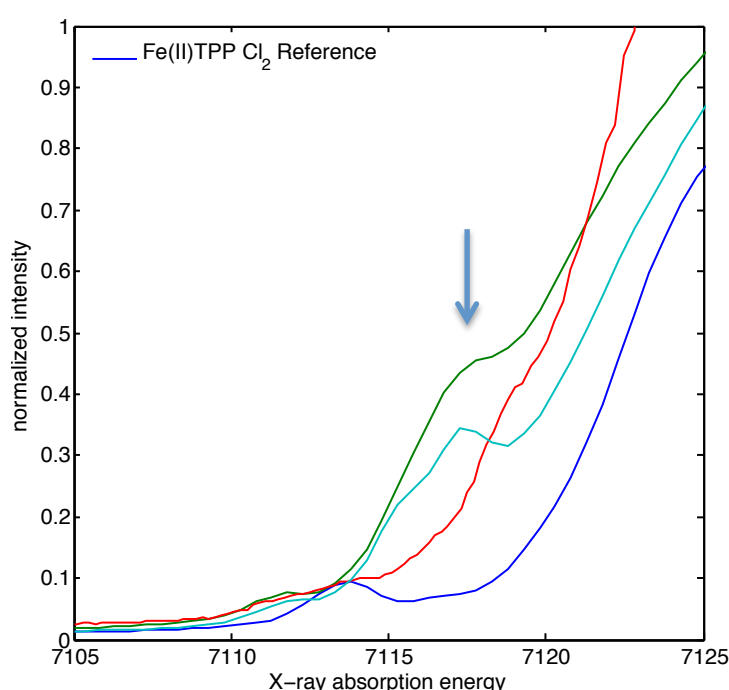


Figure 3. Fe K-edge XANES spectra of the Fe(II)TPP Cl₂ precursor complex and reduced derivatives.

in this case is considerably stabilized by the loss of the axial Cl ligands. Thus, we believe these data show that upon reduction of the Fe(II)TPP Cl₂ precursor, the axial Cl ligands are lost.

Manuscripts for both of these series of data are in preparation.

The Fe K-edges of a series of FeTPP complexes were also collected to attempt to characterize the identity and structure of the complexes following multi-electron reduction. A primary question for this subproject is the presence or absence of the axial Cl ligands, which are known to be present in the starting ferrous species. In these spectra, the peak and/or shoulder at ~7117 eV (indicated) in the green and teal

traces has been tentatively assigned as a 1s → 4p_z excitation, which