

JCTC

Journal of Chemical Theory and Computation

Theoretical Insights into Hydrogen Bonding and Its Influence on the Structural and Spectral Properties of Aquo Palladium(II) Complexes: $cis-[(dppp)Pd(H_2O)_2]^{2+}$, $cis-[(dppp)Pd(H_2O)(OSO_2CF_3)]^+(OSO_2CF_3)^-$, and $cis-[(dppp)Pd(H_2O)_2]^{2+}(OSO_2CF_3)^-_2$

Guang-Jiu Zhao,[†] Ke-Li Han,^{*,†} and Peter J. Stang^{*,‡}

State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China, and Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Received May 1, 2009

Abstract: Density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods have been performed to investigate the ground and excited states of aquo palladium(II) complexes $cis-[(dppp)Pd(H_2O)_2]^{2+}$, $cis-[(dppp)Pd(H_2O)(OSO_2CF_3)]^+(OSO_2CF_3)^-$, and $cis-[(dppp)Pd(H_2O)_2]^{2+}(OSO_2CF_3)^-_2$. Insights into the influence of hydrogen bonding on the structural and spectral properties of these three aquo Pd(II) complexes are presented. The structures and the HOMO–LUMO energy gap of the three aquo Pd(II) complexes can be markedly influenced by hydrogen bonding interactions. Hydrogen bonds can also significantly influence their absorption spectra.

It is well-known that transition-metal solvent complexes, especially aquo transition-metal complexes, are of considerable experimental and theoretical interest because of their relevance in catalytic processes and as intermediates in reactions carried out in solution.¹ Recently, aquo palladium complexes have garnered increasing attention, and their synthesis, properties, and applications as catalysts and as synthetic intermediates have been widely studied.²

Stang et al. have reported that the reaction of *cis*-(1,3-bis(diphenylphosphino)-propane)palladium(II) triflate with 1 and 2 equiv of water gives the corresponding monoquo and diaquo

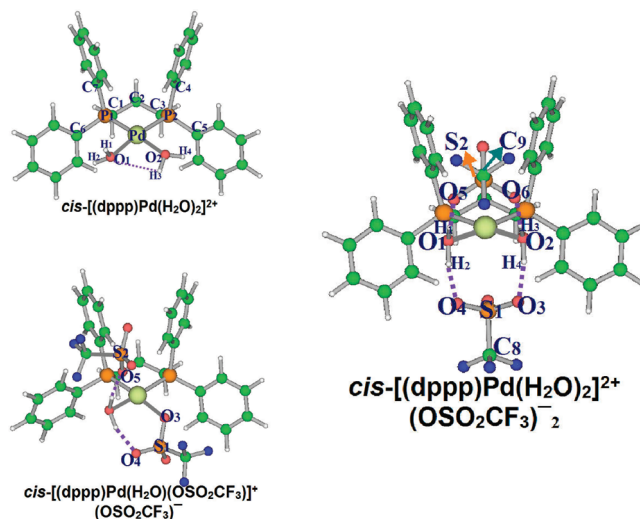


Figure 1. Conformational structures of the various aquo Pd(II) complexes.

cationic palladium(II) complexes $cis-[(dppp)Pd(H_2O)(OSO_2CF_3)]^+(OSO_2CF_3)^-$ and $cis-[(dppp)Pd(H_2O)_2]^{2+}(OSO_2CF_3)^-_2$, respectively, which are yellow microcrystalline solids.³ Moreover, the structures of monoquo and diaquo Pd(II) complexes have been determined by single-crystal X-ray crystallography.³

As is well-known, coordinated water forms hydrogen bonds with hydrogen bond acceptors in the presence of weakly coordinating counteranions (e.g., OTf^- , ClO_4^- , PF_6^- , BF_4^- , TsO^- , NO_3^- , etc.).² In the diaquo Pd(II) complex $cis-[(dppp)Pd(H_2O)_2]^{2+}(OSO_2CF_3)^-_2$ each coordinated water is doubly hydrogen-bonded to oxygen atoms of two different $OSO_2CF_3^-$ anions (see Figure 1).³ In the monoquo Pd(II) complex $cis-[(dppp)Pd(H_2O)(OSO_2CF_3)]^+(OSO_2CF_3)^-$ the hydrogen atoms of coordinated water form two contacts, intramolecularly with an oxygen atom of the coordinated anion and intermolecularly with an oxygen atom of the $OSO_2CF_3^-$ counterion (see Figure 1).³

Zhao et al. have extensively studied hydrogen bonding in both the ground and excited states of organic chromophores as well as its influence to their structures and dynamics in solution.⁴ However, hydrogen bonding in aquo transition-metal complexes, and its influence on the spectral properties of aquo transition-metal complexes, has been less investigated. Therefore, the density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods have been applied to the study structural and spectral properties of these aquo Pd(II) complexes. All quantum chemical calculations have been performed using the Turbomole program suite along with the B3LYP hybrid functional due to its moderate efficiency and

* Corresponding author e-mail: klhan@dicp.ac.cn (K.-L.H.), stang@chem.utah.edu (P.J.S.).

[†] Chinese Academy of Sciences.

[‡] University of Utah.

Table 1. Calculated Important Bond Distances (Å) and Angles (deg) and the Corresponding X-ray Data³ (in Parentheses)

	[(dppp)Pd(H ₂ O) ₂] ²⁺	[(dppp)Pd(H ₂ O)(OSO ₂ CF ₃)] ⁺ (OSO ₂ CF ₃) [−]	[(dppp)Pd(H ₂ O) ₂] ²⁺ (OSO ₂ CF ₃) [−] ₂
Pd–O ₁	2.216	2.137 (2.106)	2.122 (2.135)
Pd–O ₂	2.189		2.122 (2.127)
Pd–O ₃		2.129 (2.159)	
Pd–P ₁	2.304	2.305 (2.237)	2.299 (2.231)
Pd–P ₂	2.304	2.305 (2.228)	2.299 (2.226)
P ₁ –C ₁	1.847	1.854 (1.812)	1.852 (1.804)
P ₁ –C ₆	1.831	1.832 (1.801)	1.831 (1.815)
P ₁ –C ₇	1.818	1.830 (1.805)	1.831 (1.799)
P ₂ –C ₃	1.846	1.854 (1.819)	1.852 (1.814)
P ₂ –C ₄	1.818	1.828 (1.815)	1.831 (1.803)
P ₂ –C ₅	1.831	1.832 (1.812)	1.831 (1.804)
O ₁ –H ₁	0.977	1.012 (0.71)	1.007 (0.83)
O ₁ –H ₂	0.981	0.997 (0.74)	1.001 (0.74)
O ₂ –H ₃	0.977		1.007 (0.76)
O ₂ –H ₄	0.979		1.001 (0.72)
S ₁ –O ₃		1.534 (1.469)	1.489 (1.431)
S ₁ –O ₄		1.480 (1.425)	1.489 (1.434)
S ₂ –O ₅		1.514 (1.426)	1.495 (1.448)
S ₂ –O ₆			1.495 (1.419)
O ₁ ···H ₃	2.679		
O ₃ ···H ₄			1.700 (1.93)
O ₄ ···H ₂		1.746 (2.04)	1.700 (2.00)
O ₅ ···H ₁			1.625 (1.83)
O ₆ ···H ₃			1.625 (2.03)
P ₁ –Pd–P ₂	91.21°	91.87° (90.98°)	93.91 (90.33)
O ₁ –Pd–O ₂	80.48°		93.07 (87.66)
O ₁ –Pd–O ₃		88.44° (86.1°)	
P ₁ –Pd–O ₁	95.51°	90.83° (93.2°)	86.38° (93.38°)
O ₂ –Pd–P ₂	92.80°		86.44° (89.42°)
O ₃ –Pd–P ₂		89.85° (89.5°)	
H ₁ –O ₁ –H ₂	107.4°	108.4° (107°)	113.2° (109°)
H ₃ –O ₂ –H ₄	108.7°		113.1° (114°)
O ₂ –H ₃ ···O ₁	89.62°		
O ₂ –H ₄ ···O ₃			161.2° (172°)
O ₁ –H ₂ ···O ₄		158.1° (157°)	161.2° (172°)
O ₁ –H ₁ ···O ₅		153.0° (153°)	164.6° (173°)
O ₂ –H ₃ ···O ₆			165.1° (163°)

accuracy and def-SV(P) basis set for nonmetal elements as well as def-TZVP and the pseudopotential def-ECP basis sets for Pd.⁵

Optimized conformational structures of the *cis*-[(dppp)-Pd(H₂O)₂]²⁺, *cis*-[(dppp)Pd(H₂O)(OSO₂CF₃)]⁺(OSO₂CF₃)[−], and *cis*-[(dppp)Pd(H₂O)₂]²⁺(OSO₂CF₃)[−]₂ complexes are presented in Figure 1, and some important computationally predicted bond distances and bond angles are listed in Table 1. All three aquo Pd(II) complexes have a square-planar coordination sphere. The calculated bond angles around the palladium atom of each complex range from 80.5°–95.5°, which are close to expected values of 90° and in accordance with X-ray data.³ Calculated palladium–phosphorus bond distances of 2.299–2.305 Å are in the normal range for *cis*-chelated phosphorus. Calculated Pd–OH₂ distances in *cis*-[(dppp)Pd(H₂O)₂]²⁺ are 2.216 and 2.189 Å, respectively, due to the different conformation of the two coordinated water molecules: one of which is perpendicular to the coordination plane while the other is roughly located within the plane. There is also a weak hydrogen bond formed between the two water molecules with a distance H₃···O₁ of 2.679 Å. From Table 1 it can be seen that all bond distances are in good agreement with the previously reported X-ray data³ with the exception of the bond distances to hydrogen atoms. The calculated bond distances of the O–H bonds are noticeably longer than those obtained from X-ray data. This is due to the well-known X-ray crystallographic underestimation of bond

distances to hydrogen atoms.³ As a corollary, the O···H hydrogen bond distances will be overestimated by X-ray crystallographic studies. Hence, hydrogen bond distances between coordinated water and OSO₂CF₃[−] anions are calculated to be in the range of 1.625–1.746 Å, which are significantly shorter than the values from X-ray data.³ It is also important to note that Pd–OH₂ distances are shortened in *cis*-[(dppp)Pd-(H₂O)₂]²⁺(OSO₂CF₃)[−]₂ and *cis*-[(dppp)Pd(H₂O)(OSO₂CF₃)]⁺-(OSO₂CF₃)[−] due to the hydrogen bonding interactions between the coordinated water molecule(s) and OSO₂CF₃[−] anions. At the same time, the bond angles of P–Pd–P and O–Pd–O are increased, and the bond angles of P–Pd–O are correspondingly decreased. In addition, the H–O–H angles of the coordinated water molecules are somewhat enlarged in the presence of the hydrogen bonding interactions.

Figure 2 shows the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the three aquo Pd(II) complexes studied computationally. It is noteworthy that the HOMO orbitals similarly have electron density localized on the *cis*-[(dppp)Pd(H₂O)₂]²⁺ moiety for all three aquo Pd(II) complexes. However, the electron density of the LUMO orbital has been delocalized from the *cis*-[(dppp)Pd(H₂O)₂]²⁺ moiety to the OSO₂CF₃[−] anions for the hydrogen-bonded aquo Pd(II) complexes, which is believed to be induced by the hydrogen bonding interactions. Hence, LUMO orbitals of these aquo Pd(II) complexes can be influenced

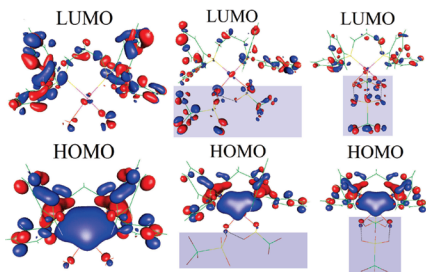


Figure 2. Frontier molecular orbitals (MOs) of the various aquo Pd(II) complexes.

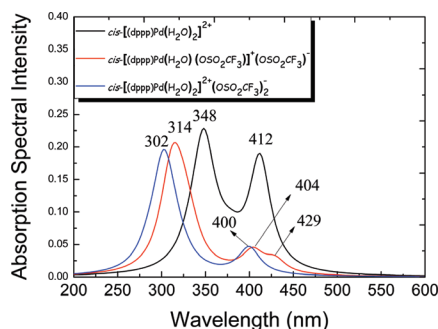


Figure 3. Calculated absorption spectra of the various aquo Pd(II) complexes. The absorption maxima values are labeled.

significantly by hydrogen bonding. Furthermore, the HOMO–LUMO energy gap of the *cis*-[(dppp)Pd(H₂O)₂]²⁺ complex increases from 3.72 to 4.40 eV by introducing two intermolecular hydrogen bonds in *cis*-[(dppp)Pd(H₂O)₂]²⁺(OSO₂CF₃)₂[−]. The energy gap of *cis*-[(dppp)Pd(H₂O)(OSO₂CF₃)]⁺(OSO₂CF₃)[−], on the other hand, decreases to 3.54 eV. The decrease of the HOMO–LUMO energy gap is ascribed to the substitution of one of the coordinated water molecules with an OSO₂CF₃[−] anion.

The calculated absorption spectra of aquo Pd(II) complexes obtained using TDDFT methods are shown in Figure 3. The absorption spectrum of *cis*-[(dppp)Pd(H₂O)₂]²⁺ has a clear two-peak structure with maxima at 412 and 348 nm. The absorption maxima of *cis*-[(dppp)Pd(H₂O)₂]²⁺(OSO₂CF₃)₂[−] are blue-shifted to 400 and 302 nm, respectively. It is therefore observed that intermolecular hydrogen bonding in *cis*-[(dppp)Pd(H₂O)₂]²⁺(OSO₂CF₃)₂[−] can induce the absorption spectra shift to the blue, which is contrary to the spectral red-shift of most organic chromophores.⁴ This may be due to the electron delocalization of the LUMO orbital from the *cis*-[(dppp)Pd(H₂O)₂]²⁺ moiety to the two OSO₂CF₃[−] anions induced by the intermolecular hydrogen bonding interactions. Consequently, the participation of the hydrogen-bonded OSO₂CF₃[−] anion in LUMO orbital significantly increases the HOMO–LUMO energy gap of the *cis*-[(dppp)Pd(H₂O)₂]²⁺(OSO₂CF₃)₂[−] complex in comparison with that of *cis*-[(dppp)Pd(H₂O)₂]²⁺. Moreover, it is also demonstrated that the hydrogen-bonded OSO₂CF₃[−] anion can shift the absorption spectra to the blue. For the case of *cis*-[(dppp)Pd(H₂O)(OSO₂CF₃)]⁺(OSO₂CF₃)[−], it is interesting to note that a new red-shifted peak appears at 429 nm in addition to the blue-shifted absorption maxima at 404 and 314 nm. It is distinct that the hydrogen-bonded and coordinated OSO₂CF₃[−] anions coexist in *cis*-[(dppp)Pd(H₂O)(OSO₂CF₃)]⁺(OSO₂CF₃)[−] complex. Furthermore, both the hydrogen-bonded OSO₂CF₃[−]

anion and coordinated OSO₂CF₃[−] anion participate in the electron delocalization of the LUMO orbital. Therefore, the blue-shifted absorption peaks may be dominantly due to the hydrogen-bonded OSO₂CF₃[−] anion in *cis*-[(dppp)Pd(H₂O)(OSO₂CF₃)]⁺(OSO₂CF₃)[−] complex. On the other hand, the new red-shifted peak at 429 nm is believed to have originated from the coordinated OSO₂CF₃[−] anion. Moreover, the participation of the coordinated OSO₂CF₃[−] anion in LUMO orbital can remarkably decrease the HOMO–LUMO energy gap of the *cis*-[(dppp)Pd(H₂O)(OSO₂CF₃)]⁺(OSO₂CF₃)[−] complex. It is demonstrated that the coordinated OSO₂CF₃[−] anion can shift the absorption spectra to the red, which is contrary to the hydrogen-bonded OSO₂CF₃[−] anion. At the same time, the longest absorption wavelengths of these aquo Pd(II) complexes, which are 412, 400, and 429 nm for the *cis*-[(dppp)Pd(H₂O)₂]²⁺, *cis*-[(dppp)Pd(H₂O)(OSO₂CF₃)]⁺(OSO₂CF₃)[−], and *cis*-[(dppp)Pd(H₂O)₂]²⁺(OSO₂CF₃)₂[−] complexes, are consistent with their corresponding HOMO–LUMO energy gaps of 3.72, 4.40, and 3.54 eV, respectively.

In summary, we have presented a theoretical investigation into the influence of hydrogen bonding on the structural and spectral properties of various aquo Pd(II) complexes. The structures and the HOMO–LUMO energy gaps of aquo Pd(II) complexes can be markedly changed by hydrogen bonding interactions. In addition, hydrogen bonds can also significantly influence absorption spectra. It has been demonstrated that the hydrogen-bonded OSO₂CF₃[−] anion can shift the absorption spectra to the blue, while the coordinated OSO₂CF₃[−] anion can shift the absorption spectra to the red. Further theoretical studies of the excited states of aquo transition-metal complexes will be performed in order to help understand the dynamic mechanism of hydrogen production by photocatalytic water splitting in many transition-metal complexes.⁶

Acknowledgment. K.L.H. thanks NKBRFSF (2007CB815202 and 2009CB220010) and NSFC (20833008) for financial support. P.J.S. thanks the NSF (CHE-0306720) for financial support.

Supporting Information Available: Cartesian coordinates and transition energies of optimized aquo Pd(II) complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (a) Beck, W.; Sünkel, K. *Chem. Rev.* **1988**, *88*, 1405. (b) Kubas, G. J.; Burns, C. J.; Khalsa, G. R. K.; Van Der Sluys, L. S.; Kiss, G.; Hoff, C. D. *Organometallics* **1992**, *11*, 3390. (c) Tamayo, A. B.; Alleyne, B. D.; Djurovich, P. I.; Lamansky, S.; Tsyba, I.; Ho, N. N.; Bau, R.; Thompson, M. E. *J. Am. Chem. Soc.* **2003**, *125*, 7377. (d) Alezra, V.; Bernardinelli, G.; Corminboeuf, C.; Frey, U.; Kundig, E. P.; Merbach, A. E.; Saudan, C. M.; Viton, F.; Weber, J. *J. Am. Chem. Soc.* **2004**, *126*, 4843. (e) Bunzli, J. C. G.; Piguet, C. *Chem. Soc. Rev.* **2005**, *34*, 1048. (f) Wik, B. J.; Lersch, M.; Krivokapic, A.; Tilset, M. *J. Am. Chem. Soc.* **2006**, *128*, 2682. (g) Beret, E. C.; Martinez, J. M.; Pappalardo, R. R.; Marcos, E. S.; Doltsinis, N. L.; Marx, D. *J. Chem. Theory Comput.* **2008**, *4*, 2108.
- (a) Vicente, J.; Arcas, A. *Coord. Chem. Rev.* **2005**, *249*, 1135. (b) Jain, V. K.; Jain, L. *Coord. Chem. Rev.* **2005**, *249*, 3075. (c) Machotta, A. B.; Straub, B. F.; Oestreich, M. *J. Am. Chem. Soc.* **2007**, *129*, 13455. (d) Sakaguchi, S.; Yoo, K. S.; O'Neill, J.; Lee,

- J. H.; Stewart, T.; Jung, K. W. *Angew. Chem., Int. Ed.* **2008**, 47, 9326. (e) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, 100, 853. (f) Lopez-Serrano, J.; Duckett, S. B.; Aiken, S.; Lenero, K. Q. A.; Drent, E.; Dunne, J. P.; Konya, D.; Whitwood, A. C. *J. Am. Chem. Soc.* **2007**, 129, 6513.
- (3) Stang, P. J.; Cao, D. H.; Poulter, G. T.; Arif, A. M. *Organometallics* **1995**, 14, 1110.
- (4) (a) Zhao, G.-J.; Han, K.-L. *J. Phys. Chem. A* **2007**, 111, 2469. (b) Zhao, G.-J.; Liu, J.-Y.; Zhou, L.-C.; Han, K.-L. *J. Phys. Chem. B* **2007**, 111, 8940. (c) Zhao, G.-J.; Han, K.-L. *ChemPhysChem* **2008**, 9, 1842. (d) Zhao, G.-J.; Han, K.-L. *Biophys. J.* **2008**, 94, 38.
- (5) (a) Furche, F.; Ahlrichs, R.; Wachsmann, C.; Weber, E.; Sobanski, A.; Vogtle, F.; Grimme, S. *J. Am. Chem. Soc.* **2000**, 122, 1717. (b) Furche, F.; Ahlrichs, R. *J. Am. Chem. Soc.* **2002**, 124, 3804. (c) Furche, F.; Ahlrichs, R. *J. Chem. Phys.* **2002**, 117, 7433.
- (6) (a) Sakai, K.; Ozawa, H. *Coord. Chem. Rev.* **2007**, 251, 2753. (b) Meyer, T. J. *Nature* **2008**, 451, 778.

CT900216M