ESRF	**Experiment title:** Structure and formation dynamics of an electronically excited trinuclear Pt-Pt-Tl complex	**Experiment number**: CH-2404
Beamline: ID09B	**Date of experiment**: from: 13/09/2007 at 8:00 to 16/09/2007 at 8:00	**Date of report**: Friday, October 12, 2007
Shifts:	**Local contact(s)**: Prof. Michael WULFF	*Received at ESRF:*

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Purpose/Results expected

The experimental aim was to investigate the structural kinetics of a tri-nuclear exciplex formed between tetrakis-μ-pyrophosphito-diplatinate(II) (abb. PtPOP) and Thallium(I). Briefly summarized, the components of an exciplex (excited state complex) remain spatially separated in the ground state, and will only form a complex as long as one of the components is in an electronically excited state. The Tl-PtPOP exciplex constitutes an ideal system for the study of reversible association reactions, since the exciplex (characterized by 3 heavy nuclei in close proximity) scatter X-rays significantly more efficiently than the separated ground state components (2+1 nuclei far apart).

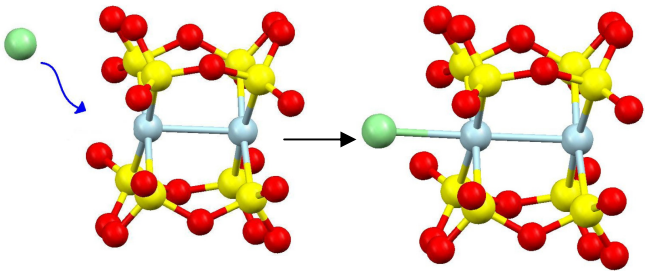

Figure 1. *The excited state complex (exciplex) formation between PtPOP and Thallium(I).Steel green = Tl, Steel Grey = Pt, Yellow = P, Red = O.*

The nine shifts of beamtime granted in September 13th-16th was a compensation for the beamtime loss attributed to beamline problems during the initial CH-2404 run late April 2007. As mentioned

in the report submitted on this earlier beamtime, the spring experiment acted as a *proof of concept* where the fundamental experimental phenomenon was successfully documented, but where the high level of noise in the data did not allow for a detailed fitting of the structural parameters.

Method

The laser-pump X-ray-probe setup for diffraction of liquids at beamline ID09B was used. Through the absorption of excess X-ray pulses, an array of three rotating chopper wheels can isolate a single X-ray pulse from the synchrotron. Prior to arrival of the X-ray pulse at the sample, a femtosecond laser pulse excites the sample, thus making possible the recording of scattering images of excited state systems at various delays after laser excitation.

A solution of Thallium(I)-sulphate and PtPOP was made in argon-purged water, and brought into circulation of the liquid jet. The resulting liquid sheet (300 μ thickness) was subsequently pumped by a laser pulse (λ = 390 nm) stretched to 2 ps and probed by the X-ray beam at various time delays.

Results

Prior to analysis, the recorded *laser-on* and *laser-off*-images are radially integrated and subtracted to yield difference curves. These curves display the change in scattering power as a function of the 2Θ-angle at a certain time-delay τ. The curves shown below (*fig. 2, left*) are from an experiment with a PtPOP concentration of 12 mM and 0.6 equivalents of Thallium(I) for every PtPOP molecule. At the earliest delay (100 ps) only the difference signal of excited state PtPOP is seen, but at later delays, the signal from the diffusion controlled exciplex formation can be seen as a drastic increase in the difference signal at low q. This behaviour is in extremely good agreement with a diffusion controlled association reaction

During the recent beamtime in September, we collected data of very good quality as illustrated below (*figure 2, left and right*). Compared with the initial beamtime in April, we have seen a remarkable improvement in the signal-to-noise ratio, and expect the fitting of structural parameters to improve likewise. The experiment was performed on samples fabricated through different (and independent) synthetic routines. The results can be reproduced consistently.

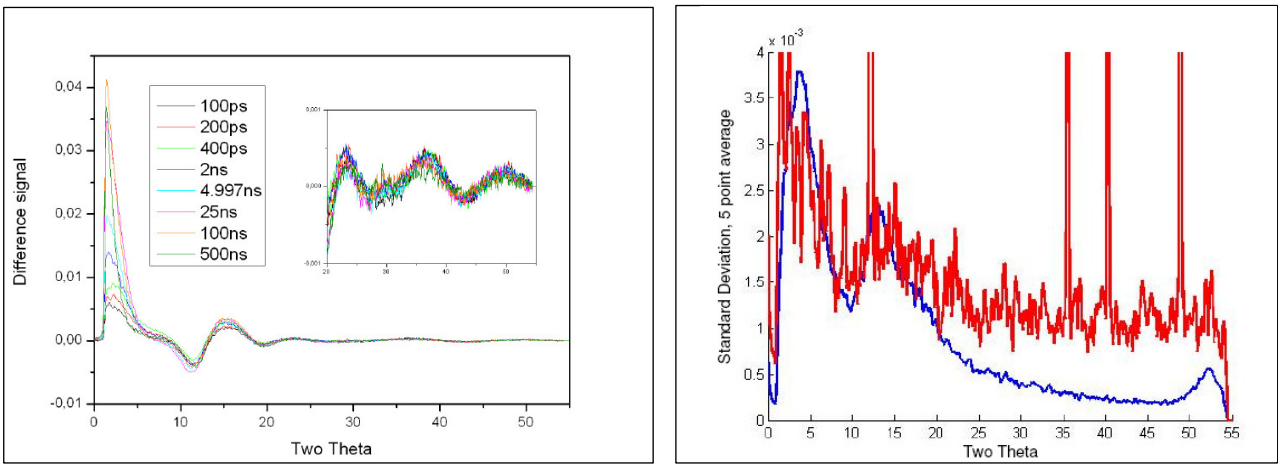

Figure 2: *Left: difference curves constructed through subtraction of the radially integrated images. The X-ray scattering fingerprint of the exciplex is seen as the grow-in at low 2Θ-angles. Right: plot of the noise from the CH-2404 experiments conducted in April (red) and September (blue). The low noise-level at scattering angles above 20 degrees is crucial in the structural interpretation of the data.*

Preliminary fitting of the results:
Radial difference curves are constructed by calculating the scattering intensity from a laser-excited and a non-excited sample (*fig. 3*). The initial fitting routines have produced decent fits for an excited state Pt-Pt distance of ~ 2.7 Å and an excited state Pt-Tl distance of ~ 2.7 Å. This should be compared to the ground state Pt-Pt distance of ~ 3.0 Å and a ground state Pt-Tl distance too large to be measured (which confirms that PtPOP and Tl+ are not associated in the ground state).

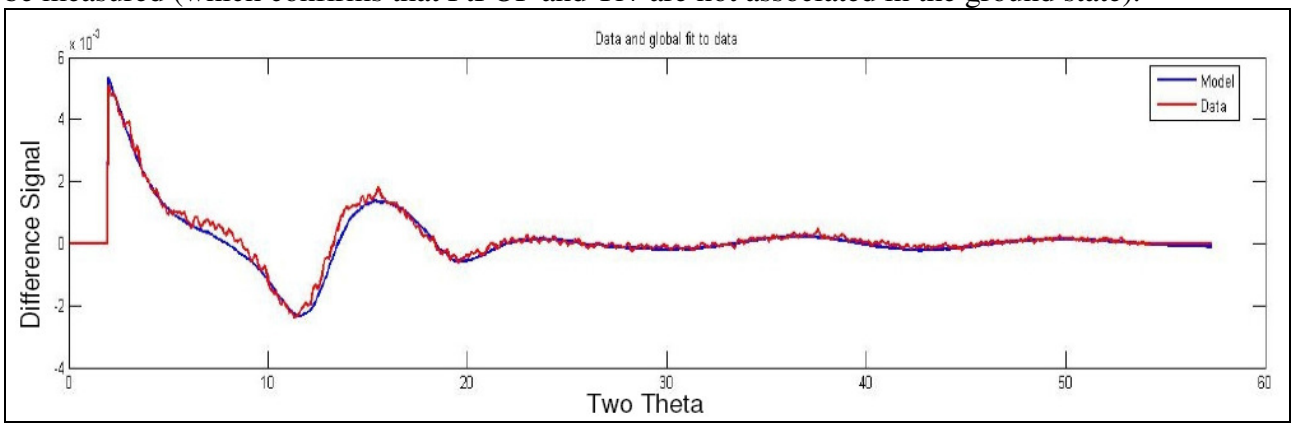

Figure 3: *The difference signal from a 12 mM PtPOP sample with 0.15 equivalents Thallium(I) 2ns after laser excitation (red curve) and the fit operating with a 2.7 Å distance between the platinum and thallium nuclei (blue curve).*

Simulations of the solvent cage:
A closer look at figure 3 reveals a discrepancy between the fit and the recorded data in the 2Θ-region between 5 and 20 degrees. This discrepancy originates in the rearrangements of the solvent cage around the PtPOP-Tl system. We have initiated a molecular dynamics (MD) simulation of these solvent rearrangements, in order to incorporate this effect in the ongoing analysis, and allow for a more detailed optimization of the structural parameters.

The kinetics of the system and suggestions for further experiments:
It is clearly evident that the largest changes in the difference curves take place in the 2Θ-region below 5 degrees (see *fig. 2 (left)*). These parts of the curves contain valuable information on the formation kinetics of the Tl-PtPOP system, and we are currently in the process of incorporation a diffusion controlled kinetic model into our data. However, due to the shadow from the beamstop and the lower number of pixels at lower apex, we suggest to improve the counting statistics in this region through a time-resolved Small Angle X-ray Scattering experiment. Such a study will provide an efficient handle on the formation kinetics of the system, and complete the picture on the structural kinetics of exciplexes in liquid solution. An application for beamtime with this aim was submitted September 1st 2007.

Conclusion
Considering the quality of the recorded data and the fit achieved during the preliminary analysis, the experiment must be considered a success. Work is ongoing with respect to improve the fit, and with the aim of publication of the results as soon as possible.