EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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.

ESRF	**Experiment title:** Single-bunch Energy Dispersive XAFS: characterisation of electronically excited states of Cu(I) complexes	**Experiment number**: CH-2849
Beamline: ID24	**Date of experiment**: from: 9 September 2009 to: 16 September 2009	**Date of report**: 27/02/2014
Shifts:	**Local contact(s)**: O. Mathon	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

***J. Evans, University of Southampton, UK**

***M Tromp, University of Southampton, UK**

M. W. George, University of Nottingham, UK

Report:

A pump-probe procedure was successfullly set up on ID24 using an in-house 3 ns Q-switched Nd:YAG laser operating at 450 nm with a 10 Hz repetition rate. Detection was with a Ge microstrip detector consisteing of 1024 elements of 50 μm pitch.[1] The experiments were performed in 4-bunch mode and allowed isolation of single bunches.

Two Cu(I) complexes were investigated with the aim of examining the ^{3}MLCT (Metal to Ligand Charge Transfer) phosphorscence state: $[Cu(dmp)_2]^+$ (**1**) (dmp = 2,9-dimethylphenanthroline) and $[Cu(dbtmp)_2]^+$ (**2**) (dbtmp = 2,9,-di-*n*-butyl-3,4,7,8-tetramethylphenanthroline) in acetonitrile solution. The former complex (**1**) provided a calibration experiment for this energy-dispersive method against a scanning XAFS pump-probe procedure.[2] The more bulky ligand (**2**) was utilised to increase the lifetime of the excited state. The difference spectrum between the ground state and the Cu(II)-like excited state is shown in Figure 1.

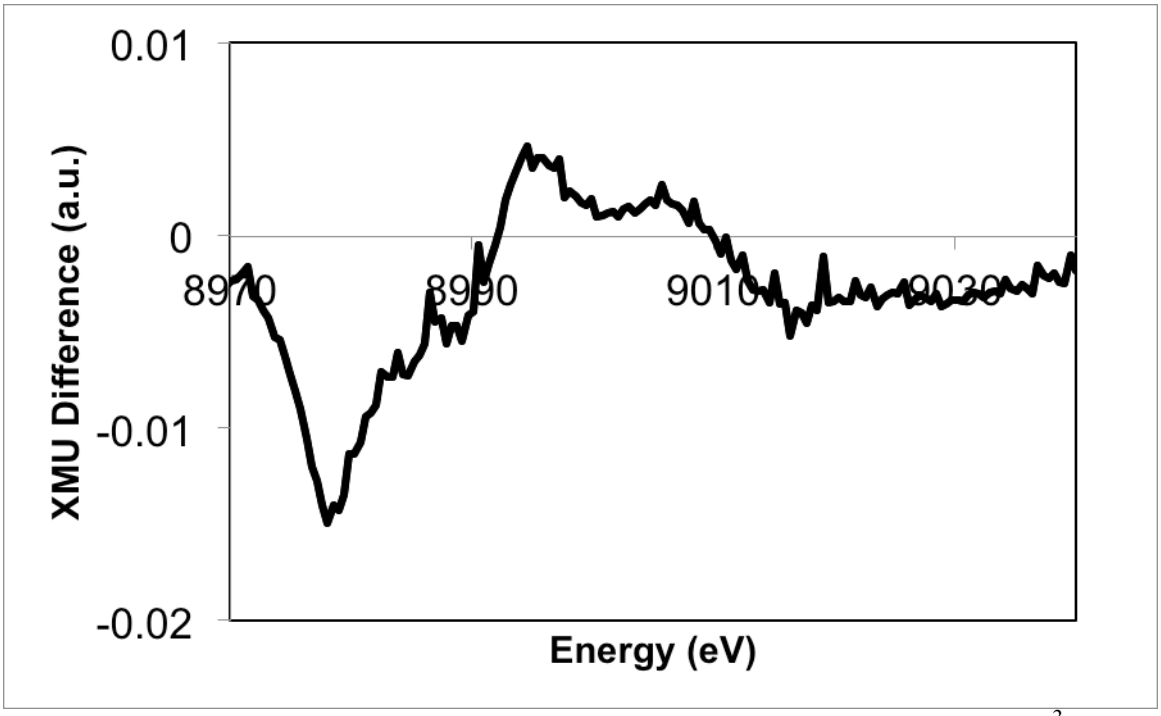

Figure 1. Difference Cu K-edge XAFS spectrum between ground and ^{3}MLCT state of $[Cu(dbtmp)_2]^=$ (15.5 mM in MeCN)

Using this difference spectrum and altering the delay between the laser and X-ray pulses, a time profile for this excited state could be measured (Figure 2).

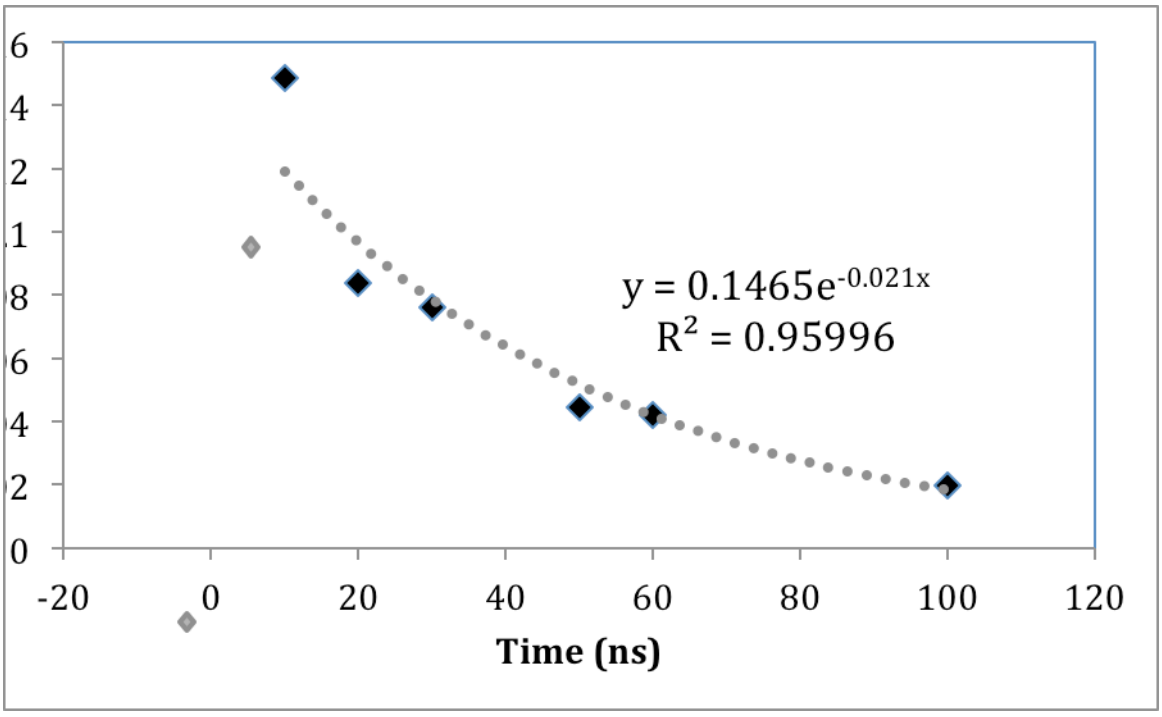

Figure 2. Time profile of the decay of $^3[Cu(dbtmp)_2]^=$ at room temperaure in MeCN.

The experiment demonstrated the viability of energy dispersive EXAFS as a means of studying transients of short duration via a laser pump- x-ray probe method, even though it requires measurment in transmssion. Subsequent to the experiment considerable work has been carried out on veriying the photochemistry via uv-visible transient absorption procedures, density functional calculations of ground and excited states, and simulations of

the XANES spectra from the calculated structures, and the work is now published.[3] The $^3[Cu(dbtmp)_2]^=$ state shows a Jahn-Teller bending distortion from tetrahedral (as a d^9 excited state) to an inter-ligand diheral angle of 60°. The XAFS evidence strongly difavoured exciplex formation and a 5-coordinate excited state

References

1. Headspith, J., et al. *Nucl. Instrum. Method Phys. Res. A*, 2003, **512**, 239-244; Headspith, J., et al. *IEEE. Trans. Nucl. Sci.*, 2007, **N55-2**, 2421-2428.
2. Chen, L. X., Shaw, G. B., Novoyhilova, I., Liu, T., Jennings, G., Attenkofer, K., Meyer, G. J. , Coppens, P. *J. Am. Chem. Soc.,* 2003, **125**, 7022-7034.
3. Tromp, M., Dent, A. J., Hedspith, J., Easun, T. L., Sun, X.- Z., George, M. W., Mathon, O., Smolentsev, G., Hamilton, M. L., Evans, J., *J. Phys. Chem. B*, 2013, **117**, 7381-7387.