

Exciting Heavy Metal Retrieving Structures in Photocatalysis

Renske M. van der Veen, Chris J. Milne, Amal El Nahhas, Frederico A. Lima, Van-Thai Pham Christian Bressler and Majed Chergui, Laboratoire de Spectroscopie Ultrarapide, EPFL; Jonathan Best, Julia A. Weinstein, University of Sheffield; Camelia N. Borca, Research Department Nuclear Energy and Safety, PSI; Rafael Abela, Research Department Synchrotron Radiation and Nanotechnology, PSI

Photocatalysts play an important role in a broad range of applications, from photochemical conversion of light energy into chemical energy through to initiating novel chemical reactions. One family of compounds that has attracted much attention is the dinuclear d^8-d^8 platinum, rhodium and iridium complexes that have a highly reactive electronic excited state. When photo-excited with light these systems have been shown to abstract H-atoms from a variety of substrates and initiate electron transfer processes. In this work we examine the structure of the triplet excited state of a diplatinum member of this photocatalyst family.

X-ray absorption spectroscopy (XAS) has long been established as a precise method of measuring local structure in disordered systems such as molecular systems in solution. This technique has recently been introduced into the domain of ultrafast science where the electronic and nuclear dynamics of molecules and crystals are examined on the timescales of atomic motion.[1,2] Here we use ultrafast XAS to examine the photocatalytic excited state of the $[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4]^{4-}$ (PtPOP) anion (see Figure 1) dissolved in ethanol.

Time-resolved x-ray absorption spectroscopy

An x-ray absorption spectrum is obtained by measuring either the transmission or total fluorescence of a sample as a function of incident x-ray photon energy. The photoelectrons generated by absorption of the x-rays in the sample scatter off neighbouring atoms and can interfere with themselves, modulating the atom's absorption coefficient and thus the measured x-ray spectrum. These spectral oscillations can be Fourier transformed to give the radial distribution function and thus the local structure around the absorber. A typical measurement allows reconstruction of atomic distances on the scale of $<0.01 \text{ \AA}$. Using this technique the structure of the ground state of PtPOP was measured for the molecule in solution, indicating a Pt-Pt distance of $2.876(28) \text{ \AA}$ and a Pt-P bond length of $2.32(4) \text{ \AA}$. [3] These values are in agreement with previous spectroscopically derived values as well as DFT calculations[4], and represent a small difference from those measured using crystallographic techniques. In the ground elec-

tronic state this molecule has two electrons in the Pt-Pt $\sigma^*(d_z^2)$ antibonding molecular orbital. Upon excitation with 350-390 nm ultraviolet light PtPOP can be excited into the $\sigma(p_z)$ bonding orbital, resulting in the formation of a transient Pt-Pt bond and a predicted decrease in the Pt-Pt distance. This excited $^3A_{2u}$ state has a room-temperature lifetime of a few μs in solution and has been thoroughly studied using a range of time-resolved techniques such as x-ray diffraction, optical spectroscopy, x-ray scattering, and EXAFS. The reported estimates on the change of the Pt-Pt distance in the excited state extend from 0.21 \AA in crystalline form through to 0.52 \AA in solution. In addition, many studies were inconclusive about the role of the ligands, which are expected to be affected by the transient bond formation. The structure of this excited state is relevant to its photocatalytic properties and the lack of agreement between previous studies provided the impetus for applying our well-established technique of time-resolved XAS [1] to the PtPOP anion. Measurements were performed at the MicroXAS beamline at the Swiss Light Source by exciting a 10 mM PtPOP solution in ethanol with 100 fs laser pulses at 390 nm and probing at the Pt L_3 absorption edge (11.56 keV). The transient XAS spectrum (excited minus unexcited), shown in Figure 2a, directly reflects the electronic and structural changes that occur 150 ns after excitation. In this study, we exploited the EXAFS region of the XAS spectrum to determine the excited-state structure of PtPOP.

Retrieving excited-state structures

Our ability to retrieve photoinduced structural changes with high accuracy is based on a rigorous model-based fitting approach. By including prior knowledge in the form of physically reasonable distortion models, the number of free fitting parameters can be considerably reduced, allowing us to introduce additional parameters, such as the photoexcited population and the energy shift between excited and ground state XAS spectra, which are typical for time-resolved XAS analyses and often difficult to obtain by independent methods.

The general procedure followed is to first obtain accurate structural values for the ground state of the system, then to use these values as a starting point for the excited state structure. By making physically reasonable changes to the ground state structure according to a specific distortion model, then simulating the EXAFS spectrum for the new structures, the resulting transient EXAFS spectra can be calculated by subtracting the ground state fit. For each excited-state structure, the difference between the experimental and simulated transient spectra can be minimized by introducing fitting parameters such as the energy shift and the photoexcited population. This procedure can then be repeated with various realistic structural distortion models that all involve a contraction along the Pt-Pt axis, allowing the result to converge to the smallest difference between experiment and calculation.

In this way, the best fit was obtained for a Pt-Pt contraction of 0.31(6) Å and a Pt-Ligand elongation of 0.013(5) Å (see Figure 2).[5] The latter is larger than just resulting from the Pt-Pt contraction, which indicates that the coordination bonds are weakened upon the Pt-Pt bond formation in the excited state. This small Pt-P elongation has been predicted by DFT calculations [4], but this represents the first experimental confirmation of such a structural change and illustrates the sensitivity of both time-resolved XAS as a technique to resolve excited-state structures and the analysis procedure used. Remarkably, the bridging P-O-P ligands do not follow the Pt atoms in the contraction movement, which supports the weakening of the Pt-P bonds and the rigidity of these bidentate ligands. In addition, the analysis indicates an excitation population of 7% and a zero energy shift. Both of these conclusions seem accurate: optical measurements indicate an excited state contribution of approximately 8% and no energy shift of the excited state x-ray absorption spectrum is expected as the photoexcitation does not affect the charge density on the Pt atoms.

It should be emphasized that the present transient

EXAFS analysis goes beyond the simple determination of nearest-neighbour distances. By using a model-based fitting approach a more global picture of the excited molecule can be obtained. Application of this analysis technique to other photocatalytic systems should provide a wealth of information not directly available through other methods.

References

- [1] C. Bressler et al. *Chem. Rev.* 1781, **104** (2004).
- [2] C. Bressler et al. *Science* 489, **323** (2009)
- [3] R. M. van der Veen et al. *CHIMIA* 287, **62** (2008).
- [4] I.V. Novozhilova et al. *J. Am. Chem. Soc.* 1079, **125** (2003).
- [5] R. M. van der Veen et al. *Angew. Chem. Int. Ed.* (in press, 2009).

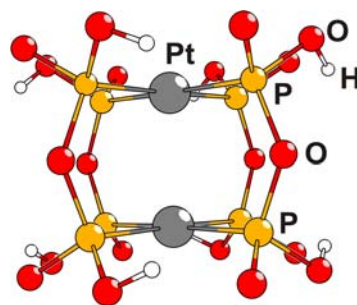


Figure 1: Structure of the $[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4]^{4-}$ (PtPOP) anion

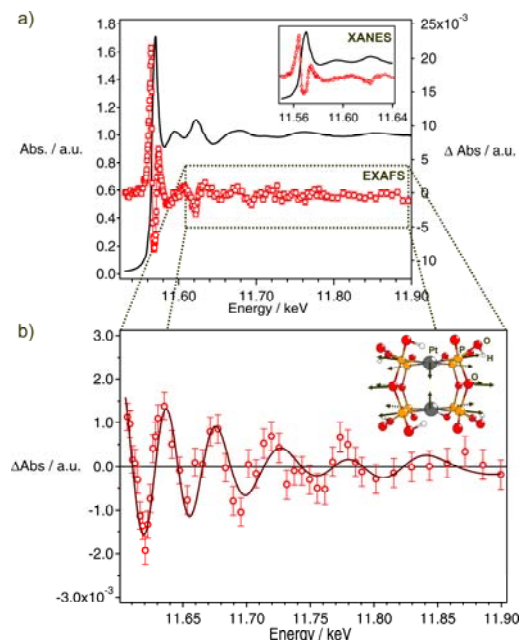


Figure 2: a) Static Pt L_3 XAS spectrum of PtPOP in solution (black line, left axis) and the transient (excited - unexcited) XAS spectrum (red circles, right axis, same units as left) integrated up to 150 ns after excitation; b) Transient EXAFS data (circles) and best fit (solid line, see text). The best-fit structural distortions are indicated in the upper right corner.