



Contribution ID: 14

Type: **Poster contribution**

A possible mechanism for X-ray induced photoreduction

Thursday, 5 July 2012 10:30 (1h 30m)

Oxidation state changes of metal organic complexes play an important role in many chemical and biological processes. X-ray absorption near edge spectroscopy (XANES) is a powerful tool to follow these changes since it can directly probe the oxidation state of a metal center[1]. However, X-rays themselves are known to cause photoreduction in photosensitive samples[2, 3]. In order to reduce X-ray induced photoreduction, it is important to gain a deeper understanding of this process. XANES was used to investigate the influence of temperature, solvent content and chemical composition on three model systems.

Based on our results, we could propose a model for X-ray induced photoreduction of metal organic complexes: A low energy electron[4] generated upon X-ray irradiation attaches to the metal center, yielding a short-lived excited state. Photoreduction of the metal center becomes permanent by an oxidation in the ligand, accompanied by the release of a leaving group and an electron. A possible temperature dependence can be explained by the temperature dependence of the oxidation reaction.

[1] D.C. Koningsberger, R. Prins, X-ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES, Chemical Analysis, John Wiley & Sons, New York, 1988.

[2] J. Yano et al., PNAS 102, 12047-12052, 2005.

[3] I. Schlichting, K. Chu, Curr. Op. Struct. Biol. 10, 744-750, 2000.

[4] B. Boudaiffa et al., Science 287, 1658-1660, 2000.

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Session Classification: Poster Session

Track Classification: Biological / Pharmaceutical Research