Photoisomerization in a platinum-amido pincer complex

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ABSTRACT Computational investigations of the electronic spectroscopy and photochemical isomerization in the complex (bis(8-quinolinyl)amido)PtMe₂I are presented. Time-dependent density functional theory, in conjunction with the polarizable continuum solvent model, reproduce the experimental spectra for the mer and fac isomers well. The nature of the initially populated states for the mer isomer are ππ* in nature and localized on the BQA ligand. Geometry optimization shows that the system relaxes in the excited manifold to a fac-like geometry in the S₁ electronic state. Complete active space self-consistent field (CASSCF) calculations show that there exists a sloped conical intersection that connects the excited- and ground-state fac species, allowing for radiationless deactivation in fac-like geometries.

SECTION Dynamics, Clusters, Excited States

We have computationally investigated a recent intriguing experimental result from Harkins and Peters. They found that light irradiation of the complex (bis(8-quinolinyl)amido)PtMe₂I resulted in an unexpected stereochemical transformation from the meridional (mer) form (all coordinating nitrogens and metal being coplanar) to the facial (fac) form (all coordinating nitrogens cis to each other). The BQA ligand belongs to the group of robust “pincer-type” amido ligands that display a rich variety of chemistry. Transition-metal complexes with these ligands are very popular in organometallic and inorganic chemistry due to their potential applications in catalysis, electrochemical devices, or the activation of small molecules. They can adopt a variety of geometries, from square-planar structures to more distorted ones. The common bonding feature of such complexes is that the metal is bonded to the quinolinyl arms via the nitrogen donor atoms and that the amide nitrogen is sp² hybridized, thus leading to significant conjugation through the π-system. Quinoline and related ligands showing ligand-localized photochemistry have been studied recently with important consequences for use as OLEDs. We find that the photochemistry of the BQAptMe₂I complex is dominated by localized chemistry on the BQA ligand, with the metal having very little effect on the nature of the electronic transitions. The initial excitation is of ππ* type and involves a reduction in the conjugation across the planar amido linkage in the BQA. The system then relaxes in this state, with the ligand sphere...
undergoing rearrangement toward folded BQA conformations. This leads to an excited fac minimum, followed by a sloped conical intersection connecting the excited and ground electronic states (Figure 1), allowing for efficient radiationless deactivation to the ground-state fac geometry. This is a naturally occurring photochemical feature of the BQA ligand itself. This type of pathway may be potentially important for other complexes that involve the interesting family of flexible chelating pincer-type ligands.5,33,34,36,37

The (BQA)PtMe2I complex shows an unexpected coordination with a planar tridentate BQA in a mer geometry at the octahedrally coordinated Pt(IV) 23 Harkins and Peters found this complex to be stable in acetone when stored in the dark but that it is unexpectedly transformed to the fac geometry under irradiation of light. The photoexcited mer form involves essentially a redistribution of the π system on the organic BQA ligand, which “loosens” the conjugation across the amide linkage (the amide nitrogen changes its hybridization from sp² to sp³) and weakens the metal—BQA bonds via population of orbitals with nominal M—π antibonding character.

The simulated spectra are shown in Figure 2 (see Computational Details below). Here, the solvent in the PCM model is...
Table 1. TD-B3LYP (PCM = CH₂Cl₂) Excitation Energies and Oscillator Strengths for Vertical Excitation of mer and fac Isomers

<table>
<thead>
<tr>
<th>state</th>
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<th>state</th>
<th>f</th>
<th>character</th>
</tr>
</thead>
<tbody>
<tr>
<td>S₁</td>
<td>2.29 eV</td>
<td>0.0136 (H(L)-0.121; (H(L+1)-0.690)</td>
<td>S₁</td>
<td>2.78 eV</td>
<td>0.0033 (H(L+1)-0.534; (H(L+2)-0.443)</td>
</tr>
<tr>
<td>S₂</td>
<td>2.35 eV</td>
<td>0.2590 (H(L)-0.693; (H(L+1)-0.121)</td>
<td>S₂</td>
<td>2.85 eV</td>
<td>0.1178 (H(L)-0.701)</td>
</tr>
<tr>
<td>S₃</td>
<td>2.79 eV</td>
<td>0.0023 (H(L+2)-0.684)</td>
<td>S₃</td>
<td>3.03 eV</td>
<td>0.0366 (H(L+1)-0.449; (H(L+2)-0.537)</td>
</tr>
</tbody>
</table>

The optimized geometries of the ground-state mer and fac structures are shown in Figure 3. These compare favorably with experimental structures. The mer isomer is 2.9 kcal mol⁻¹ lower in energy than the fac using the PCM model, while for the gas-phase structures, the fac is 0.9 kcal mol⁻¹ more stable. We were unable to find any evidence of a direct transition structure linking these two geometries on the S₀ potential surface. We suspect that any thermal process would have to go through (at least one) reactive intermediate via dissociation of the iodine to give a five-coordinate species. The potential surface. We suspect that any thermal process would have to go through (at least one) reactive intermediate via dissociation of the iodine to give a five-coordinate species.

The mer form has an intense absorption at 534 nm, which is at 530 nm from TD-B3LYP. The fac form has a broad band centered at 422 nm, with a small shoulder at 510 nm. The TD-B3LYP gives this band maximum at 425 nm. The nature of the transitions that give rise to these bands can be determined by examination of the dominant particle–hole configurations of the response eigenvectors relative to HOMO and LUMO. We observed very little difference between analysis of the excitation using the canonical Kohn–Sham orbitals and the natural transition orbitals. The data given in Table 1 lists the principal particle–hole configurations in response eigenvectors relative to HOMO (H) and LUMO (L) are also given.

CH₂Cl₂, to match that used in ref 23. The effect of solvent is minimal, with only a small blue shift (on average, 0.05 eV) observed between the gas-phase and PCM results. We also note that the experimental photochemistry was performed in acetone, though the spectra were recorded in CH₂Cl₂, and we do not observe any difference in the computed spectra between these using the PCM model. The computed spectra compare favorably with the experimental ones. The mer form involves essentially intraligand excitation of the dominant particle, whereas the fac form involves essentially ligand-to-metal charge transfer (LMCT) as postulated previously. The π* orbital contains a very small component that is antibonding with respect to the t₂g metal d orbitals. The main particle–hole configuration of the state involves a donation of electron density from the central amide nitrogen to each π system on both adjacent quinoline rings. It is also worth noting that the lower dark state (S₁) and all higher dark states in the spectral range up to 400 nm involve this qualitative feature of localized ligand excitation, with charge redistribution across the BQA “backbone”.

The optimized geometries of the ground-state mer and fac structures are shown in Figure 3. These compare favorably with experimental structures. The mer isomer is 2.9 kcal mol⁻¹ lower in energy than the fac using the PCM model, while for the gas-phase structures, the fac is 0.9 kcal mol⁻¹ more stable. We were unable to find any evidence of a direct transition structure linking these two geometries on the S₀ potential surface. We suspect that any thermal process would have to go through (at least one) reactive intermediate via dissociation of the iodine to give a five-coordinate species. The thermal isomerization is not seen experimentally.

In the S₂ state of the complex, relaxation involves the BQA ligand “folding” in, and the molecule relaxes to a quasi-fac form of the complex in the first singlet excited state (S₁) (Figure 3). The bright and dark states are very close and may switch in energetic order with different DFT functionals (vide infra). If the ordering is correct and the bright state is S₁, then obviously, there must be a crossing between the S₁ and S₂ states. There is a minimum on the mer side of the reaction with BQA slightly nonplanar that is reached from the dark state. We were unable to locate an S₁ transition state due to the limitation of not having TD-DFT excited Hessians at present. Constrained geometry calculations indicate that any barrier will be relatively low. While the driving force in the populated S₂ state forces the system to relax toward fac-like geometries, obviously more accurate photochemical dynamics simulations would be required to determine if there is any population transfer to the dark state. However, whether via direct relaxation to the excited fac side of the reaction, or transformation over a barrier on a longer time scale, the system ends up at the same point, namely, the S₁ fac minimum (Figure 3). This fact is further emphasized if the bright and dark states are switched in order.

The TD-DFT and CASSCF excited geometry optimizations of this minimum are in good agreement. From this S₁ fac minimum, the excited molecule can access a conical intersection that connects the S₁ state to the ground state (shown schematically in Figure 1). This allows for radiationless relaxation to the ground-state fac geometry. The CASSCF energy difference between the S₁ minimum and the minimum-energy crossing point is around 10 kcal mol⁻¹, although, obviously, this value should be treated with caution due to incomplete accounting for dynamic correlation.

Interestingly, this conical intersection seam exists in the bare BQA ligand, and the excited relaxation and subsequent decay are essentially driven by the ligand’s photochemistry. CASSCF computations on the pure ligand indicate that at folded geometries, there is an extensive seam of intersection that connects the ground state with a ππ* state. The global minimum-energy crossing point on this seam occurs at a CNC angle of 120°, but with the two quinoline groups twisted almost 90°. We have performed constrained conical intersection searches and observed that the intersection seam includes an energetically accessible portion with a small dihedral angle between quinoline groups. This constrained crossing point has a very similar geometry to the intersection in the full metal complex. From the geometries in Figure 3, it can be seen that the S₁ fac minimum occurs with a NPtN angle of 110°, which is more open than that at the conical intersection (92°) and that at the S₀ minimum (90°). Thus, molecular motion moves the system through the S₁ fac minimum, crosses from S₁ to S₀ via a radiationless transition in the conical intersection region, and finally relaxes to the stable S₀ fac minimum. The branching space for the conical intersection...
Figure 3. Optimized geometrical parameters for critical points involved in the mer–fac photoisomerization of (BQA)PtMe₂I. S₀ mer and S₀ fac optimized using B3LYP, both in the gas phase and with CH₂Cl₂ using the PCM model. S₁ fac optimized using TD-B3LYP and CASSCF; S₀/S₁ conical intersection optimized with CASSCF. Bond lengths are in Angstroms, angles in degrees.

is shown in Figure 1. This is the space (a 2D plane containing the derivative coupling (dc) and gradient difference (gd) vectors) in which the electronic degeneracy is lifted at first-order in vibrational motion. The motion is seen to mainly involve the amido link in the BQA ligand. Thus, one can see that when the locally excited ligand is driven toward such geometries, the crossing to the ground state becomes favorable.

The reaction path linking the conical intersection and the S₀ and S₁ fac minima (Figure 3) can be determined unambiguously by computing an intrinsic reaction coordinate (IRC). For this system, an IRC is computationally expensive, but an idea of the downhill path from the conical intersection can be gained from examination of geometry optimization on the ground- and excited-state surfaces (using both CASSCF and (TD)-DFT). It is observed that the downhill direction from the conical intersection on S₁ leads directly to the S₁ fac minimum, while downhill on S₀ leads to the S₀ fac minimum. This is consistent with the observation that the conical intersection seam has a locally sloped topology, as depicted in Figure 1.

In summary, the metal complex acts as a scaffold for the pincer ligand, and localized excitation on the conjugated
ligand drives the intraligand folding, which takes the system downhill to the fac geometry. At such excited geometries, a conical intersection seam is accessible, which allows for radiationless decay to the stable fac photoproduct observed experimentally.

**COMPUTATIONAL DETAILS**

The ground-state isomeric forms were studied using density functional theory (DFT). For the DFT calculations, the one-electron basis set used was as follows: the Stuttgart Dresden effective core potential (SDD) on platinum (60 core electrons) and iodine (46 core electrons), in conjunction with the standard SDD valence basis and the 6-31G(d) basis on carbon, nitrogen, and hydrogen. The electronic spectroscopy was studied using time-dependent DFT. The effect of different functionals on excitation is given more fully in Supporting Information. The character of the lowest states contributing to the observed spectral bands involves ππ* redistribution localized on the BQA ligand with all functionals investigated. Both B3LYP and PBE1PBE give the S1 state as a dark state, with localized on the BQA ligand with all functionals investigated.

CAM-B3LYP and M06-2X give a blue shift of around 0.4 eV for the first transition with a Gaussian function to account for homogeneous line broadening (although we note that only a few states contribute in the low-energy region of interest). Geometry optimization in the excited manifold is now possible using analytical TD-DFT gradients, which were used to study the relaxed excited-state geometries. Ground- and excited-state solvent effects were investigated using the B3LYP functional in conjunction with the polarizable continuum model (PCM), with all the default settings as implemented in Gaussian 09. We note that optimized geometries in both the ground and excited states were found to be insensitive to the functional used. In order to investigate nonadiabatic relaxation pathways, we used complete active space self-consistent field (CASSCF) theory. Obviously, such a large system presents some difficulties in choosing an appropriate active space. Qualitatively, we looked at the TD-DFT orbitals involved in the photochemistry on both the reactant and product sides of the photo reaction. As discussed above, these were seen to involve ligand-centered π orbitals. Quantitatively, initial guess orbitals were natural orbitals from an unrestricted Hartree–Fock calculation. These are the orbitals which diagonalize the one-electron density matrix and whose eigenvalues are occupation numbers that give a measure of the importance of that orbital in a multiconfigurational wave function. From these, we generated active spaces consisting of 14 electrons distributed in 12 orbitals, generating 314028 singlet configurations. These CASSCF wave functions were checked for stability by switching some of the initial valence orbitals for alternative core or virtual orbitals and observing convergence to the same state. For the CASSCF calculations, the one-electron basis on platinum and iodine was as above, while for carbon, nitrogen, and hydrogen the 3-21G(d) basis was used. For the conical intersection optimization with CASSCF, the orbital derivative terms were neglected in the solution of the coupled perturbed multiconfiguration self-consistent field (CP-MCSCF) equations. All DFT computations were performed with the Gaussian 09 program, while the CASSCF calculations were performed with the Gaussian 03 program. All computations were performed on a Linux cluster with Intel Xeon Harpertown processors.

**SUPPORTING INFORMATION AVAILABLE**

Cartesian coordinates, relative energies, and TD-DFT functional comparison. This material is available free of charge via the Internet at http://pubs.acs.org.

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**REFERENCES**


