Supplementary Material (ESI) for *PCCP*

# Supporting Information

# Structure of a Short-lived Excited State Trinuclear Ag-Pt-Pt Complex in Aqueous Solution by Time Resolved X-ray Scattering

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## *Experimental procedures*

### Materials

$K_4$PtPOP (CAS#: 80011-26-3, octahydrogen-tetrapotassium-tetrakis[μ- [diphosphito-κP:κP']]-diplatinate) was prepared according to published procedures.[1,2] The dry powder was stored under argon atmosphere in tightly sealed glass containers. The purity of the substance was checked by absorption and emission spectroscopy. Silver trifluoromethanesulfonate ($AgCF_3SO_3$) was prepared by adding a surplus concentrated NaOH (CAS#: 1310-73-2, sodium hydroxide) to a solution of technical grade $AgNO_3$ (CAS#: 7761-88-8, silver(I) nitrate). The white product was rinsed with water at least 5 times before it was dissolved in smoking trifluoromethanesulfonic acid (CAS#:1493-13-6, $CF_3SO_3H$) and diluted to a concentration of 1 M as a stock solution.

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## Characterization of PtPOP

Absorption and emission spectra ($\lambda_{ex}$ = 350 nm) were recorded for the pure PtPOP sample to ascertain purity of the compound. The spectra were in excellent agreement with the literature[3] and indistinguishable from the spectra shown in Supporting Information to Christensen et al.[4] and Haldrup et al.[5]

## Preparation of solutions

Oxygen causes degradation of PtPOP and acts as a quencher of the triplet-excited state. Thus, samples were to the widest extent possible handled in a protective Ar- or $N_2$-atmosphere. Weighing chambers were purged with Ar or $N_2$ before weighing. The solvent (18.2 mS milli-Q water) was purged with Ar through a Dreschel bubbler for at least 2 hours before dissolution of PtPOP-salt to prepare a solution being 24 mM in PtPOP. Likewise a solution of $CF_3SO_3Ag$ (12 mM) and $CF_3SO_3H$ (12 mM ) in water was purged with argon for 2 hours before the start of the experiment. Immediately before the start of the experiment, equal volumes of these solutions were mixed to produce a solution being 12 mM in PtPOP, 6 mM in $AgCF_3SO_3$, and 6 mM in $CF_3SO_3H$. This solution was introduced into the sample system.

## Beamline ID09B at ESRF

The time-resolved liquid-diffraction experiment was carried out using the well established pump-probe protocol for the ID09B beamline described by Wulff et al.[6] and Cammarata et al.[7] More information, especially on the data retrieval protocol implemented at ID09B can be found in the supporting information to the paper by Ihee et al.[8]

## The laser pump pulse

The laser pulse used was the third harmonic (260 nm) of a 780 nm pulse generated by a mode-locked Ti:sapphire laser (Dragon, KM labs). The 100 fs pulse was stretched to 3.3 ps by passing it through two rods of fused silica. The laser power was 32 mW corresponding to 32 μJ pr pulse on the sample.

## The x-ray probe pulse

For these experiments, the storage ring was in the Hybrid mode 24*8 +1, consisting of one 4 mA single bunch diametrically opposed to a 196 mA multi-bunch beam composed of 24 groups of 8 bunches spread over 3/4 of the storage ring circumference. The x-ray choppers were phase-locked to the x-ray emission from the single 4 mA bunch, from which the U17 undulator produced a “pink” x-ray pulse with a triangular energy distribution with a maximum at 18.2 KeV, 3% bandwidth, and a pulse length of about 100 ps. This process is described in detail by Cammarata et al.[7]

The scattered x-rays from the interaction of the x-ray probe with the liquid sample were detected by a 133 mm MARCCD detector placed 50 mm from the sample. This geometry allowed for collection of x-ray photons with a scattering angle less than $2\theta = 55°$.

## The pump-probe cycle

A single pump-probe sequence consisted of a laser-pulse arriving at the sample followed by an X-ray probe pulse with a time difference $\tau$. This sequence was repeated at 986.3 Hz, being the 360th subharmonic of the ESRF ring. The MarCCD was exposed to the scattering sequence for ~ 5 s, corresponding to ~5000 individual pump-probe sequences, after which the CCD was read out. Subsequently, the time delay $\tau$ was changed, and a new image acquisition with the same total exposure time was carried through.

The experiment utilized an on-off sequence of image acquisitions: $\tau_{ref}$, $\tau_1$, $\tau_{ref}$, $\tau_2$, $\tau_{ref}$,...$\tau_n$, where $\tau_{ref}$ corresponds to a reference/negative time delay (”laser off”), i.e., the laser pulse arrived at the sample 3 ns after the x-ray probe pulse. The positive delays $\tau_1$-$\tau_n$ were selected in the interval from 100 ps to 1 $\mu$s. The uncertainty in the delay between pump and probe events was less than 10 ps. This on-off sequence was chosen to minimize instrumental drift between successive laser-on and laser-off exposures. For the experiments reported in the present work, the entire data collection cycle was repeated 36 times.

### Experimental setup

The experimental setup used at ID09B consisted of a sample container protected from oxygen by a hydrated Ar atmosphere. The sample solution was circulated through a sapphire nozzle resulting in a uniform liquid film of 300 μm thickness, which also was protected by an Ar atmosphere. The sample volume investigated was defined by the volume intersected by both by the x-ray probe pulse and laser pump pulse, entering at a 10° angle and focused to ellipsoid shapes of 100 × 60 μm and 110 × 185 μm, respectively. A flow-speed of 3.0 m/s ensured that the sample was fully exchanged between each pump-probe sequence. Furthermore, at this flow-speed the outflow of liquid from the illuminated volume between pump and probe events was negligible, even for the longest time-delay of 1 μs.

## *Data analysis*

### “Zinger” removal

“Zinger” is a collective term for a single- or few-pixel outlier. ”Zingers” are endemic to CCD measurements. The first step in the data-analysis was the removal of these from the raw CCD images. Subsequently, the images were corrected for polarization effects and changes in the beam-phosphor interaction length as a function of scattering angle. This was done using a standardized protocol implemented at ID09B at the time of the experiments (available upon request).

### Azimuthal integration

Images were integrated azimuthally by defining a set of N equidistant values in the $2\theta$ variables $[2\theta_1,...,2\theta_N]$, and assigning the average of the intensities of the pixels in the bin defined by the interval between two adjacent $2\theta$ values $[2\theta_i ; 2\theta_{i+1}]$ to the lowest of these($2\theta_i$), yielding a set of scattering-angle dependent intensities $I(2\theta_i)$. The full set of intensities of a given exposure gives the scattering signal $S(2\theta)$. The standard deviation of the intensity of a bin $\sigma(2\theta_i)$ was defined as the standard deviation of pixel counts in the given bin.

## Scaling

The construction of difference scattering curves necessitates a scaling of the individual scattering curves in such a way that a direct comparison between laser-on and laser-off measurements is possible.

The azimuthally integrated S(2θ) curves described above were converted to an absolute scale by scaling the high-angle scattering of the measured curves to the calculated high-angle scattering of a “liquid unit cell” (described below). At high angles, scattering is dominated by the incoherent (Compton) scattering which is insensitive to structural changes. The theoretical value of the incoherent scattering was calculated using the numerical approximation introduced by F. Hajdu[9] and G. Palinkas.[10]

In the typical experiment the “liquid unit cell” corresponds to the atoms pr one PtPOP-ion in an aqueous solution of $K_4$PtPOP (12 mM), (6 mM), and $CF_3SO_3H$ (6 mM). Or, 1 equivalent $K_4$PtPOP, corresponds to 0.5 eq (6 mM/12 mM) of $CF_3SO_3Ag$, 0.5 eq. (6 mM/12 mM) of $CF_3SO_3H$, and 4625 eq. (55.55 M/12 mM) of water. This yields a liquid unit cell containing the following atoms: 2 Pt, 8 P, 20 O, 8 H, 4 K (from PtPOP), 0.5 × (3 O, 3 F, 1 S and 1 Ag) from $CF_3SO_3Ag$, 0.5 × (3 O, 3 F, 1 S 1H) from the trifluoromethanesulfonic acid, and 4625 water molecules, for which Hajdu[9] also presented a numerical approximation of the incoherent scattering.

The scaling was carried out in a 5-degree interval around 2θ = 47°, where the integrated difference curve is very close to zero. The result of the data analysis was qualitatively independent of the size and position of the normalization interval as long as the interval stayed in the high-angle region (>35°) and was symmetric around an isosbestic point.

## Construction of difference scattering curves (ΔS(θ))

The scaled scattering signal curves of the positive time delays were converted to difference signal scattering curves by subtracting the average of the negative time delay curves exposed immediately before and after the positive time delay. By having a reference on either temporal side of the positive time delays the effects of intensity- and instrumental drifts are minimized.

### Outlier Removal

For a set of measurements at a given time delay, some exposures were significantly different from the rest of the set. To prevent these outliers from influencing the final analysis, they were removed before averaging. This was done by applying the unbiased Chauvenet criterion:[11] *Given set of measurements* $m_i = (m_1 \ldots m_n)$ *with standard deviation* $\sigma_m$*, it is possible to calculate how many measurements one would expect at a given value of the measured parameter* $m_i$*, based on the distribution of the measurements and the number of repetitions. If a measurement* $m_i$ *lies outside the region where the expected number of measurements (estimated from the set of measurements and excluding* $m_i$*, and hence "un-biased") is >0.5, the measurement fails the criterion.*

The Chauvenet criterion was implemented in a point-by-point fashion over the entire 2θ range described above. Thus, for each time delay and for each $2\theta_i$ value, the ensemble of measurements $\Delta S(2\theta_i)$ (36 individual values) was analyzed and outliers failing the Chauvenet criterion were identified. If more than 2.5% of a given $\Delta S(\tau)$ curve failed the criterion, the curve was discarded. The remaining curves for a given time delay were subsequently averaged to produce the final $\Delta S(2\theta)$ curve used in the data analysis.

### Uncertainty estimate

The standard deviation for each 2θ-point was calculated using the method given Haldrup (2010). By this method, a second-order polynomial is fitted to consecutive 20-point segments of the 1000-point dataset and the standard deviation calculated from the residuals of this local fit. In essence, this is a high-pass filter, removing the information-containing low-frequency oscillations while retaining the high-frequency noise from which the error is estimated.[12]

### Conversion from 2θ to Q

In most neutron and x-ray scattering studies, the scattering is described in terms of the wave vector transfer Q, $Q = (4\pi/\lambda)\sin\theta$, where λ is the wavelength of the incident beam. The conversion was carried out using 30 point numeric deconvolution around the 18.2 keV maximum of the x-ray spectrum. This was done by dividing the undulator spectrum into 30 $I(\lambda_i)$-bins, converting $\Delta S(2\theta)$ to $\Delta S(Q)\lambda_i$ for each $\lambda_i$, and subsequently forming the weighted average of the 30 curves, where the weight for each $\lambda_i$ was given by the corresponding intensity $I(\lambda_i)$.

### Scattering contribution from bulk solvent

As described by Cammerata et al.[13] the bulk solvent contribution to the difference signal due to impulse heating of a liquid sheet for a given time $\tau$ between 100 ps and 1 ms can be completely described by two hydrodynamic variables (temperature T and density ρ) and their differentials through the linear combination:

$$\Delta S(\tau) = \left.\frac{\partial \Delta S}{\partial T}\right|_{\rho} \Delta T(\tau) + \left.\frac{\partial \Delta S}{\partial \rho}\right|_{T} \Delta \rho(\tau)$$

This was first applied to the impulse-heating response of methanol,[13], and the implementation of this method to water is described in the supporting information of both Christensen et al.[4] and Haldrup et al.[5]

### Simulated Difference Signals

As described in the main text, the simulated difference spectrum is described by the 5 terms in equation 1:

$$\Delta S(Q,\tau)_{simulated} = \Delta S(Q,\tau)_{solutes} + \Delta S(Q,\tau)_{solvent}$$

$$= \left(\alpha_1 \Delta S_{PtPOP^*} + \alpha_2 \Delta S_{AgPtPOP^*} + \alpha_3 \Delta S_{AgPtPOPAg^*}\right) + \left(\left.\frac{\partial \Delta S}{\partial T}\right|_{\rho} \Delta T + \left.\frac{\partial \Delta S}{\partial \rho}\right|_{T} \Delta \rho\right)$$

(Equation 1)

The α's designate the molar fraction of the given species scaled to the liquid unit-cell like the scattering data (i.e. $\alpha_3 = [AgPtPOP^*Ag] / [PtPOP]_{total}$). It is thus a simple matter of multiplying the fractional output of the fitting with the total PtPOP concentration to get the absolute concentration of the transient species at a given time-point.

Mass conservation is explicitly incorporated in the difference signal from the excited species as follows.

$$\Delta S(Q,\tau)_{solutes} = S_{on} - S_{off}$$

Where

$$S_{on} = \alpha_1 S_{PtPOP^*} + \alpha_2 S_{AgPtPOP^*} + \alpha_3 S_{AgPtPOPAg^*} + (1 - \alpha_1 - \alpha_2 - \alpha_3) S_{PtPOP}$$

$$S_{\mathrm{off}} = S_{\mathrm{PtPOP}}$$

For example, the contribution to $\Delta S(Q,\tau)$ from PtPOP* to the $\tau$ = 300 ps signal, when no complexes have yet been formed, is obtained as

$$\Delta S_{\mathrm{PtPOP}^*}(Q) = S_{\mathrm{On}}(Q) - S_{\mathrm{Off}}(Q) = \alpha_1 S_{\mathrm{PtPOP}^*}(Q) - (1-\alpha_1) S_{\mathrm{PtPOP}}(Q),$$

Thus,

$$\Delta S(Q,\tau)_{\mathrm{solutes}} = \alpha_1 S_{\mathrm{PtPOP}^*}(Q) + \alpha_2 S_{\mathrm{AgPtPOP}^*}(Q) + \alpha_3 S_{\mathrm{AgPtPOPAg}^*}(Q) - (1 - \alpha_1 - \alpha_2 - \alpha_3) S_{\mathrm{PtPOP}}(Q)$$

$$- \alpha_1 S_{\mathrm{PtPOP}^*}(Q) - (1 - \alpha_1) S_{\mathrm{PtPOP}}(Q) + \alpha_2 S_{\mathrm{AgPtPOP}^*}(Q) - (1 - \alpha_2) S_{\mathrm{PtPOP}}(Q)$$
$$+ \alpha_3 S_{\mathrm{AgPtPOPAg}^*}(Q) - (1 - \alpha_3) S_{\mathrm{PtPOP}}(Q)$$

$$= \alpha_1 \Delta S_{\mathrm{PtPOP}^*} + \alpha_2 \Delta S_{\mathrm{AgPtPOP}^*} + \alpha_3 \Delta S_{\mathrm{AgPtPOPAg}^*}$$

The simulated difference signal takes as input the molecular structures of the ground state, excited state and exited state complexes of PtPOP. The scattering contribution from each of these molecular structures is evaluated through the orientation-averaged Debye equation calculated within the framework of the independent atom model. This orientation-averaged scattering intensity of a molecule consisting of N independent atoms with form factors ($f_1 \ldots f_N$) is calculated[13] through

$$\langle I(Q) \rangle_{\mathrm{orient.avg.}} = \left\langle \left| \sum_{k=1}^{N} f_k e^{iQ\cdot r_k} \right|^2 \right\rangle_{\mathrm{orient.avg.}} = |f_1|^2 + |f_2|^2 + \cdots + |f_N|^2$$

$$+2 f_1 f_2 \frac{\sin(Qr_{12})}{Qr_{12}} + 2 f_1 f_3 \frac{\sin(Qr_{13})}{Qr_{13}} + \cdots + 2 f_1 f_N \frac{\sin(Qr_{1N})}{Qr_{1N}}$$

$$+2 f_2 f_3 \frac{\sin(Qr_{23})}{Qr_{23}} + \cdots + 2 f_2 f_N \frac{\sin(Qr_{2N})}{Qr_{2N}}$$

$$\ldots + 2 f_{N-1} f_N \frac{\sin(Qr_{N\text{-}1\ N})}{Qr_{N\text{-}1\ N}}$$

where $\mathbf{r}_k$ is the position vector of the different atoms and $r_{kl}$ is the distance between two atoms. Thus, the total scattering intensity can be calculated as

$$I(Q) = \sum_{\substack{i,j,k=1 \\ k>j}}^{N} |f_i|^2 + f_j f_k \frac{\sin(Qr_{jk})}{Qr_{jk}}$$

The individual atomic form factors $f_{i,j,k}$ are calculated through the Cromer-Mann expression

$$f(Q) = \sum_{j=1}^{4} a_j \, e^{-b_j \left(\frac{Q}{4\pi}\right)^2} + c$$

where the coefficients ($a_{1-4}$,$b_{1-4}$,c) are the tabulated Cromer-Mann parameters found in International Tables of Crystallography.[14] The full set of interatomic distances $r_{rj}$ were calculated directly from molecular structures in Cartesian coordinates.

The structures of the PtPOP ground and excited states (PtPOP*) used in the fitting routine were taken from Christensen et al.[4] where $d_{Pt\text{-}Pt} = 2.75 \pm 0.03$ Å was obtained for PtPOP*. As the exciplex (Ag-PtPOP), the PtPOP* structure was added one silver ion positioned at a distance $d_{PtAg}$ from one Pt atom on the PtPt axis.

**Maximum likelihood estimation**

The maximum likelihood scheme employed for model evaluation is a search through parameter space spanned by the n parameters ($a_1 \ldots a_n$) to find the set of parameters maximizing the probability product sum[15]

$$P \propto \prod_{i=1}^{N} \left\{ \exp\left[ -\frac{1}{2} \left( \frac{y_i - y(x_i; a_1 \ldots a_n)}{\sigma_i^2} \right)^2 \right] \right\},$$

where $y_i$ and $\sigma_i$ are the measured data points and uncertainties respectively, $y(x_i;a_1,\ldots a_n)$ is the corresponding modelled datapoint based on the (unique) combination of model parameters ($a_1,\ldots a_n$). Maximizing P is equivalent to minimizing the more familiar expression

$$\chi^2 = \sum_{i=1}^{N} \left( \frac{y_i - y(x_i; a_1 \ldots a_n)}{\sigma_i^2} \right)^2$$

Thus, the set of parameters maximizing P is found by minimizing the deviation between measured and modelled data. This set of parameters is the most likely to explain the N observed datapoints, given some model with *n* adjustable parameters.[15] In the present analysis, the $\chi^2$-expression is further normalized with the (large, N ~ 1000) number of data points and the number of varied model parameters, such that the final expression for $\chi^2$ reads

$$\chi^2 = \sum_{i=1}^{N} \left( \frac{y_i - y(x_i; a_1, \ldots a_n)}{\sigma_i^2} \right) \Big/ (N - n - 1)$$

## Parameter and error estimates

Through the above analysis, a single likelihood estimate P, which through the probability sum is proportional to $\exp(-\chi^2)$ is assigned to each point in the (discrete) 6- or 7-dimensional space spanned by the investigated ranges of the parameters $(a_1, \ldots, a_n)$, in the present case ($\alpha_1$, $\alpha_2$, $\alpha_3$, $\Delta T$, $\Delta\rho$, $d_{AgPt}$ and $d_{PtPt}$(AgPtPOP*)). As discussed by Press et al.[15] slices through this space for particular values of a subset of parameters correspond to fixing these experimentally, whereas projections onto each of the axes correspond to no prior knowledge of this parameter. Consequently, the most probable values and associated error estimates for each parameter can be determined from the 1-D likelihood distribution obtained by projecting the total likelihood distribution onto each individual single-parameter axis. Estimates of the error in the parameter determinations were based on the width of a line segment on the parameter axis (centred on the most likely parameter value) for which the corresponding part of the likelihood distribution contains 68% of the cumulative likelihood, in accordance with the discussion by Press et al.[15] and the method described by Haldrup et al.[12]

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