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Theoretical Modeling of Water Exchange on $[Pd(H_2O)_4]^{2+}$, $[Pt(H_2O)_4]^{2+}$, and *trans*-$[PtCl_2(H_2O)_2]$

Robert J. Deeth*,† and Lars I. Elding‡

Inorganic Computational Chemistry Group, Department of Chemistry, University of Warwick,
Coventry CV4 7AL, U.K., and Inorganic Chemistry 1, Chemical Center, Lund University,
P.O. Box 124, S-221 00 Lund, Sweden

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Density functional theory is applied to modeling the exchange in aqueous solution of H_2O on $[Pd(H_2O)_4]^{2+}$, $[Pt(H_2O)_4]^{2+}$, and *trans*-$[PtCl_2(H_2O)_2]$. Optimized structures for the starting molecules are reported together with trigonal bipyramidal (tbp) systems relevant to an associative mechanism. While a rigorous tbp geometry cannot by symmetry be the actual transition state, it appears that the energy differences between model tbp structures and the actual transition states are small. Ground state geometries calculated *via* the local density approximation (LDA) for $[Pd(H_2O)_4]^{2+}$ and relativistically corrected LDA for the Pt complexes are in good agreement with available experimental data. Nonlocal gradient corrections to the LDA lead to relatively inferior structures. The computed structures for analogous Pd and Pt species are very similar. The equatorial $M-OH_2$ bonds of all the LDA-optimized tbp structures are predicted to expand by 0.25−0.30 Å, while the axial bonds change little relative to the planar precursors. This bond stretching in the transition state counteracts the decrease in partial molar volume caused by coordination of the entering water molecule and can explain qualitatively the small and closely similar volumes of activation observed. The relatively higher activation enthalpies of the Pt species can be traced to the relativistic correction of the total energies while the absolute $\Delta H^{\ddagger}$ values for exchange on $[Pd(H_2O)_4]^{2+}$ and $[Pt(H_2O)_4]^{2+}$ are reproduced using relativistically corrected LDA energies and a simple Born model for hydration. The validity of the latter is confirmed *via* some simple atomistic molecular mechanics estimates of the relative hydration enthalpies of $[Pd(H_2O)_4]^{2+}$ and $[Pd(H_2O)_5]^{2+}$. The computed $\Delta H^{\ddagger}$ values are 57, 92, and 103 kJ/mol compared to experimental values of 50(2), 90(2), and 100(2) kJ/mol for $[Pd(H_2O)_4]^{2+}$, $[Pt(H_2O)_4]^{2+}$, and *trans*-$[PtCl_2(H_2O)_2]$, respectively. The calculated activation enthalpy for a hypothetical dissociative water exchange at $[Pd(H_2O)_4]^{2+}$ is 199 kJ/mol. A qualitative analysis of the modeling procedure, the relative hydration enthalpies, and the zero-point and finite temperature corrections yields an estimated uncertainty for the theoretical activation enthalpies of about 15 kJ/mol.

Introduction

A number of exchange processes at square-planar palladium(II) and platinum(II) complexes with oxygen-, nitrogen-, sulfur-, and carbon-bonded ligands have been studied.[1−14] Except for cases where there is extensive transfer of electron density from strongly σ-bonding carbon-donor ligands to the metal center,[10,15] these processes, like square-planar substitution reactions in general, seem to take place *via* associative mechanisms.

The mechanistic classification of processes involving exchange of identical ligands between the inner coordination sphere and bulk solution relies mainly on the entropies and volumes of activation. For the exchange of neutral molecules, contributions to these parameters from solvational changes during the activation process are usually assumed to be of minor importance. For simple square-planar solvent exchange processes, the observed volumes of activation vary greatly, however. For instance, the activation volumes $\Delta V^{\ddagger}$ for water exchange at $[Pd(H_2O)_4]^{2+}$ and $[Pt(H_2O)_4]^{2+}$ are -2.2 and -4.6 cm^3 mol^{-1}, respectively, whereas for the exchange of dimethyl sulfide (Me_2S) at the corresponding tetrasolvated cations, the values are -9.4 and -22.0 cm^3 mol^{-1}. Attempts have been made to correlate these differences with the size and steric requirements of the ligands and/or with the steric encumbrance of the inner coordination sphere of the complex.[9,10,12] However, later high-pressure studies of complex formation reactions of the non-sterically hindered tetraaqua complexes of palladium(II) and platinum(II) indicate that there is no such obvious correlation.[17] As discussed earlier,[18,19] other factors that might influence the magnitude of the activation volumes are bond stretching in the

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† University of Warwick.
‡ Lund University.
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transition state, changes in electrostriction of solvent molecules due to changes of ionic radii in the activation process, and (for associative square-planar reactions in particular) the possibility of loss of axially bound solvent molecules when a five-coordinate transition state is formed.[12]

At present, *ab initio* theory is the only technique for obtaining detailed structural and energetic data for the transition states (TS) for these processes. The calculation of TS geometries and their energies relative to reactants and products presents a significant challenge to quantum chemistry. This paper addresses a theoretical estimation of the activation energy barriers for the well-studied[1,2,5,8] water exchange on $[Pd(H_2O)_4]^{2+}$, $[Pt(H_2O)_4]^{2+}$, and *trans*-$[PtCl_2(H_2O)_2]$ in associative activation processes (eqs 1−3). In the case of $[Pd(H_2O)_4]^{2+}$, a dissociative process has been tested as well (eq 4.)

$$[Pd(H_2O)_4]^{2+} + H_2O \rightarrow \{[Pd(H_2O)_5]^{2+}\}^{\ddagger} \qquad (1)$$

$$[Pt(H_2O)_4]^{2+} + H_2O \rightarrow \{[Pt(H_2O)_5]^{2+}\}^{\ddagger} \qquad (2)$$

$$\textit{trans}\text{-}[PtCl_2(H_2O)_2] + H_2O \rightarrow \{[PtCl_2(H_2O)_3]\}^{\ddagger} \qquad (3)$$

$$[Pd(H_2O)_4]^{2+} \rightarrow \{[Pd(H_2O)_3]^{2+}\}^{\ddagger} + H_2O \qquad (4)$$

Since the TS structures are unknown, they must be calculated. A general *ab initio* method is required since any parametric approach, whether completely empirical or only semiempirical, employs experimental data (*e.g.*, geometries, heats of formation, ionization energies) to determine values for the relevant adjustable parameters and these data are not available for transition states. *Ab initio* schemes based on density functional theory (DFT) are enjoying some success at handling transition metal systems efficiently and accurately.[20]

Vacuum-phase *ab initio* results can often describe reaction mechanisms in solution successfully. However, this generally relates to reactions of neutral molecules in nonpolar solvents. The present work shows that the same is not true for charged complexes where hydration effects must be treated explicitly.

Experimental Section

Computational Details. All DFT calculations were based on the Amsterdam density functional (ADF) program system version 2.0.1.[21] The ADF program employs numerical integration and is supplied with five types of Slater-type-orbital (STO) basis set (I−V) of which set IV has been used here. Set IV describes uncontracted triple-ζ expansions for the valence orbitals with an additional function (2p for H, 3d for O and Cl, 5p for Pd, and 6p for Pt).[22,23] Geometry optimizations were generally carried out using the uniform electron gas local density approximation[24] (LDA) and analytical energy gradients.[25] The LDA correlation energy was computed according to Vosko, Wilk, and Nusair's[26] parametrization of electron gas data. Gradient-corrected (GC) functionals for the LDA exchange and correlation terms employed the formulations of Becke[27] and Perdew,[28,29] respectively. Unless otherwise stated, the GC functionals were applied after geometry optimization at the LDA level. The lower core shells on the atoms (1s on O, 1s to 2p on Cl, 1s to 3d on Pd, and 1s to 5p on Pt) were treated by the frozen core approximation.[30] The total molecular electron density was fitted in each self-consistent field cycle by auxiliary s, p, d, f, and g STO functions.[31] Scalar relativistic corrections[32,33] to the LDA (LDA/rel) were applied for all aspects of the calculations on Pt^{II} species or at the LDA-optimized geometries for the Pd^{II} complexes unless otherwise indicated. The total molecular binding energies were computed relative to an arbitrary reference state calculated for the neutral, spin-restricted atoms using the same basis sets as for the molecule. These binding energies are not absolute, but this is not relevant provided that, as here, the reference state for both sides of the reaction is the same. Connolly surfaces were computed using the Nemesis program[34] and employed a dot density of 10 and probe radius of 1.40 Å.

Results

In order to determine activation energies, the minimum energy structures for the species involved must be calculated. Test optimizations for $[Pd(H_2O)_4]^{2+}$ showed that the water adopts a planar coordination mode such that the metal lies in the ligand plane. Local C_{2v} symmetry was therefore imposed on each $M-OH_2$ interaction, which gives three parameters to be optimized: the M−O and O−H distances and the M−O−H angle. It was further assumed that the planes of the water ligands related by an O−M−O angle of 180° were parallel. This leads to the various ligand conformations shown in Figure 1.

The three- and five-coordinate species have overall C_{2v} or D_{3h} symmetry while the planar molecules are either D_{2h} or D_{4h}. The relevant point group was employed for each geometry calculation, and all variables were optimized subject to the constraints of maintaining the point group symmetry. The exceptions were the five-coordinate species of C_{2v} symmetry (Figure 1, structures **8**−**15**, **19**, and **20**) where the three M−O distances for the notional equatorial bonds of the (near) trigonal bipyramid (tbp) were constrained to be equivalent. This procedure permits the geometry of an approximate transition state to be calculated *via* a constrained energy minimization rather than by the general but more time-consuming method of locating the saddle point on the potential energy surface using the matrix of second derivatives. As will be reported at a later date, the true transition states for these exchange processes are quite difficult to locate even for apparently simple species like $[PdCl_5]^{3-}$. However, a near-tbp TS struture is confirmed for the latter which has virtually the same energy as the tbp structure. It seems that the constrained minimizations give satisfactory near-TS structures and provide activation energies for associative exchange only a few kJ/mol higher than that derived from the actual TS.

Another feature to consider is the possible role of solvent molecules loosely coordinated along the *z*-axis of the planar complexes. This has been verified for d^9 Cu species.[35] However, for low-spin d^8 systems, the driving force for axial elongation is at least twice as large as that for a comparable Cu^{II} compound[36] and the generally larger d-orbital energy splittings for second- and third-row transition metals will further weaken any axial interaction. Noteworthy attempts to detect axially coordinated solvent molecules by NMR, low-angle X-ray

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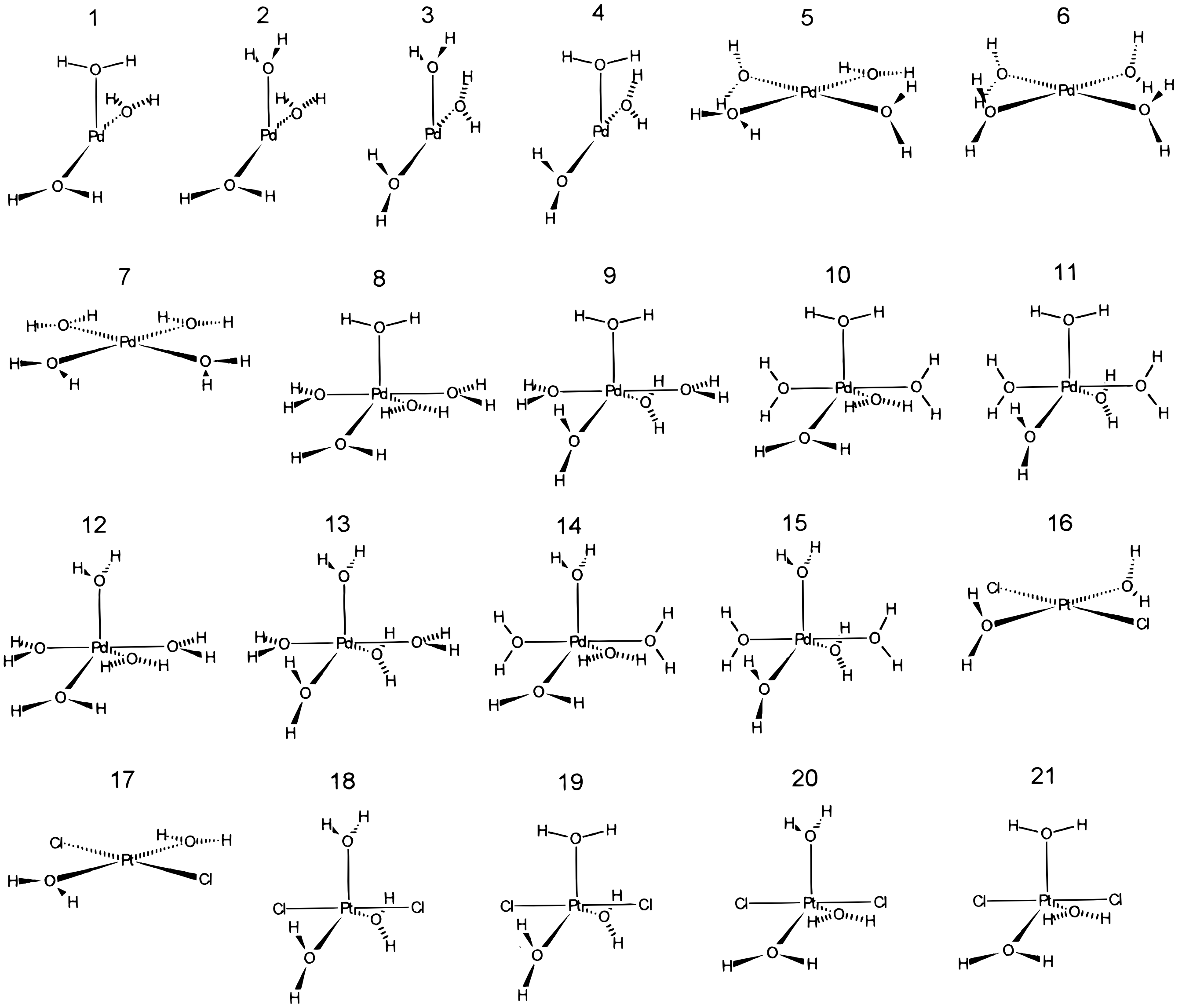

Figure 1. Structural diagrams for $[Pd(H_2O)_3]^{2+}$, $[Pd(H_2O)_4]^{2+}$, $[Pd(H_2O)_5]^{2+}$, *trans*-$[Pt(H_2O)_2Cl_2]$, and $[Pt(H_2O)_3Cl_2]$ displaying the various orientations of water ligands considered.

scattering, and EXAFS have given negative results.[1,37] For the present complexes, calculated metal–axial water distances fall in the range of 2.6–2.8 Å with binding energies of about 5 kJ/mol (LDA) and about −20 kJ/mol (GC). That is, the axial waters are weakly bound at the LDA level while the GC calculations suggest no axial binding. One of the axial waters is the notional entering ligand, but apart from taking note of the axial binding with regard to estimating the errors inherent in the overall modeling procedure, the second axial ligand was not considered explicitly.

With the tbp structures taken as reasonable approximations to the true transition states, certainly as far as the total energy is concerned, both LDA and GC binding energies were computed at the LDA- or LDA/rel-optimized geometries for all 21 structures in Figure 1. In all cases except $[Pd(H_2O)_5]^{2+}$, the minimum-energy structure is the same at both levels of theory and corresponds to structure **2** for $[Pd(H_2O)_3]^{2+}$, structure **5** for $[Pd(H_2O)_4]^{2+}$, structure **17** for *trans*-$[PtCl_2(H_2O)_2]$, and structure **21** for $[PtCl_2(H_2O)_3]$. For $[Pd(H_2O)_5]^{2+}$, structure **9** has the lowest LDA energy while structure **13** has the lowest GC energy, although the difference between LDA and GC energies for both structures is less than 10 kJ/mol. The difference between the lowest and highest binding energies for a given molecule is around 40–50 kJ/mol. The highest energy structures are **3**, **7**, **10**, **16**, and **18** for $[Pd(H_2O)_3]^{2+}$, $[Pd(H_2O)_4]^{2+}$, $[Pd(H_2O)_5]^{2+}$, *trans*-$[PtCl_2(H_2O)_2]$, and $[PtCl_2(H_2O)_3]$, respectively.

Under the assumption that the relative energies of the Pt–aqua complexes follow the same pattern as their Pd counterparts, the structures relevant to the activation energy calculations of all four reactions of eqs 1–4 are depicted in Figure 2 along with a comparison of calculated and observed bond lengths and angles. The O–H distances and M–O–H angles in all the complexes are about 0.98 ± 0.01 Å and 124 ± 2°, respectively, and have been omitted from Figure 2 for clarity.

Structural data for the ground state species are quite limited. The geometry of water is well-known,[38] and the LDA calculations are in good agreement. However, of the metal complexes, only $[Pt(H_2O)_4]^{2+}$ has been structurally characterized by EXAFS rather than by single-crystal X-ray diffraction.[37,39] However,

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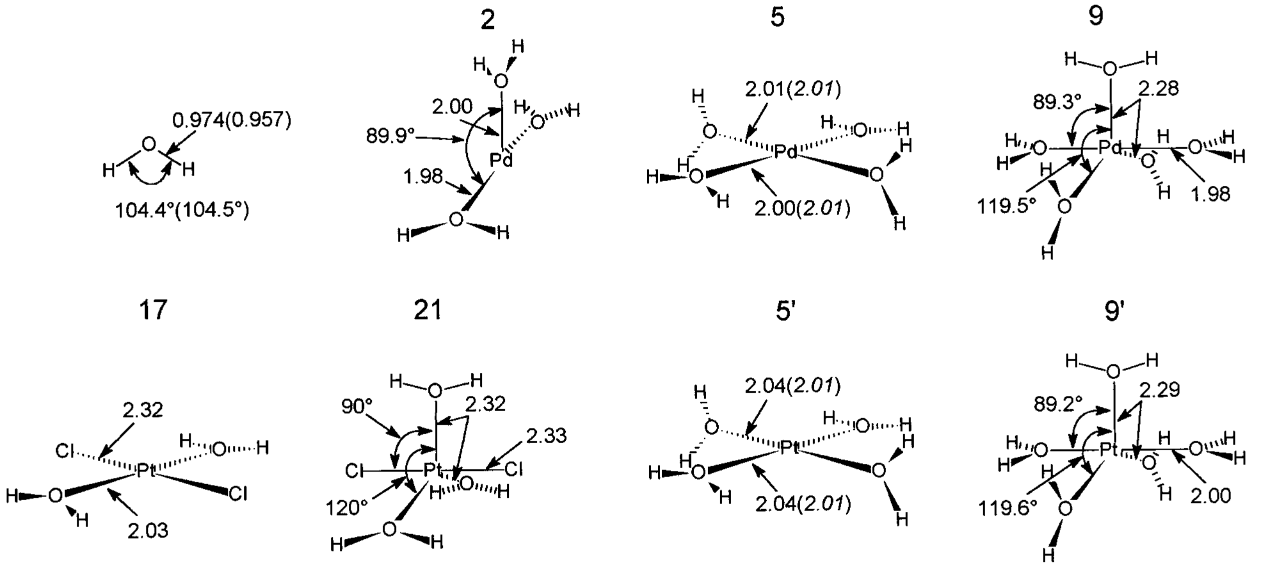

Figure 2. Calculated structural parameters for the minimum-energy conformations of H_2O, $[Pd(H_2O)_3]^{2+}$, $[Pd(H_2O)_4]^{2+}$, $[Pt(H_2O)_4]^{2+}$, $[Pd(H_2O)_5]^{2}+$, $[Pt(H_2O)_5]^{2+}$, *trans*-$[Pt(H_2O)_2Cl_2]$, and $[Pt(H_2O)_3Cl_2]$. Available experimental data (in Å and deg) are given in parentheses. (Note that the experimental bond length for $[Pd(H_2O)_4]^{2+}$ actually refers to the Pt analogue.)

the structures of Pd and Pt analogues are often similar,[40−43] and this is supported by the LDA calculations which give M−O distances for both tetraaqua ions within 0.04 Å of the experimental result for $[Pt(H_2O)_4]^{2+}$. Given this good agreement and that the Pt−Cl distance in $(NH_4)_2PtCl_4$ is 2.31 Å,[44] the computed structure of *trans*-$[PtCl_2(H_2O)_2]$, where the optimized Pt−Cl distance is 2.32 Å, appears reasonable also.

The effect on the calculated geometry of both the GC functional and relativity was undertaken for the $[M(H_2O)_4]^{2+}$ complexes. The (nonrelativistic) LDA Pd−O and Pt−O distances are 2.00 and 2.09 Å, respectively. Gradient corrections in the geometry optimizations using the basis sets described above increase the M−L bond length by about 0.08 Å for $[Pd(H_2O)_4]^{2+}$ and about 0.07 Å for $[Pt(H_2O)_4]^{2+}$. The scalar relativistic corrections shorten the M−L bonds by about 0.02 Å for Pd−O and 0.05 Å for Pt−O. The simple LDA gives a good Pd−O distance, while the best Pt−O length is obtained at the LDA/rel level. The GC function yields bond lengths that are too long. The LDA (or LDA/rel) geometries are therefore used throughout.

LDA and GC binding energies were computed for the eight species in Figure 2. In addition, scalar relativistic corrections to the energies were evaluated for all the complexes except $[Pd(H_2O)_3]^{2+}$. A correction for the latter was deemed unnecessary, given the small effect found for $[Pd(H_2O)_4]^{2+}$. As implemented in the ADF program, the relativistic correction includes the most important contributions, namely, the mass−velocity and Darwin corrections.[32,33] Spin−orbit coupling is omitted, except for the calculation of core potentials where the complete relativistic Hamiltonian is used albeit within the Xα (*i.e.*, LDA exchange only) approximation with $\alpha = 0.7$. Thus, there is a slight mismatch between the valence and core relativistic treatments but the error is small.

During the course of this work it became apparent that some form of solvation energy was also needed. The simplest equation describing the solvation energies of ions was developed by Born:[45]

$$\Delta G_S = -\frac{N_A Z^2 e^2}{8\pi\epsilon_0 r}\left(1 - \frac{1}{D}\right) \qquad (5)$$

The free energy of solvation ΔG_S depends on the ionic charge Z, the ionic radius r, and the solvent dielectric constant D and is overwhelmingly dominated by the enthalpy, with entropy making less than a 2% contribution.[45] For an aqueous solution with r expressed in picometers, eq 5 reduces to the following expression of the hydration enthalpy ΔH_H in kJ/mol (eq 6);

$$\Delta H_H = \frac{-Z^2}{r}\,6.97 \times 10^4 \qquad (6)$$

Estimates of the ionic radii are needed to use eq 6. A straightforward yet robust method for obtaining *relative* estimates of r is to compute the Connolly surface area[46] for the metal complex ions in Figure 2 and derive the radius of a sphere having the same area. The Connolly surface gives some indication of the surface accessible to solvent. Although equating this value with the area of a sphere is crude, this method is easy to apply and gives remarkably good results (*vide infra*). This is presumably because only relative hydration enthalpies are required. Variation of the M−O distances by up to 0.1 Å changes ΔH_H by less than 10 kJ/mol.

An attempt to confirm the Born model hydration energy estimates was carried out for $[Pd(H_2O)_4]^{2+}$ using a crude atomistic simulation. A $[Pd(H_2O)_4]^{2+}$ ion was surrounded by 18 water molecules using the DROPLET option of the Sybyl molecular modeling package.[47] Gasteiger charges were placed on the waters while the LDA gross atomic charges were used for the metal complex. The PdO_4 framework was constrained at its LDA geometry, but the H atoms were allowed to move, subject to the standard Sybyl force-field parameters. The whole system was then minimized relative to a unit dielectric constant

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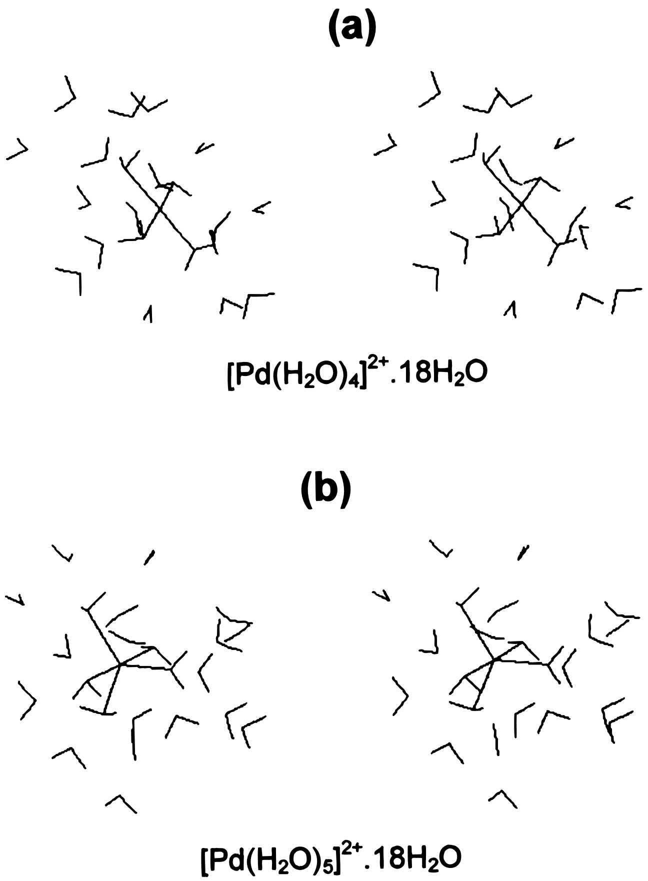

Figure 3. Stereoviews of a representative Sybyl “DROPLET” hydration simulation for $[Pd(H_2O)_4]^{2+}$ (a) and $[Pd(H_2O)_5]^{2+}$ (b). See text for details.

for the electrostatic energy. A similar procedure was adopted for five-coordinate $[Pd(H_2O)_5]^{2+}$, and the hydration energy was taken as the difference between the two minimized energy values. Several water molecules were then moved more or less at random, and the whole process was repeated. Seven repetitions gave a value for the hydration energy difference of 80 ± 5 kJ/mol. A representative stereodiagram for “solvated” $[Pd(H_2O)_4]^{2+}$ and $[Pd(H_2O)_5]^{2+}$ is shown in Figure 3.

The Pt−aqua species in Figure 2 have very similar structures to their Pd counterparts and hence almost the same hydration energies. The absolute values for the Connolly surface areas, effective spherical radii, and hydration enthalpies are as follows: 114.3 Å^2, 302 pm, and −908 kJ/mol for $[Pd(H_2O)_3]^{2+}$, 133 Å^2, 325 pm, and −842 kJ/mol for $[M(H_2O)_4]^{2+}$, and 160 Å^2, 357 pm, and −768 kJ/mol for $[M(H_2O)_5]^{2+}$. The remaining molecules in Figure 2 are neutral and, within the Born approximation used here, have zero hydration enthalpies.

The Born hydration model contribution to the activation enthalpy for water exchange at $[M(H_2O)_4]^{2+}$ complex is therefore +74 kJ/mol for an associative mechanism and −66 kJ/mol for a dissociative mechanism. These figures simply reflect the change in cation size with changing coordination number. The former value of 74 kJ/mol also compares favorably with the 80 ± 5 kJ/mol estimated by the atomistic simulation. While each method is in itself crude, together they are reasonably consistent and suggest that the hydration energy difference for the aqua complexes is approximately 77 ± 10 kJ/mol. We conclude that there are large error cancellations such that while the absolute hydration energy for any one ion may be inaccurate, the difference between $[M(H_2O)_4]^{2+}$ and $[M(H_2O)_5]^{2+}$ is well represented even by the simplistic models.

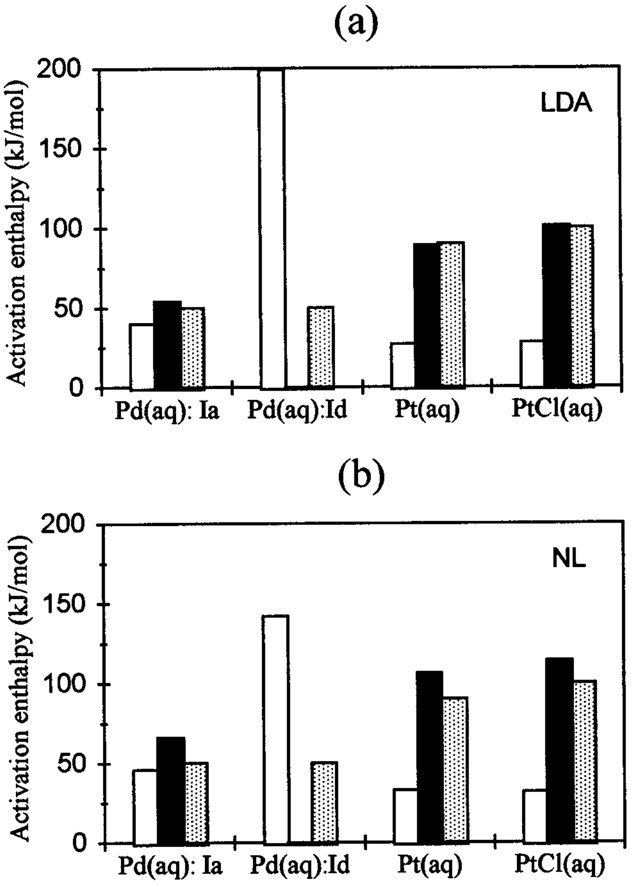

Figure 4. Calculated and observed[2,5,8] activation enthalpies. The four sets of columns refer respectively to results for an associative mechanism for $[Pd(H_2O)_4]^{2+}$, a dissociative mechanism for $[Pd(H_2O)_4]^{2+}$, and associative mechanisms for $[Pt(H_2O)_4]^{2+}$ and *trans*-$[Pt(H_2O)_2Cl_2]$. All of the calculated data include any relevant hydration enthalpy corrections while (a) refers to LDA binding energies and (b) includes gradient corrections to the total binding energies. The black bars include relativistic contributions computed at the LDA geometries, the white bars refer to nonrelativisitic results, and the shaded boxes represent observed values. See text for more details.

This view is generally supported by Warshel,[48] who concludes that provided the first hydration sphere is well represented, the effect from the remaining solvent can be accommodated by a range of schemes of varying degrees of sophistication. Here, the first hydration shell is the coordinated water molecules which are treated fully by DFT. The second hydration shell, represented by 18 water molecules, is reasonable in the light of recent EXAFS measurements,[49] which indicate about 12−13 next-nearest water molecules surrounding the $[Zn(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{3+}$ complexes. It is also significant that there is no change in overall ionic charge between reactants and the TS models which, given the Z^2 dependence of the hydration enthalpy, could lead to much larger uncertainties in ΔH_S when using the Born model.

The combination of the relative DFT binding energies and the hydration enthalpy contributions gives theoretical estimates of the activation enthalpy as shown in Figure 4.

Discussion

The fundamental nature of the solvent exchange process, particularly in aqueous solution, has attracted considerable research efforts.[9] Water exchange on first-row metal hexaaqua

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complexes has recently become the focus of some controversy. *Ab initio* Hartree−Fock calculations[50,51] suggest a uniform dissociative mechanism for all of the hexaaqua metal ions, contrary to experimental assignments based on activation volumes.[52,53] This description of the mechanism has, in turn, been questioned.[54,55]

The present calculations strongly suggest that water exchange at the simple square-planar metal centers studied here proceeds *via* an associative mechanism, in agreement with experimental assignments.[2,5] This is shown graphically in the first two sets of columns in Figure 4a and 4b. The assumption of an associative mechanism for water exchange on $[Pd(H_2O)_4]^{2+}$ (labeled Pd(aq): Ia in Figure 4) gives the results in the first set of columns. The agreement between theory and experiment is within 10 kJ/mol with the best result obtained from a relativistically corrected energy at the LDA geometry. A dissociatve mechanism (Pd(aq): Id in Figure 4) gives a discrepancy of over 100 kJ/mol. The last two sets of columns describe, respectively, associative water exchange on $[Pt(H_2O)_4]^{2+}$ (Pt(aq) in Figure 4) and on *trans*-$[PtCl_2(H_2O)_2]$ (PtCl(aq) in Figure 4). Both also give agreement to better than 10 kJ/mol at the relativistically corrected LDA level, which argues strongly that (a) the theoretical procedures are reasonable and (b) an associative mechanism applies throughout.

The agreement with the measured activation enthalpies is remarkable given the assumptions made. For example, no zero-point corrections have been applied nor have the computed activation enthalpies been corrected to 25 °C. In addition, we know that the five-coordinate structures are not the true transition states. The rigorous location of a TS requires computing the second derivative matrix and showing that there is exactly one negative eigenvalue. Indeed, structure **21** for $[PtCl_2(H_2O)_3]$ cannot possibly be a transition state since its symmetry (D_{3h}) is too high and would lead to a degenerate transition vector in violation of corollary A of ref 56. At best, it may be a so-called "monkey saddle" on the potential energy surface, but more work is required to characterize the transition states fully. It is well-known, however, that the potential energy surface connecting the extreme five-coordinate geometries of tbp and square pyramidal is quite flat.[57] The overall good agreement between theory and experiment suggests that the tbp structures computed here are close enough.

Furthermore, the zero-point energies are likely to be very similar for the reactants and the transition state. For example, for an associative process, three extra degrees of vibrational freedom will arise in the transition state. However, the TS will have one imaginary vibrational frequency, and for the species studied here, the equatorial bonds lengthen quite dramatically so that, overall, the change in vibrational energy should be small between the reactants and the transition state. Presumably, this will carry over into the temperature correction of $\Delta H^{\ddagger}$. The differences in raw DFT binding energies are thus quite good approximations for estimating $\Delta H^{\ddagger}$, which is supported by the success of the computational approach for water exchange on the neutral *trans*-$[PtCl_2(H_2O)_2]$ where no hydration energy correction is required.

The relative robustness of the Born model correction has already been mentioned. It is remarkable that a model for spherical ions appears to work so well for nonspherical species, but there are considerable error cancellations in a comparative study of this sort. Another example of such cancellations is that the water ligands will be subject to hydrogen-bonding forces in aqueous solution which will presumably alter the hydrogen atom positions from those shown in Figure 2. However, the effect on the reactants and tbp structures appears to be relatively constant, judging by the success of using idealized geometries in the calculations. Moreover, where geometries could be compared, the theoretical *in vacuo* M−O distances are in good agreement with experimental condensed phase data, indicating that the solvent has a minimal influence on the coordination geometry.

Although the vacuum-phase *geometries* can be used, quantitative estimates of activation *enthalpies* require an explicit solvation enthalpy correction. Thus, just the LDA energies for exchange on $[Pd(H_2O)_4]^{2+}$ describe a net energy loss of about −20 kJ/mol for an associative exchange implying that, in a vacuum, $[Pd(H_2O)_5]^{2+}$ should be stable. It is the change in hydration enthalpy of ~77 kJ/mol which is responsible for the observed positive activation enthalpy.

An interesting point alluded to above is the effect of gradient and relativistic corrections on the computed geometries. Gradient corrections lengthen M−L bonds, while relativity shortens them. The gradient correction is larger than the relativistic effect for $[Pd(H_2O)_4]^{2+}$ but about the same for $[Pt(H_2O)_4]^{2+}$. For the hexacarbonyls of Mo and W,[58] the LDA method gives M−CO distances that are too short such that the gradient corrections improve the agreement with experiment. For more classical coordination complexes such as those treated here, it appears that the best structures are obtained at the LDA or LDA/rel level. Our experience to date suggests that this might be a general difference between organometallic species or other complexes with a soft−soft metal−donor interaction and classical coordination complexes in that the geometries of the former are treated better by gradient-corrected DFT while the latter are better handled by the LDA approach. An analysis[59] of the optimized M−L bond lengths in 17 Werner-type complexes leads to the speculation that the difference is due to the change in bonding and the role of the d-orbitals in different types of complexes.

Organometallic and related species are more covalent and employ the d-orbitals extensively in bonding, while simple coordination complexes are relatively ionic and do not employ the d−orbitals very much. (For a review of the latter assertion, see Gerloch.[60]) One could speculate, therefore, that since the metal in an organometallic compound is more like a free atom than the metal in a classical Werner-type complex and that since both Becke[27] and Perdew[28,29] gauge much of the performance of their respective corrections terms with respect to atomic properties, gradient-corrected DFT works better for covalent species. Fortunately, we appear to be left with the happy accident that the local density approximation is quite good for the more classical coordination complexes.

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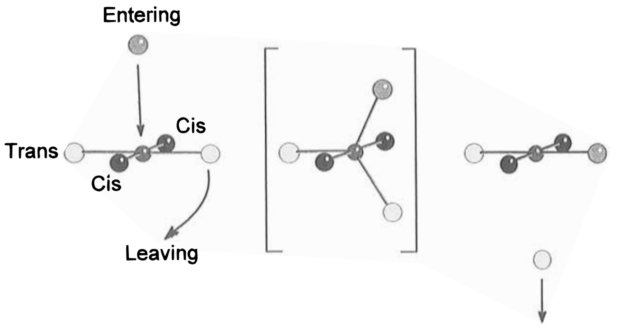

Figure 5. Schematic representation of the ligand exchange process on planar d^8 aqua complexes.

Although the LDA geometries are adequate to describe the water exchange process, the LDA energies alone are not and require relativistic corrections, especially for Pt^{II}. Additional gradient corrections add about 15−20 kJ/mol to all the theoretical activation enthalpies (see Figure 4b) but give an identical trend to the LDA data. When a hydration enthalpy contribution of 77 kJ/mol is assumed for the aqua species, the best comparison between theory and experiment is therefore as follows: for exchange on $[Pd(H_2O)_4]^{2+}$, $[Pt(H_2O)_4]^{2+}$, and *trans*-$[PtCl_2(H_2O)_2]$ the observed $\Delta H^‡$ values are 50(2),[5] 90(2),[1,2] and 100(2)[8] kJ/mol, while the theoretical values are 57(15), 92(15), and 103(15) kJ/mol, respectively. The estimated numerical error of around ±15 kJ/mol is based on the insensitivity of the relative hydration enthalpy calculations, the likely DFT energy variations accompanying any deviation of the $M-OH_2$ coordination away from planarity, and the contribution from weakly coordinated axial ligands (*vide supra*).

The agreement between theoretical and experimental activation enthalpies is very good and suggests that the computational procedure is reasonable. This implies that the computed structures are relevant to the exchange reactions, which is important since, at present, the only method for obtaining direct, detailed geometries of transition states is by computation. Since the structures are computed relative to a vacuum, this further implies either that the solvent does not significantly alter the molecular geometry or that the LDA method fortuitously reproduces condensed phase geometries. The latter is unlikely since DFT performs well for gas phase molecules, too.[61] The absence of a solvent effect on geometry is significant since it is easier to do calculations in the vacuum phase than to include solvation effects explicitly in the computational method, although the latter are necessary for *absolute* energetics.

Figure 2 shows that there is a large lengthening of nearly 0.3 Å in the equatorial bonds of the tbp structures. These three groups correspond to the entering, trans, and leaving groups, as shown schematically in Figure 5. The bonds to the cis ligands hardly change at all, consistent with the relative insignificance of cis effects. The origin of these geometrical changes can be traced to the stereochemical of activity[62] of the underlying d^8 configuration.

Increasing the coordination number from four to five should be accompanied by a general lengthening of the bonds. Superimposed on this is a differential distortion related to the underlying d-orbital occupations. In tbp symmetry, d_{z^2} is the highest energy d-orbital. In a low-spin tbp d^8 complex, d_{z^2} is empty and there will therefore be less repulsion of the ligand electrons along the z-axis. The axial bond lengths decrease while the equatorial contacts increase to compensate. The results is an axially compressed tbp which should be compared to the expected, elongated geometry predicted by the Gillespie−Nyholm theory for a closed shell d^{10} system. This variation of M−L distance with d configuration in tbp complexes is nicely illustrated by the $[M(Me_6tren)Br]Br$ complexes {M = Mn, Fe, Co, Ni, Cu, Zn; Me$_6$tren = tris(*N*,*N*-dimethylamino)amine},[62] although the effect in these high-spin complexes should be less pronounced than in the present low-spin tbp models.

Interpretation of activation volumes for exchange of neutral ligands is often based on the assumptions that the bond distances to the spectator ligands and the structure of the solvent are not greatly changed in the activation process. These assumptions might be reasonable in the light of Hartree−Fock calculations on the first-row hexaaqua complexes,[50] but our DFT results suggest that the same may not be true for the planar species. To our knowledge, the present attempt to model ligand exchange at planar d^8 centers gives the first demonstration of relatively extensive bond stretching in the TS.[64] The calculations show that the structures of the $[Pt(H_2O)_5]^{2+}$ and $[Pd(H_2O)_5]^{2+}$ transition states would be almost the same and that the structural similarity between the tetraaqua ions in their ground states extends to their transition states as well. Whether this is true also for palladium and platinum complexes with more strongly bonding donor ligands than oxygen remains to be studied.

Water exchange on $[Pt(H_2O)_4]^{2+}$ has an activation volume of -4.6 ± 0.2 cm^3 mol^{-1}, which is quite close, in absolute terms, to the value of -2.2 ± 0.2 cm^3 mol^{-1} observed for the palladium exchange.[2,5] The bond stretching in the transition state as well as the release of solvent molecules from the expanded TS complexes of Pd and Pt counteracts the decrease in molar volume caused by the association of the entering water molecule into the inner coordination sphere. These effects can explain, at least qualitatively, the small and closely similar volumes of activation observed for these two aqua complexes. On the other hand, the situation might be different for complexes with more strongly interacting donor ligands. For instance, reactions involving thioethers at analogous palladium and platinum complexes display large differences in the observed activation volumes, those for platinum always being much more negative.[17] These observations and those based on the Hartree−Fock calculations for first-row hexaaqua complexes[50] suggest that the simple mechanistic interpretation of activation volumes may require further examination.

Conclusions

Ab initio density functional theory has been used to model water exchange on $[Pd(H_2O)_4]^{2+}$, $[Pt(H_2O)_4]^{2+}$, and *trans*-$[PtCl_2(H_2O)_2]$. Geometries optimized at the local density approximation level (or its scalar relativistic extension) are in good agreement with the available structural data. Gradient corrections lead to inferior geometries for $[Pd(H_2O)_4]^{2+}$ and $[Pt(H_2O)_4]^{2+}$. A relativistic correction to the total molecular energy is important for describing the rather higher activation enthalpies of the Pt species, while absolute reproduction of the observed $\Delta H^‡$ values for water exchange on the cationic $[Pd(H_2O)_4]^{2+}$ and $[Pt(H_2O)_4]^{2+}$ complexes requires an explicit energy correction for solvation. Both the simple Born model for hydration and an approximate atomistic simulation, computed using the LDA geometries plus the relativistically corrected LDA energies, give excellent agreement with the

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(64) Muguruma *et al.*[63] have reported a theoretical study of water substitution by chloride on $[Pt(NH_3)(H_2O)]^{2+}$ but constrain the geometry of the T-shaped $[Pt(NH_3)_3]^{2+}$ fragment to its ground state configuration.

experimentally observed activation enthalpies for water exchange: $[Pd(H_2O)_4]^{2+}$ $\Delta H^{‡}$(obs) 50(2) kJ/mol, $\Delta H^{‡}$(calc) 57(15) kJ/mol; $[Pt(H_2O)_4]^{2+}$ $\Delta H^{‡}$(obs) 90(2) kJ/mol, $\Delta H^{‡}$(calc) 92(15) kJ/mol; *trans*-$[PtCl_2(H_2O)_2]$ $\Delta H^{‡}$(obs) 100(2) kJ/mol, $\Delta H^{‡}$(calc) 103(15) kJ/mol. The theoretical uncertainty of 15 kJ/mol is estimated from considering zero-point, finite temperature, and other corrections. Although the tbp structures cannot be the true transition states, calculations for other systems suggest that they are within about 5 kJ/mol. A dissociative mechanism was discounted since the dissociative activation enthalpy for $[Pd(H_2O)_4]^{2+}$ was computed to be 199 kJ/mol.

Given the good agreement between theoretical and experimental activation enthalpies, one assumes that the other calculated data such as the geometries are also reasonable. This has two important consequences. First, the effect of the solvent on structure is not significant. That is, the LDA delivers structures relative to a vacuum which are in good agreement with aqueous solution phase geometries. Second, the computed trigonal bipyramidal structures for $[Pd(H_2O)_5]^{2+}$ and $[Pt(H_2O)_5]^{2+}$ are very similar, which has implications for the interpretation of the activation volumes.

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