VIP Time-Resolved EXAFS

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Structural Determination of a Photochemically Active Diplatinum Molecule by Time-Resolved EXAFS Spectroscopy**

Renske M. van der Veen, Chris J. Milne, Amal El Nahhas, Frederico A. Lima, Van-Thai Pham, Jonathan Best, Julia A. Weinstein, Camelia N. Borca, Rafael Abela, Christian Bressler, and Majed Chergui**

Electronically excited states of transition-metal complexes are finding a broad range of applications, ranging from the conversion of light (e.g. solar) or chemical energy, to the storage and processing of optical or magnetic information, or as homogeneous photocatalysts in chemical conversions at room temperature.[1] These processes have in common that the function of the excited system strongly correlates with its transient structure. In this respect, the triplet excited states of dinuclear d^8–d^8 platinum, rhodium, and iridium complexes (bridged by various ligands) have attracted much attention owing to their unusually high reactivity: they can abstract hydrogen atoms from a wide range of substrates as well as halogen atoms from alkyl and aryl halides, and they can also induce both oxidative and reductive electron transfer.[2,3] The photophysical and photochemical properties of these complexes are a manifestation of the newly formed bond in the lowest excited singlet and triplet $^{1,3}A_{2u}$ states, owing to the promotion of an electron from the antibonding $d\sigma^*$ (d_{z^2}-derived) to the bonding $p\sigma$ (p_z-derived) orbitals. The key question towards understanding the photoreactivity of these complexes is therefore the structure of the triplet excited state.

The $[Pt_2(P_2O_5H_2)_4]^{4-}$ ion investigated herein is among the most extensively studied molecules in the family of dinuclear metal complexes.[2] Excitation into the first singlet state in the near UV region around 370 nm leads to emission from both singlet and triplet states, which was analyzed at low temperatures.[4] The formation of the triplet state from the singlet state occurs with unity quantum yield,[4a] and the triplet state exhibits a lifetime of a few microseconds in solution at room temperature,[4g] making it an efficient photocatalyst.

The excited-state structure of the $[Pt_2(P_2O_5H_2)_4]^{4-}$ ion is still not resolved, despite several studies using different approaches, such as Franck–Condon analyses of low-temperature excitation and emission spectra[4b] and Raman spectroscopy.[5] The derived values for the shortening of the Pt–Pt separation lie in the range 0.175–0.225 Å. These spectroscopic studies all rely on the metal–metal stretch vibrational frequencies in the ground and excited states to derive the Pt–Pt distortion (the contraction is proportional to the excited-state vibrational frequency). However, the change in restoring force arising from a structural modification in the bridging POP ligands or the platinum–ligand bonds is not taken into account in these studies, although such distortions have a large effect on the frequency of the metal–metal vibration and thus the derived values for the contraction.

X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) provide a more direct way of determining the structural changes in the excited state. A stroboscopic X-ray diffraction study with 33 μs time resolution on helium-cooled crystals of the $[Pt_2(P_2O_5H_2)_4]^{4-}$ ion derived a shortening of the Pt–Pt bond by 0.28(9) Å.[6a] In a different XRD experiment, Ohashi and co-workers derived different values for the Pt contraction (0.23–0.28 Å, depending on the counterion in the crystalline compound) and a very large Pt–P shortening by 0.1–0.2 Å, but the quantitative results depended strongly on the fraction of excited molecules, which could not be determined accurately.[6b–d] An EXAFS study with microsecond time resolution, based on the Fourier transform of the difference (excited minus unexcited) EXAFS spectrum, reported a shortening of the Pt–P and Pt–O separations in the triplet state[7] but was not sensitive to the Pt–Pt bond itself. The authors therefore used the optically derived Pt–Pt bond length of 2.75 Å in the excited state[4a] to derive a large contraction of 0.52 Å along the Pt–Pt axis between the two planes containing four phosphorus atoms each, implying unrealistic structural changes within the ligands. DFT calculations by Coppens and co-workers predicted a Pt–Pt bond shortening (0.17–0.5 Å) and a slight Pt–P bond lengthening (0.005–0.05 Å) in the triplet state.[8] The large range of reported values is due to the different functionals used in their calculation. However, all calculations pointed to a Pt–P bond lengthening, which has not otherwise been observed and is in clear contrast to EXAFS[7] and X-ray diffraction results.[6d] Thus, the structural determination of the triplet

[*] R. M. van der Veen, Dr. C. J. Milne, A. El Nahhas, F. A. Lima, V.-T. Pham, Prof. Dr. C. Bressler, Prof. Dr. M. Chergui
Laboratoire de Spectroscopie Ultrarapide
Ecole Polytechnique Fédérale de Lausanne (Switzerland)
E-mail: majed.chergui@epfl.ch
Homepage: http://isic2.epfl.ch/page62272-en.html
R. M. van der Veen, Dr. C. N. Borca, Dr. R. Abela
Swiss Light Source, Paul Scherrer Institute
Villigen (Switzerland)
J. Best, Dr. J. A. Weinstein
Chemistry Department
The University of Sheffield (United Kingdom)

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state of $[Pt_2(P_2O_5H_2)_4]^{4-}$ is still the subject of contradictory claims from theory as well as optical and X-ray studies.

Over the past ten years, we have developed and implemented time-resolved X-ray absorption spectroscopy (XAS) in both the X-ray absorption near edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) regions as a reliable tool to investigate the electronic and molecular structure changes of light-induced short-lived reaction intermediates in solutions.[9a] This method is based on the recording of the transient (difference) XAS spectra of the excited minus the unexcited (i.e. ground-state) system and has shown its high sensitivity in detecting very small changes in the recorded spectra.[9b–d] Indeed, we used it to retrieve the structural changes resulting from an intramolecular electron-transfer process in $[Ru^{II}(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine)[9e] and from the ultrafast spin crossover in aqueous $[Fe^{II}(bpy)_3]^{2+}$[9b,c] as well as to elucidate the solvent-shell rearrangements around atomic ionic solutes.[9f] The precision in the structural determination is further enhanced by a quantitative structural analysis of the excited state we recently proposed,[9c,d] which is based on the fitting of the transient EXAFS spectrum directly in energy space by minimization of the square residual function between a large series of simulated transient EXAFS spectra and the experimental data. It gives superior accuracy for the derived structural parameters when compared to conventional EXAFS fitting methods that extract structural changes from the Fourier transform of the reconstructed excited-state EXAFS signal (which suffers an additional uncertainty is due to the imprecisely known fractional population of the excited-state species in the time-resolved XAS experiment).[9c] The fitting procedure applied herein relies on additional knowledge about the possible structural changes, which need to be chemically reasonable, while allowing ample variation in their magnitude. Ideally, this approach reduces the degrees of freedom considerably, and therefore it allows finding an unambiguous solution for the excited-state structure and extracting additional information, such as the chemical shift and excitation yield (i.e. fraction of excited molecules).[9c] The latter is especially useful in cases where the excitation yield has not been determined in situ (or cannot even be reliably determined by laser-only pump–probe measurements, as is the case here, see the Supporting Information). Details of the analysis procedure are given in the Supporting Information and in references [9c,d].

The sample (a thin quartz flow capillary with 0.5 mm path length containing 10 mM $[Pt_2(P_2O_5H_2)_4]^{4-}$ in ethanol at room temperature) is excited by a femtosecond laser pulse at 390 nm and probed with a 70 ps hard X-ray pulse at 50 ps after excitation and simultaneously with multiple 50 ns wide integration gates at later times. We record X-ray absorption spectra at the Pt L_3 edge in total fluorescence detection mode (see the Supporting Information for details). Figure 1a shows the Pt L_3-edge XAS spectrum in the ground state (black trace) as well as the transient spectrum, integrated from 0 to 150 ns to improve the signal-to-noise ratio (the triplet lifetime is ca. 1 μs). Indeed, no spectral changes were observed in the transient EXAFS spectra for all times up to 150 ns. The inset in Figure 1a shows the XANES region for the ground-state

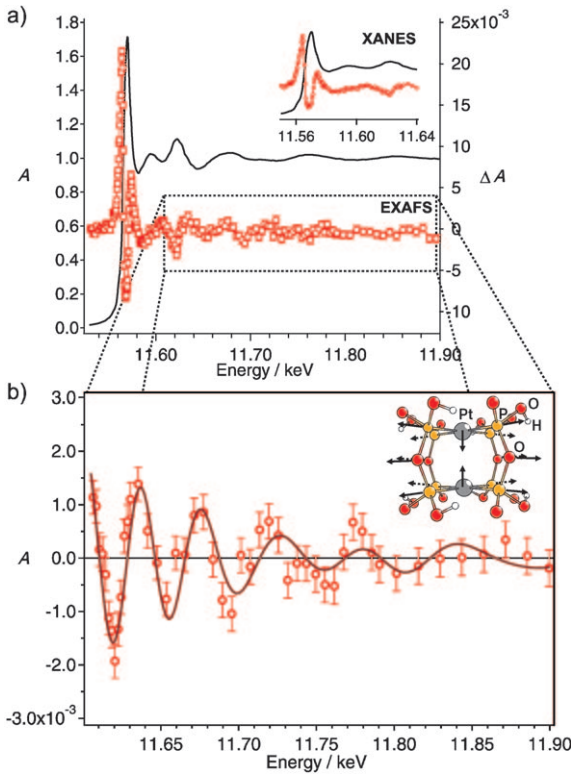

Figure 1. a) Static Pt L_3 XAS spectrum of $[Pt_2(P_2O_5H_2)_4]^{4-}$ in solution (black line, left axis) and the transient (excited–unexcited) XAS spectrum (red circles, right axis, same units as left) integrated up to 150 ns after excitation. The inset zooms into the XANES region. b) Transient EXAFS data (circles; binned from the data in (a)) and best fit (solid line) with the following results: a Pt–Pt contraction of 0.31(5) Å, a platinum–ligand elongation of 0.010(6) Å, zero energy shift, and 7% excitation yield. The error bars represent the standard error of the measurement. The best-fit structural distortions are indicated in the upper right corner.

complex and its transient spectrum. Dramatic changes appear therein. In particular, a new absorption shows up at 11.574 keV below the absorption edge of the ground-state spectrum. This absorption is due to the creation of a hole in the 5dσ* orbital upon laser excitation, which can then be accessed from the $2p_{3/2}$ core orbital (L_3 edge). The analysis of the transient XANES signal will be presented in a future publication. Herein, we exploit the direct structural information extracted from the EXAFS region (up to $k = 9$ Å^{-1}; Figure 1b). Clear changes are visible, reflecting structural modifications between the ground and excited triplet states. From the transient EXAFS spectrum we can directly extract the magnitude of the Pt–Pt bond contraction as well as, for the first time, the changes affecting the ligand coordination bonds. In particular, we show that the latter undergo a slight elongation.

The antibonding-to-bonding 5dσ*→6pσ nature of the electronic transition led us to consider only structural distortions that involve a contraction along the Pt–Pt axis. As to whether and how the ligands are influenced by the excitation, four chemically reasonable deformation models were applied (Figure 2). In model I, only the Pt atoms are allowed to move along their connecting axis, implying a

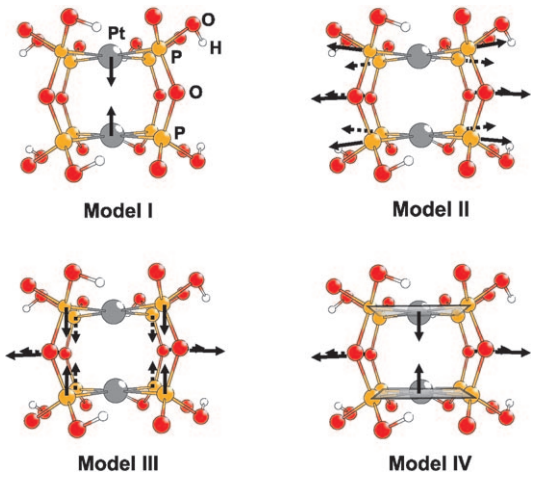

Figure 2. Schematic representation of the structural distortion models I–IV considered in the statistical analysis (distortion indicated by arrows). The bridging P–O bond lengths are fixed for the distortions of models III and IV.

change in the P-Pt-P angle (since the ligand atoms are kept rigid), with consequent small elongation of the Pt–P bonds. Model II introduces an additional flexibility to the coordination bonds by allowing the ligands to move perpendicular to the Pt–Pt axis, while still keeping the P-O-P angles fixed to their ground-state values. In model III, the P-O-P angles can change as a result of the inwards movement of the P atoms along the Pt–Pt axis, while the bridging O atoms move outwards to maintain a constant P–O bond length. Finally, model IV is a special case of model III in which the planes containing the Pt and P atoms are rigid and approach each other without changing the Pt–P bond length. Both models III and IV imply a large structural change in the P-O-P bridging ligand angle, contained in the hypotheses of references [4a] and [7].

We aim at a unique solution for the excited-state structural distortion by combining the motions of models I–III in an iterative way. The calculated transient EXAFS spectra are generated by subtracting the fit to the ground-state EXAFS spectrum[10] from the simulated excited-state EXAFS spectra for each excited-state structure.[11] This collection of simulated transient spectra is then compared to the experimental transient spectrum for a series of excitation yields and edge energy shifts between the ground and excited state in a statistical analysis based on a least-squares fitting procedure (see the Supporting Information). The overall best fit was obtained for a combination of models I and II, and the resulting best-fit transient spectrum is shown in Figure 1b. For this result, the Pt atoms were first gradually moved closer together in small steps of 0.001–0.002 Å (model I). A moderately good fit to the data was obtained for a Pt–Pt contraction of 0.31 Å, an excitation yield of 8%, and a −1 eV energy shift. Second, the Pt–Pt contraction was fixed to the previously found value of 0.31 Å, but now the POP ligands were allowed to move towards and away from the Pt atoms perpendicular to the Pt–Pt axis (model II). The χ^2 values of the fit improved significantly (by 17%) for an expansion of 0.010 Å, 7% excitation yield, and zero energy shift (Supporting Information, Figures S5b and S6). A third iteration of the Pt–Pt contraction motion with the new ligand structure did not change the Pt–Pt distance further and yielded the same zero energy shift, excitation yield, and minimum in χ^2 as the previous iteration, thus confirming the convergence of this fit sequence.

The excitation yield thus obtained is in good agreement with the one estimated (ca. 8%) from independent optical pump–probe measurements (see the Supporting Information). Furthermore, the fitted zero energy shift may be expected for a metal-centered transition without change of oxidation state of the absorbing metal. The main effect from model I on the scattering in the first coordination shell (near P atoms within the original PtP_4 plane) is given by the reduced amplitude of the strong collinear multiple scattering path along P-Pt-P.[10] The additional Pt–P elongation arising from model II mainly affects the frequency in the difference spectrum, which, because of parameter correlation, leads to the anticipated zero energy shift.

The above result is unique in the sense that the structural distortions (0.31(5) Å Pt–Pt contraction and 0.010(6) Å ligand dilation) both lead to a unique combination of distance changes. These in turn influence the phases and amplitudes of the scattering paths and their mutual interference in an unambiguous way, leading to the good agreement with the experimental data (Figure 1b). There is, however, a resulting discrepancy between the fit and the data, which we assign to the limited structural parametrization in the calculation of the EXAFS signals. The number of parameters was limited owing to the large overlap of scattering paths, thus narrowing the information content of the data.

We also considered models III and IV, since they are implicit in references [4a] and [7]. We performed a similar iterative fitting procedure as above, but now for the Pt–Pt contraction (model I), platinum–ligand contraction/expansion (model II), and the contraction of the P_4 planes (model III). The latter results in a small (3%) and not significant improvement of the χ^2 values of the fit for a contraction of 0.02(3) Å. On the other hand, we can reliably exclude contractions of the planes larger than 0.05 Å, as they significantly worsen the fit. Model IV can be ruled out as it does not yield any reasonable fit of the observed transient EXAFS features (see the Supporting Information for details of the optimization procedure for models III and IV).

The present study shows for the first time an elongation of the Pt–P coordination bonds by 0.010(6) Å, which is significantly larger than just the elongation based on the geometric considerations for model I (0.003 Å). The additional increase in the Pt–P distance confirms the predictions of DFT calculations[8] for the first time. The high sensitivity of our transient EXAFS measurement to the dominant Pt–P scattering path[10] allows us to detect this small platinum–ligand elongation. We believe it is due to a weakening of the coordination bonds upon formation of the Pt–Pt bond in the excited state, which reduces the overlap of the coordinating ligand orbitals with the Pt $d_{x^2-y^2}$ orbitals. The weakened Pt–P bonds allow in turn the Pt atoms to come even closer, resulting in the relatively large distortion of 0.31(5) Å. Indeed, the value for the Pt–Pt bond contraction determined

here is much larger than the values determined by optical methods (0.15–0.25 Å) that derive the Pt–Pt contraction solely based on the vibrational frequency increase in the excited state (the higher the frequency, the larger the contraction). The weakened coordination bonds decrease the restoring force, resulting in a lower metal–metal stretching frequency, and the optical studies in consequence deliver underestimated values for the Pt–Pt distortion. The Pt–Pt contraction of 0.31(5) Å is close to the value determined by time-resolved X-ray diffraction (0.28(9) Å)[6a] and is within the range of values from DFT calculations.[8] It has a comparatively small uncertainty, owing to the rigorous analysis presented herein. The present analysis reliably excludes the excited-state distortion model in which the Pt atoms remain in the plane of the P atoms (model IV, Figure 2).[4a,7] The P atoms follow the Pt atoms to only 0.02(3) Å in the contraction along the Pt–Pt axis, which is very small compared to the large movement of the Pt atoms.

The present results establish unambiguously the excited-state distortions in a dinuclear d^8–d^8 complex (and especially with emphasis on the quantitative value for the Pt–Pt contraction). The ability to retrieve details of the excited-state structure comes from the high sensitivity of the experiment together with our novel structural analysis based on fitting transient EXAFS spectra directly in energy space. Its consistency is supported by the retrieved excitation yield and energy shift, which both agree with the expected values. This high sensitivity can now be exploited to investigate the faster and more subtle details of the relaxation from the initially excited singlet state to the final triplet state, which both have parallel potential curves along the Pt–Pt coordinate. We believe that deformations that are not totally symmetric must mediate the intersystem crossing, and femtosecond X-ray absorption spectroscopy should be able to address this issue. Such analysis is now possible thanks to new sources of femtosecond hard X-rays, such as the slicing scheme at synchrotrons, as recently demonstrated on a transition-metal complex in solution.[12]

Experimental Section

The laser pump/X-ray probe measurements were performed at the microXAS beam line of the Swiss Light Source at the Paul Scherrer Institute. The experimental setup is described in detail elsewhere[9g] and in the Supporting Information.

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