ESRF	**Experiment title:** High resolution X-ray emission and XANES studies of the binding mode of aminoacids to metal sites in biomimetics for catalyis and enzymes	**Experiment number**: CH2754
Beamline:	**Date of experiment**: from: 22/10/2008 to: 28/10/2008	**Date of report**: 01/03/2009
Shifts:	**Local contact(s)**: T.C: Weng	*Received at ESRF:*

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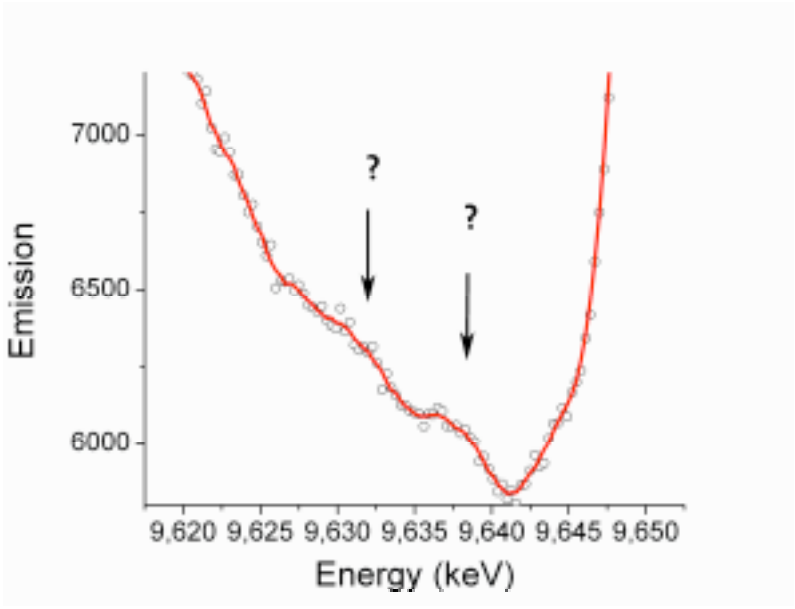
Report:

Nature has already invented very efficient catalysts able to perform high turnover rates. Bioinorganic mimics of these metalloenzyme active sites could be used as catalysts. Porphyrin arrays are of continuos interest as a mimic for the light harvesting appartus in plants, algae and bacteria (Suijkerbruijk, 2007). There are industrial efforts in mimicry of nature light harvesting systems for new solar cells. This study is focused on hybrids of a metalloporphyrin core surrounded by pincer metal groups* to study the effect of the ligand on the electronic structure of the metal. Models compounds without pincer ligands (Zn Tpp and Zn Pthalocyanine) were measured as well for comparison.

The crossover peak Kβ" at the lower energy side of the $K\beta_{2,5}$ emission peak has been assigned to the ligand 2s band energy and is caused by transitions from the metal 4pcharacter in this band to the metal 1s. This implies that the strength of the metal 4p-ligand 2s hybridization is directly visible in the crossover peak. It turns out that the crossover peak is sensitive to the difference in protonation of a solvent ligand, even in the presence of coordinated nitrogen (from imidazoles), as shown in carbonic anhydrase (CA) and in the CA bioinorganic model compounds [Mijovilovich et al]. Also the crossover peak is sensitive to the difference between N and O bound to a metal [Bergmann et al, 1999]. These results are not achievable by normal EXAFS and are of sound importance for the understanding of the mechanism in many proteins and enzymes. In this run the crossover and the $K\beta_{2,5}$ could be measured, using the new multicrystal analyzer (see figure 1).



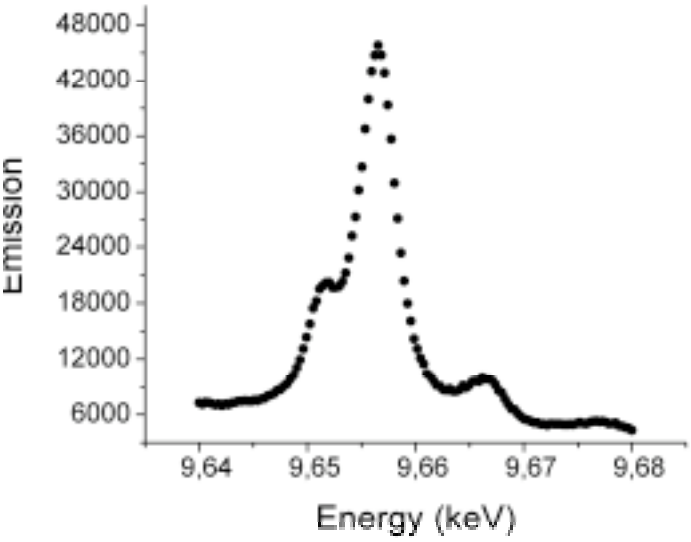


Figure1: crossover (top) and the $K\beta_{2,5}$ (bottom) for the compound with the pincer ligand to Zn(TPP)

DFT calculations for the valence band projected DOS (as visible in XES) are being performed to understand the nature of the crossover peaks (Fig 1 top), and the $K\beta_{2,5}$ (Fig1 bottom).

REFERENCES

* Sample from Prof Bert Klein Gebbink's group.

B. Suijkerbuijk, R.J.M. KleinGebbink. Merging Porphyrins with Organometallics: Synthesis and Applications. J Angewandte Chemie International Edition, 2008, 47, 39, 7396-7421.

A. Mijovilovich, P. Glatzel, U. Bergmann, G. Parkin, P. Ellis, and J.E. Penner-Hahn. "High resolution X-ray emission: carbonic anhydrase solvent protonation": In preparation

http://www-conf.slac.stanford.edu/ssrl/2004/reg/abs_detail.asp?absID=128

U. Bergmann, C.R. Horne, T.J. Collins, J.M. Workman, and S.P. Cramer. Chem. Phys. Lett. 1999, 302, 119-124.