ESRF	**Experiment title: X-Ray Absorption Spectroscopy structural studies of Cu complexes containing the hydrophilic phosphine-based ligands**	**Experiment number**: CH-3283
Beamline: BM08	**Date of experiment**: from: 22/06/2011 to: 28/06/2011	**Date of report**: 21/01/2013
Shifts: 18	**Local contact(s)**: Angela Trapananti	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Marco Giorgetti, University of Bologna, Bologna, Italy

Angela Trapananti, ESRF, Grenoble, France

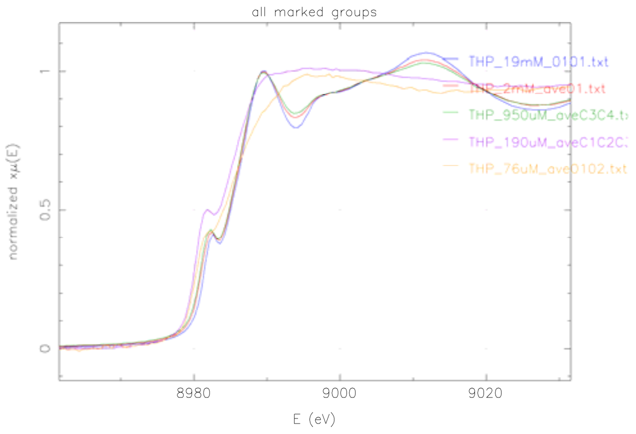
Marco Minicucci, University of Camerino, Camerino, Italy

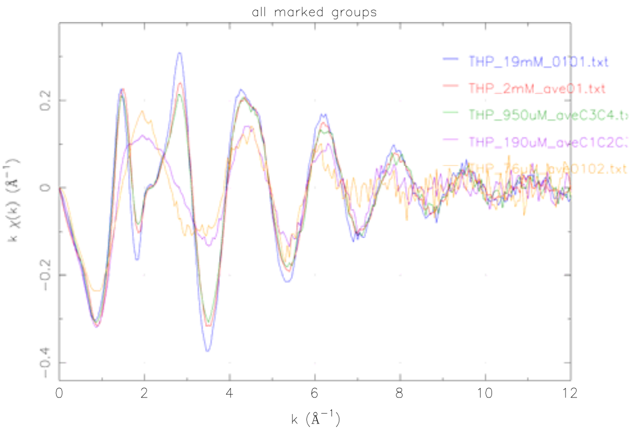
Giuliana Aquilanti, Sincrotrone ELETTRA, Basovizza, Italy

Report:

The project was aimed to the study the local atomic arrangement of the copper(I) atom in a series of phosphine metal complexes of the type $[Cu(P)n]^+$, namely [Cu(thp)4][PF6]; $[Cu(bhpe)_2][PF6]$; $[Cu(PTA)_4](BF_4)$; $Cu(mPTA)_4][(CF_3SO_3)_4(PF_6)]$ using a series of XAS spectra taken at a different concentration. Solutions at four or five different concentration (between 0.05-1 mM) were prepared in the Chemistry Lab, and recorded at the BM08(which also provides sagittally focused beam) in order to investigate the possible dissociation in solution which leads to less coordinated $[Cu(P)n]^+$ species (n = 2, 3), as postulated by recent studies [1]. Due the high dilution, measurements have been be carried out in fluorescence mode and using the 13-elements high-purity Ge fluorescence detector available at the BM08. A suitable cell for solution (from the University of Bologna) was used and placed appropriately at the beamline. The solution samples will be kept in cells with kapton windows and measured at ambient temperature. In addition, solid samples to be used as a reference for the coordination geometry of Cu(I) have been also measured in transmission mode at ambient temperature.

The allocated beamtime was successfully used . The first 2 shifts were utilized for the beamline set-up including the positioning of the cell for liquids and solid-state detector optimal position. Among the different HP Ge element of the detector , numbers 10 and 11 did not work properly and therefore have been excluded. Due to the low concentration of the photoabsorber in solutions, 4 to 6 spectra have been averaged to get a good S/N ratio. The figure below (left) displays the comparidon of the XANES spectra of [Cu(thp)4][PF6] at different concentration obtained after a pre-analysis which has included: a) the columns corresponding to the different elements of the Ge detector have been averaged; b) The average sum has been divided by the incoming beam intensity I0. c) the edge position (maximum of the first derivative) has been checked for the Cu reference foil (measured in chamber 2 after the sample) and if necessary, the energy scale has been shifted in order to have to have the Cu edge at 8979 eV; d) signals have been normalised.





As seen the X-ray absoprtion spectrum spectra strongly depends on the dilution conditions, with features changing in both edge and XANES characteristics, which makes feasible the use of the XANES with a well defined fingerprint for the coordination number (n= 2, 3 or 4) of Cu(I) complexes [2,3].

Figure in the rigth panel shows the corresponding extracted EXAFS signals. Both amplitude and phase change at different diluition conditions. The interpretation of these spectra will be performed along the lines described in recent publications [4,5] on the basis of a comparison between experimental and theoretical signals. In particular the quality of these data will allow us to retrieve reliable information on the average local environment of tetrahedral Cu(I) species whose coordination sphere is saturated by four equivalent hydrophilic tertiary phosphines (in solid).

The dissociation phenomena occurring under dilute conditions seem to play a relevant role in the cytotoxic action of these species. It has been clearly established that more labile compounds are more efficient as antitumor agents [1].

Present results prove the feasibility of these kind of EXAFS experiments on the high dilute conditions setup available at BM08 and encourage the submission of further proposals along the same research line.

[1] F. Tisato et al. Rapid Comm. Mass. Spectrom. 2010, ***24***, 1610.

[2] L. Kau, D.J. Spira-Solomons, J.E. Penner-Hahn, K.O. Hogdson, E.I. Solomons J. Am. Chem. Soc. 1987, ***109***, 6433

[3] N.J. Blackburn, R.W. Strange, J. Reedijk, A. Volbeda, A. Farooq, K. D. Karlin, J. Zubieta, Inorg. Chem. 1989, ***28***, 1349.

[4] G. Aquilanti, G. Aquilanti, M. Giorgetti, M. Minicucci, G. Papini, M. Pellei, M. Tegoni, A. Trasatti, C. Santini Dalton Trans. **40**, 2764 (2011). doi:10.1039/C0DT01401J

[5] M. Giorgetti, S. Tonelli, A. Zanelli, G. Aquilanti, C. Santini, M. Pellei, Polyhedron **48**, 174-180 (2012). doi: 10.1016/j.poly.2012.08.073