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A Systematic ab Initio Study of the Hydration of Selected Palladium Square-Planar Complexes. A Comparison with Platinum Analogues

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The hydration surface of four palladium square-planar complexes (neutral *cis*-dichlorodiamminepalladium $PdCl_2(NH_3)_2$, neutral *trans*-dichlorodiamminepalladium $PdCl_2(NH_3)_2$, tetraamminepalladium cation $[Pd(NH_3)_4]^{2+}$, and tetrachloropalladium anion $[PdCl_4]^{2-}$) has been examined by advanced quantum-chemical calculations. Preliminary geometry optimizations were carried out using the second-order Møller−Plesset level of theory with frozen core approximation, utilizing the 6-31G* basis set for H, N, O, and Cl atoms. Pd was described with the Stuttgart relativistic pseudopotential with a basis set of corresponding quality for the explicitly treated electrons. Final reoptimization of all the species considered in the hydration scheme was done at the MP2 (full) level. Then, the reaction surfaces of the structures localized by optimizations were constructed utilizing the MP4 single-point evaluations with additional inclusion of diffuse functions. The computed results were compared with corresponding data of analogous platinum complexes. The Pd and Pt energy surfaces resemble each other to a surprisingly large extent. Practically all qualitative trends, such as cis/trans energy ordering, are identical, and the solvation energies of Pd and Pt species differ only by a few (at most 10) kcal/mol. Concerning the markedly different biochemical and pharmacological roles of Pt- and Pd-based compounds, our basic conclusion is that the difference between cisplatin and analogous palladium complexes cannot be rationalized considering the energetics (thermodynamic properties) of hydration because these properties do not differ significantly.

Introduction

Palladium compounds have been explored for their catalytic properties for a long time. Besides numerous experimental works (e.g., refs 1−10 and some dealing with purine or DNA bases interaction[11−13]), a number of theoretical papers have started to emerge with the recent development of quantum chemistry. Computational studies of metal-containing clusters are becoming increasingly accurate and, when properly applied, efficiently complement the experimental data. Some of these studies also dutifully compare both structural and thermodynamical properties of palladium and platinum complexes. Generally, structural similarities are obtained.[14] As to catalytic properties, the behavior of these two metals is already not so unique. One of the reasons can be seen in the different electronic structure of the atoms. While Pd in the ground state prefers an ^1S state with a complete d-shell, the ground state of atomic Pt is ^3D in which the 6s orbital is also partially occupied.[15]

Very interesting studies were performed on small Pd diatomics and triatomics in the group of Siegbahn[16−18] including H, F, and Cl atoms using the modified coupled pair functional (MCPF)[19] method. Here, the nature of palladium bonds can be (relatively easily) studied. The ratio of covalent bonding to Coulombic interaction can be estimated by varying individual substituents. The inclusion of relativistic effects was studied in the work of Sjovoll et al.[20] Also, density-functional theory (DFT) methods were used for halide systems[21] (similar to Siegbahn's systems) showing fairly good reliability of these methods. The BP86 functional (Becke's 88 exchange functional)[22] was applied to square-planar palladium compounds,[23] $[PdCl_4]^{2-}$. This type of complex was also explored in our work. Recently, a paper investigating the solvation of square-planar palladium complexes appeared.[24] There, infrared and NMR spectroscopy results were compared with ab initio calculations at the Hartree−Fock level using the MIDI basis set.

It is well established that contrary to cisplatin, a similar compound with palladium is inactive as an anticancer drug.[7] However, the exact explanation is missing. It was observed experimentally that numerous analogous species with Pt(II) and Pd(II) have very similar structural parameters, but their kinetics are substantially different (ca. 10^4 times faster in the case of Pd(II) compounds).[14] The difference in kinetics of chemical reactions is important in understanding the different catalytic and biochemical roles of Pd- and Pt-based compounds.

In the present paper, we explore in detail the energetics of selected square palladium complexes using high-level quantum-chemical calculations. We compare the present results of the potential energy surfaces of Pd-complexes with our analogous study of platinum systems published recently.[25] The accuracy of various computational approaches has also been investigated.

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Computational Details

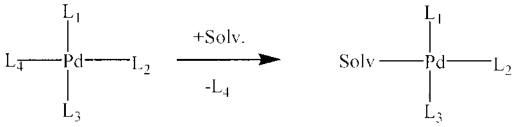
Four square-planar complexes of palladium were chosen as starting structures for interactions with a solvent represented by water molecules and hydroxyl anions: neutral *cis*- and *trans*-dichlorodiamminepalladium (the first two structures in Figure 1), dication tetraamminepalladium (2+), and anion tetrachloropalladium (2−).

As the first step, all of the considered structures (four starting complexes and their solvated derivatives) were optimized using the second-order Møller−Plesset perturbational method (MP2) with frozen core approximation. For first- and second-row elements, Pople's 6-31G* basis sets of atomic orbitals were used. The palladium atoms were described with MWB (M stands for fitting pseudopotentials on neutral atom, WB means Wood−Boring approach for inclusion of relativistic effects) energy-averaged pseudopotentials developed by the Stuttgart−Dresden laboratory.[26] The recommended basis set was augmented with a set of f-functions obtained on the basis of the coupled-cluster (CCSD) optimization of the palladium atom in the ^1S electronic ground state ($\alpha_f = 1.47$). The ground state of all these complexes is a closed-shell singlet. In this way, the most stable conformers were chosen. For these structures, additional MP2 reoptimization with no frozen core was performed (MP2(full)). It can be shown that the order of individual rotamers for a given complex is not changed substantially; for further details, see ref 25. Contrary to our preceding work on Pt complexes, zero-point vibrational energy (ZPVE) contributions were not considered in this work as this term has not been found to be substantial for the reaction preferences.[25] Other energy terms which were found to be negligible were also omitted (e.g., the spin−orbit term and CCSD instead of MP4). Finally, single-point calculations were performed on the optimized structures, utilizing the fourth-order MP method (MP4-SDTQ) including diffuse and polarization functions (the 6-31+G* basis set).[27] For the Pd atom, a set of additional diffuse functions was also added (s-, p-, and d-functions: $\alpha_s = 0.008$, $\alpha_p = 0.012$, and $\alpha_d = 0.03$) for the sake of consistency. Especially for the negatively charged species, the extension of the basis set with diffuse functions is of basic importance.[25,28−31] The fourth-order correlation energy is taken in a form recommended by Kellö et al.[32,33]

$$E_{\mathrm{corr}} = \sum_{\mathrm{pert}=2}^{4} E_{\mathrm{val}}^{\ \mathrm{pert}} + \Delta E^2$$

where $\Delta E^2 = \Delta E_{\mathrm{all}}^2 - \Delta E_{\mathrm{val}}^2$ represents the difference between the frozen core approach and the full MP2 approach. Most of the calculations were done with the program GAMESS.[34]

This computational model was used for the determination of the hydration surface on the basis of reactions according to the following scheme:



(1)

Solvation species were regarded as both neutral water molecules and OH anions. In the case of $[PdCl_4]^{2-}$, hydration with the hydronium cation $[H_3O]^+$ was considered, too. The present results have been compared with analogous data for platinum complexes.

Results and Discussion

Geometries. The most important geometrical parameters of the gradiently optimized structures are compiled in Table 1.

TABLE 1: Bond Lengths (in Å) of Individual Pd Complexes

complex	Pd−N	Pd−Cl	Pd−O
$[Pd(NH_3)_4]^{2+}$	2.054		
$[Pd(NH_3)_3(H_2O)]^{2+}$	2.042		2.083
	2.016		
	2.054		
$[Pd(NH_3)_3(OH)]^+$	2.044		1.925
	2.110		
	2.044		
cis-DDPd	2.070	2.254	
cis-$[PdCl(NH_3)_2(H_2O)]^+$	2.008	2.229	2.082
	2.076		
cis-$PdCl(NH_3)_2(OH)$	2.099	2.271	1.925
	2.060		
cis-$[Pd(NH_3)_2(H_2O)_2]^{2+}$	2.004		2.083
cis-$[Pd(NH_3)_2(H_2O)(OH)]^+$	2.012		1.917
	2.104		2.078
cis-$Pd(NH_3)_2(OH)_2$	2.080		1.946
			1.946
cis-$PdCl_2(NH_3)(H_2O)$	2.056	2.250	2.133
		2.223	
cis-$[PdCl_2(NH_3)(OH)]^-$	2.031	2.345	1.952
		2.293	
cis-$PdCl_2(H_2O)_2$		2.223	2.115
cis-$[PdCl_2(H_2O)(OH)]^-$		2.257	1.953
		2.322	2.127
cis-$[PdCl_2(OH)_2]^{2-}$		2.385	1.985
		2.429	1.961
cis-$[PdCl(NH_3)(H_2O)_2]^+$	1.997	2.204	2.086
			2.120
cis-$PdCl(NH_3)(H_2O)(OH)$	2.085	2.242	1.922
			2.121
cis-$[PdCl(NH_3)(OH)_2]^-$	2.064	2.358	1.955
			1.953
trans-DDPd	2.025	2.275	
		2.276	
trans-$[PdCl(NH_3)_2(H_2O)]^+$	2.032	2.209	2.129
	2.048		
trans-$PdCl(NH_3)_2(OH)$	2.023	2.302	1.956
trans-$[Pd(NH_3)_2(H_2O)_2]^{2+}$	2.041		2.047
trans-$[Pd(NH_3)_2(H_2O)(OH)]^+$	2.049		1.906
	2.038		2.155
trans-$Pd(NH_3)_2(OH)_2$	2.020		1.976
	2.021		1.976
trans-$PdCl_2(NH_3)(H_2O)$	1.989	2.271	2.069
		2.271	
trans-$[PdCl_2(NH_3)(OH)]^-$	2.086	2.312	1.933
		2.322	
trans-$PdCl_2(H_2O)_2$		2.267	2.032
		2.267	
trans-$[PdCl_2(H_2O)(OH)]^-$		2.301	1.909
		2.336	2.188
trans-$[PdCl_2(OH)_2]^{2-}$		2.36	2.001
trans-$[PdCl(NH_3)(H_2O)_2]^+$	2.067	2.226	2.045
trans-$PdCl(NH_3)(H_2O)(OH)$	1.985	2.307	1.942
			2.087
trans-$[PdCl(NH_3)(OH)_2]^-$	2.019	2.31	1.984
$[PdCl_2(HCl)(H_2O)]$		2.215	2.150
		2.213	
		2.433	
$[PdCl_3(H_2O)]^-$		2.297	2.121
		2.235	
		2.297	
$[PdCl_3(OH)]^{2-}$		2.366	1.959
		2.389	
		2.332	
$[PdCl_4]^{2-}$		2.326	

Valence angles involving neighboring heavy atoms in all complexes deviate from 90°, on average by about 7°. The largest deviations are seen in cis complexes (maximum deviation is 14.6° for the N−Pd−N angle of the *cis*-$Pd(NH_3)_2(OH)_2$ complex). The other systems (trans, trichloro, and triammine complexes) show a more even valence angle distribution. The deviation from planar arrangement is only a few degrees and not more than 6.4° (*cis*-$Pd(NH_3)_2(H_2O)(OH)$). And cis conformers exhibit larger deviations compared with the other systems.

The largest bond lengths are observed in the case of Pd−Cl bonds (about 2.31 Å), the Pd−O distance in water-ligated complexes are on average around 2.10 Å, and the Pd−N bond lengths amount to about 2.04 Å. Some interesting exceptions can be seen, for example, in the $Pd(NH_3)_3(OH)^+$ complex where NH_3 in the trans position to the OH group has a relatively long Pd−N distance of 2.11 Å. The reason for such an extension stems from an induction effect which causes a shift in electron density toward the negatively charged OH group, resulting in a mild weakening of the Pd−N bond. The same effect is responsible for the elongation of Pd−Cl bonds (up to 2.42 Å) in $PdCl_y(OH)_x$ complexes. In the case of Pd−O bond lengths, the shortest bond lengths occur for hydroxyl groups. Here, the influence of Coulombic forces leads to decreased Pd−O bond distances. Another interesting point is that the Pd−N distances are generally shorter than the Pd−O distances. This is not in accord with the covalent and/or atomic radii of nitrogen and oxygen. Both covalent and atomic radii are a little larger in the case of nitrogen. The observation can be explained by considering that the nitrogen atom belongs to the so-called soft (or borderline) atoms (ligands)[35,36] and that the oxygen atom belongs to hard atoms. For a detailed explanation of the hard and soft acids and bases (HSAB) concept, see ref 37. The affinity of the transition metals for soft atoms is larger, and thus, the corresponding bonds are shorter. An interesting comparison of interactions of magnesium- and zinc-group cations with the nitrogen sites of DNA base and water oxygen atoms can be found in one of our recent studies.[38] While in the case of the magnesium ion, the ratio of the Mg−O to Mg−N distances roughly follows the ratio of atomic radii, O/N, zinc clearly prefers interaction with nitrogen over oxygen; distances for Zn−N are shorter than those for Zn−O.

Figure 1 shows the most stable rotamers obtained for key reaction intermediates and products. Starting from dichlorodiamminepalladium (DDPd), it can be seen that the global minimum of the *trans*-DDPd has both in-plane hydrogens of the NH_3 group oriented toward the same chlorine atom (C_{2v} point group symmetry). Such an orientation is also known to exist in transplatin complexes.[25] The next six structures in Figure 1 represent the most stable singly hydrated intermediates. Both *cis*- and *trans*-$PdCl(NH_3)_2(OH)$ preserve the orientation of the NH_3 groups in the same way as DDPd conformers. The hydrogen of the OH group is kept symmetrically in plane and perpendicular to the plane of the heavy atoms because of electrostatic forces. Also *trans*-$[PdCl_2(NH_3)(OH)]^-$ has as the most stable rotamer a structure in which the two in-plane hydrogen atoms are both oriented toward the same chlorine. In the case of the cis conformer, the stronger electrostatic interaction of H···O prevails over the H···Cl interaction and the NH_3 group is rotated by about 60°, keeping N−H···O in a planar arrangement. A somewhat different structure is seen in the *trans*-$PdCl_2(NH_3)H_2O$ complex in which symmetrical hydrogen distribution toward chlorine atoms can be observed as a global rotational minimum.

Let us now analyze six doubly hydrated complexes (bottom part of Figure 1). Negatively charged species show a clear trend to keep as many hydrogens as possible in the in-plane position. Because of electrostatic reasons, both $Pd(NH_3)_2(OH)_2$ species have the hydrogens of the OH groups away from the complex plane.

Our geometry parameters are in fact in a good accord with the bond distances published in a preceding quantum-chemical study[24] where Pd−O distances were 2.12 Å for formic acid ligands and 2.01 Å for formate ligands. The former results were obtained at the Hartree−Fock level with a slightly smaller basis set.

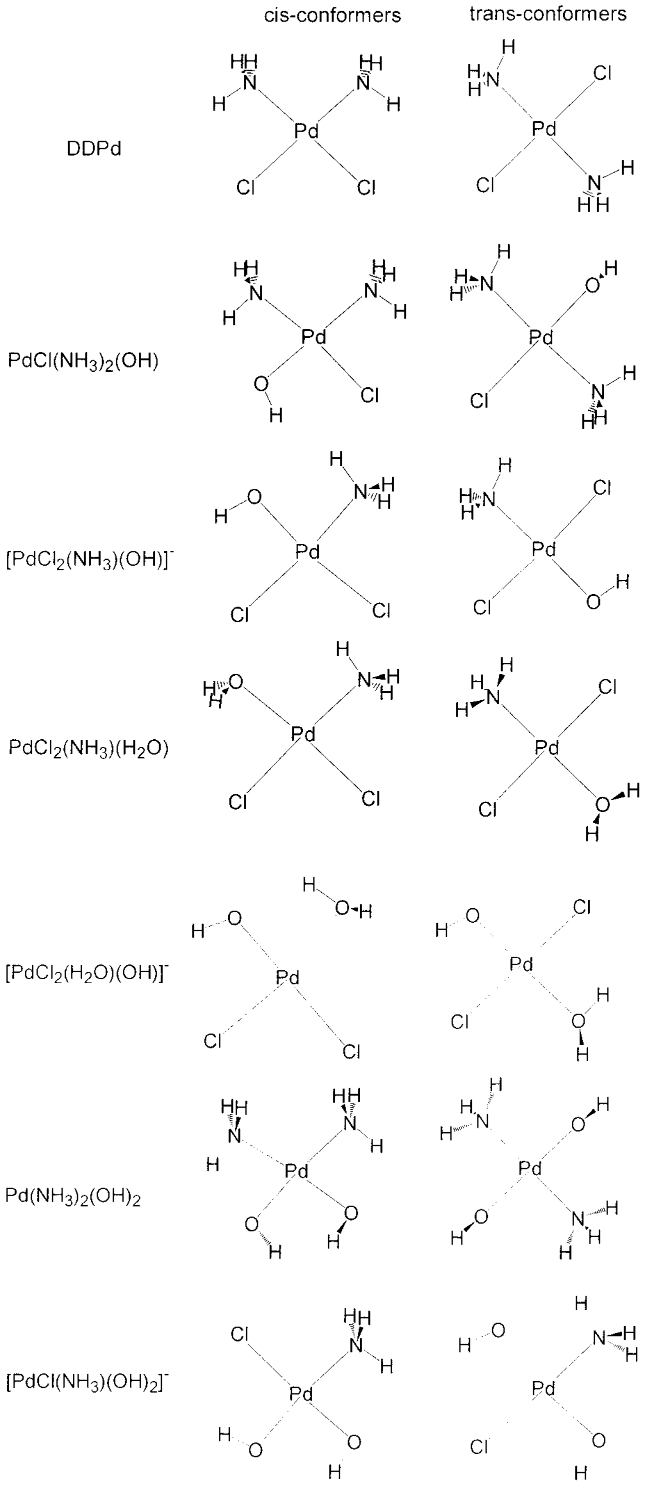


Figure 1. The global minima found for the selected Pd complexes.

Recently also, a study of excited states of *cis*- and *trans*-dichlorodiammineplatinum (DDP) and *cis*- and *trans*-DDPd has appeared.[39] The optimized geometry at the B3LYP/6-311G(3d,3p) level with corresponding effective core potential approximation (ECP) also shows good agreement with our results (their Pd−N and Pd−Cl distances are 2.20/2.10 Å and 2.31/2.36 Å for the cis/trans conformers, respectively). All of these results follow the trends found in experimental measure-

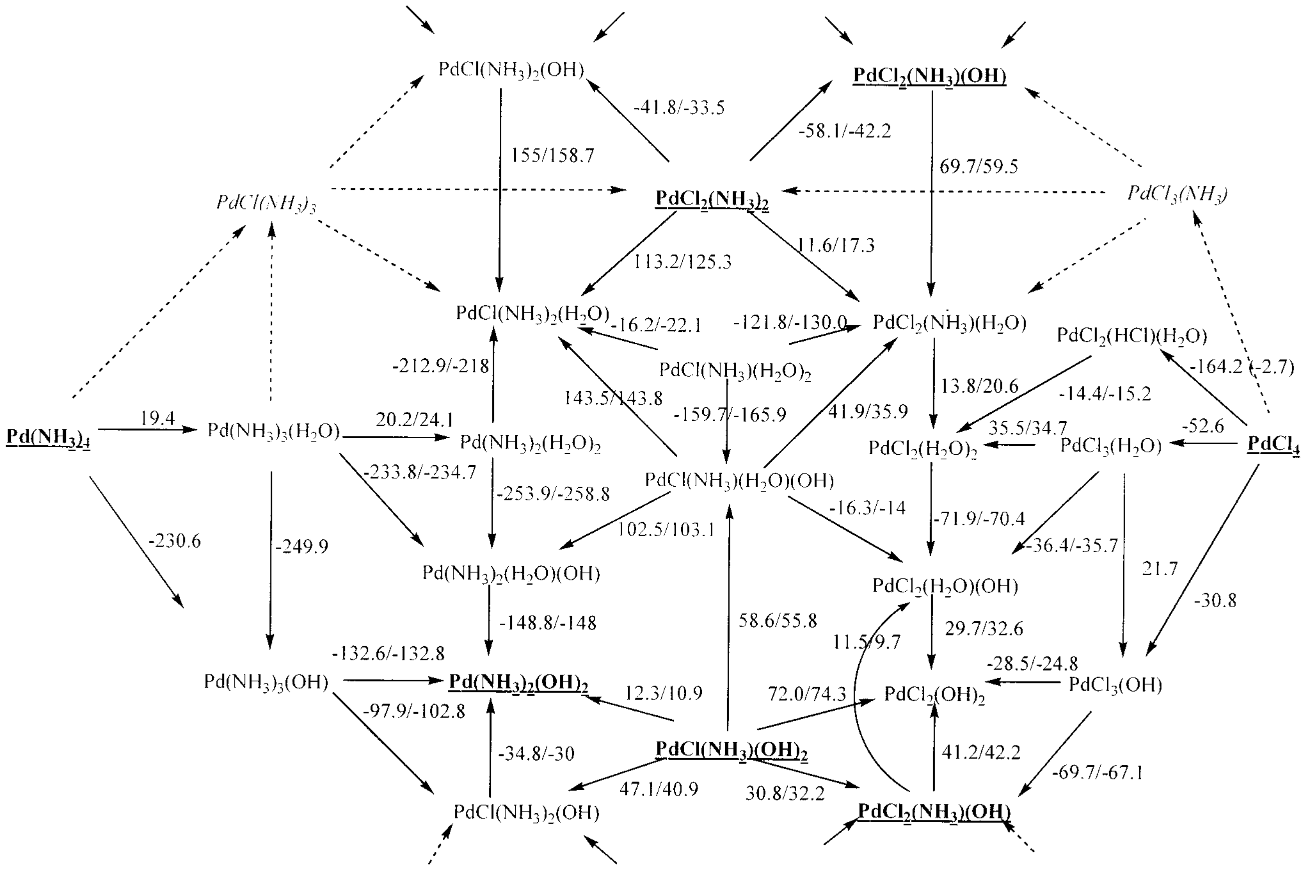


Figure 2. Thermodynamics of the hydration reactions for four starting species: neutral *cis*-dichlorodiamminepalladium $PdCl_2(NH_3)_2$, neutral *trans*-dichlorodiamminepalladium $PdCl_2(NH_3)_2$, tetraamminepalladium cation $[Pd(NH_3)_4]^{2+}$, and tetrachloropalladium anion $[PdCl_4]^{2-}$. In the case of a fraction, the numerator corresponds to reaction energies (in kcal/mol) of cis conformers and the denominator of trans conformers.

ments: $d(Pd-N) = 2.13/2.05$ Å (cis/trans) and $d(Pd-Cl) = 2.26/2.33$ Å (cis/trans).[40]

Energetics. For the optimized structures, calculations at the MP4 level of theory were performed and the energy was corrected by the full MP2 treatment (ΔE^2) as described above. The calculated energies were used for evaluation of the hydration surface according to eq 1. The individual reaction energies are used to compose an extended reaction scheme, which is shown in Figure 2. Other missing reaction energies (associated, for example, with the replacement of chlorine by a water molecule in the process $PdCl(NH_3)_2(OH) \rightarrow Pd(NH_3)_2(H_2O)(OH)$) can be easily calculated using the rule of additivity of reaction heats, known as the Hess law.

The replacement of an ammonia ligand from the $[Pd(NH_3)_4]^{2+}$ complex with a water molecule is a slightly endothermic process (about 19 kcal/mol). In contrast, a large energy release is associated with an exchange of the ammonia ligand by negatively charged $(OH)^-$ species. This process leads to a reduction in positive charge of 2+ in the complex. Thus, despite the smaller Pd affinity for oxygen compared with nitrogen, the process is facilitated by Coulombic forces. Furthermore, solvation results in three complexes differing by charge. Preserving the 2+ charge in the starting complex, two conformers (cis or trans) of $[Pd(NH_3)_2(H_2O)_2]^{2+}$ can be obtained. Similarly to the first water replacement, the reactions are again slightly endothermic. The formation of the *cis*-$[Pd(NH_3)_2(H_2O)_2]^{2+}$ species from the $[Pd(NH_3)_3(H_2O)]^{2+}$ species requires 20 kcal/mol, and in the case of the trans conformer, the reaction requires about 4 kcal/mol more. The substitution of the second ammonia ligand with the hydroxyl group leads to a large energy release, regardless of from which complex ($[Pd(NH_3)_3(H_2O)]^{2+}$ or $[Pd(NH_3)_3(OH)]^+$) this replacement occurs. The process which leads to neutral $Pd(NH_3)_2(OH)_2$ gives about a 100 kcal/mol gain in comparison with 234 kcal/mol in the case of the mixed *cis*- and *trans*-$[Pd(NH_3)_2(OH)(H_2O)]^+$ complexes formed from the $[Pd(NH_3)_3(H_2O)]^{2+}$ species. While the cis conformer is more stable for the $[Pd(NH_3)_3(H_2O)]^{2+}$ complex, the opposite is true for the other two complexes ($[Pd(NH_3)_2(OH)(H_2O)]^+$ and $Pd(NH_3)_2(OH)_2$).

Solvation of $[PdCl_4]^{2-}$ gives a different picture of the energetics. The first hydration step is energetically comparable for both the water molecule and the hydroxyl anion. The substitution with water is slightly more feasible (about 20 kcal/mol). It can be assumed that this preference is due to elimination of one of the excessive electrons thereby forming $[PdCl_3(H_2O)]^-$. The solvation with the acidic $[H_3O]^+$ species was also considered in this case. Here, the complex $[PdCl_3(H_3O)]^-$ was immediately transformed to the $[PdCl_2(HCl)(H_2O)]$ form. This is in perfect accord with the Brønsted−Lowry theory of acid−base equilibria because in highly acidic environments (represented here by the unsolvated $[H_3O]^+$ species), a chloride particle behaves as a relatively strong conjugated base and accepts a proton. Nevertheless, even such an arrangement is not energetically that much more favorable. It must be kept in mind that the large amount of energy released in this step is associated with the proton transfer from the hydronium cation to the chloride particle (this transfer represents about 162 kcal/mol of the total amount of 164 kcal/mol). Thus, only 2.7 kcal/mol is left for the hydration process. Such a process will probably be fairly favorable in a highly acidic environment. In other cases, the dissociation of the HCl ligand molecule occurs. The replacement of the second chlorine ligand with water

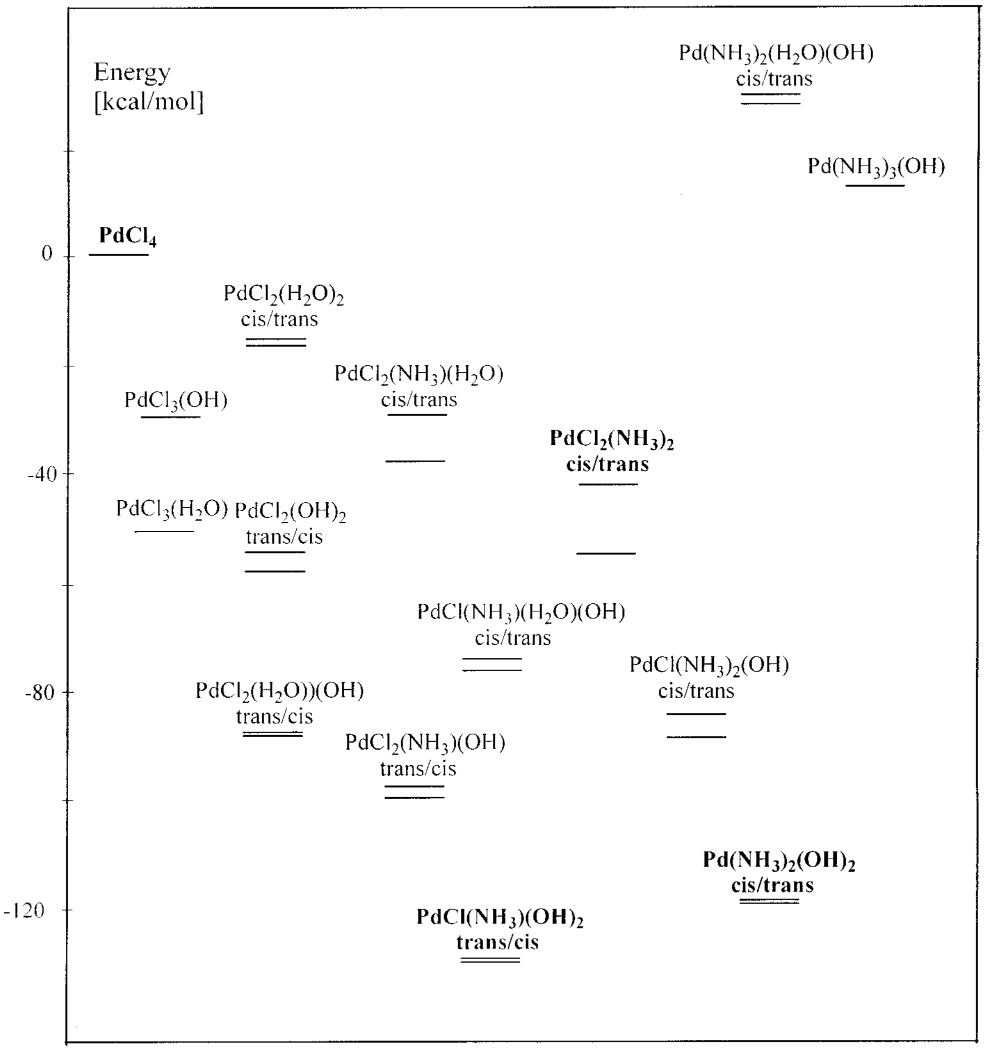


Figure 3. The relative reaction surface of Pd complexes. The $[PdCl_4]^{2-}$ species was chosen as a zero-energy point.

requires some amount of energy (about 30 kcal/mol) for both cis and trans conformers. However, substituting chlorine in $[PdCl_3(H_2O)]^-$ with the $(OH)^-$ group leads to an energy release of about 30 kcal/mol. The replacement of the second chlorine from $[PdCl_3(OH)]^{2-}$ is more advantageous in the case of water than that of the hydroxyl group (60 and 30 kcal/mol, respectively). Thus, the most stable hydration product of the $[PdCl_4]^{2-}$ complex is the mixed negatively charged compound $[PdCl_2(H_2O)(OH)]^-$.

The most important complexes are *cis*- and *trans*-DDPd. Because both the cis and the trans conformers exhibit similar properties, they will be discussed together. Some additional remarks will be presented only in cases where noticeable differences occur. The first hydration of DDPd can take place in two different ways, replacing either the NH_3 molecule or chlorine. When substitutions with the OH group are considered, the NH_3 molecule is a slightly more favorable ligand than is the Cl atom. Both ligands lead to an energy release of more than 30 kcal/mol. In contrast, the water molecule replacement of either ligand requires the addition of energy. Nevertheless, in the case of the $[PdCl_2(NH_3)(H_2O)]$ complex, only about 10 kcal/mol is needed for the reaction to proceed. All four hydration reactions (replacement of NH_3 or Cl with H_2O or OH) stabilize the cis conformers a little more than the trans conformers. Considering the lowest lying intermediate from the first step, the $[PdCl_2(NH_3)(OH)]^-$ complex, the next ammonium substitution is an endothermic process for both water and $(OH)^-$. However, the mixed $[PdCl_2(OH)(H_2O)]^-$ species lies only 10 kcal/mol higher so that under some conditions, such a process can also occur. The reason for the lower stability of $[PdCl_2(OH)_2]^{2-}$ can be seen mainly in its negative charge. The second intermediate, $[PdCl(NH_3)_2(OH)]$, can be further solvated by the hydroxyl group with an additional energy gain when the second chlorine is replaced. The $[Pd(NH_3)_2(OH)_2]$ species is formed in this step, and about 30 kcal/mol is released. The other possibility for both intermediates obtained in the first hydration step is a mixed substitution in the course of a subsequent solvation, i.e., the replacement of chlorine in the case of $[PdCl_2(NH_3)(OH)]^-$ and the replacement of an ammonium molecule in the case of $[PdCl(NH_3)_2(OH)]$. Neither of these possibilities leads to a more stable product on the reaction energy surface when the H_2O molecule is considered. However, if the OH group is considered, a slightly deeper minimum than the $[Pd(NH_3)_2(OH)_2]$ complex is obtained (about 13 kcal/mol). This amount of energy is not large, and under some conditions (neutral or basic pH), the $[Pd(NH_3)_2(OH)_2]$ complex may be preferred. In this way, the most stable product of hydration of the DDPd complex is the negatively charged $[PdCl(NH_3)(OH)_2]^-$ species followed by the neutral $[Pd(NH_3)_2(OH)_2]$ complex.

On the basis of the reaction scheme presented in Figure 2, the reaction surface can be defined as a sum of the total energy of the given complex plus the total energies of the remaining ligand species (to reach four ammonia, four chlorine, two water molecules, and two hydroxyl groups). The resulting surface is

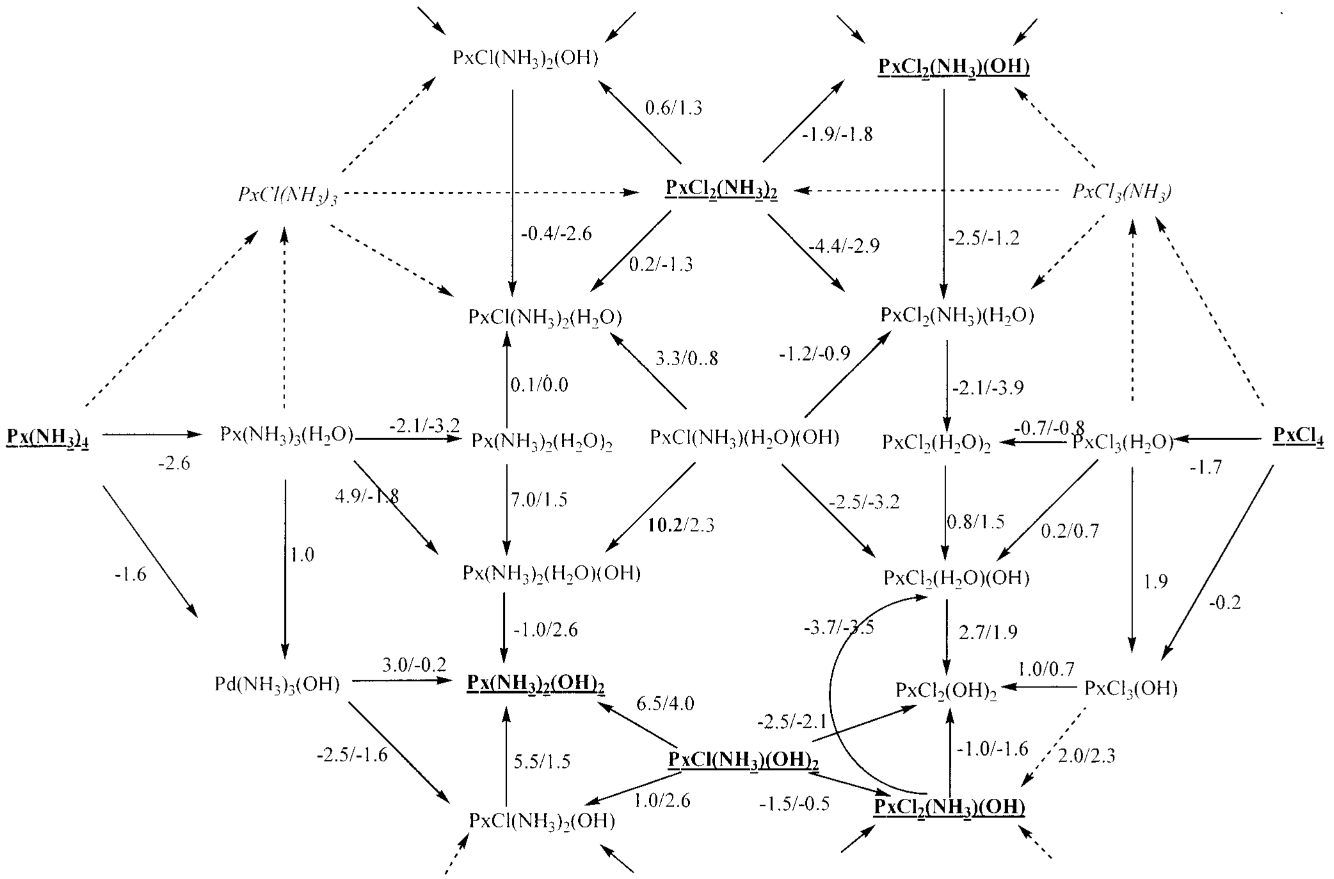


Figure 4. The comparison of the corresponding hydration schemes for the Pd and Pt complexes. The values are taken as a difference (Pd reaction energies) − (Pt reaction energies) in kcal/mol.

drawn in Figure 3. In this figure, the relative zero-energy level was defined by the position of the $[PdCl_4]^{2-}$ species. The figure clearly shows for each complex whether the cis or trans conformer is more stable (lower lying). It can also be observed that the final (most stable) product on the surface is the $PdCl(NH_3)(OH)_2$ complex. The other relatively stable species (more stable than DDPd), which could be detectable along with DDPd, are $Pd(NH_3)_2(OH)_2$, $[PdCl_2(NH_3)(OH)]^-$, $[PdCl_2(H_2O)(OH)]^-$, $PdCl(NH_3)_2(OH)$, and $PdCl(NH_3)(H_2O)(OH)$. From these complexes, the cis conformers are more stable in the case of negatively charged species. In the other cases, structures with a trans arrangement represent the lower lying conformers. For clarity of the picture, only those conformers which are below 40 kcal/mol are depicted.

Partial Charges. To find some deeper insights into these reactions, wave function analyses were performed. It was found that partial charges based on the Mulliken population analysis for both SCF and MP2 wave functions are not reliable despite the fact that this method is still often used in the literature. For example, for *trans*-$[Pd(NH_3)_2(H_2O)_2]^{2+}$, the Mulliken population gives partial charges on palladium $\delta(Pd) = 4.19$ e and on the nitrogen atoms $\delta(N) = -2.34$ e. In contrast, natural bond orbital (NBO)[41] partial charges of this species look more reasonable: $\delta(Pd) = 0.95$ e and $\delta(N) = -1.07$ e. Therefore, we concentrate only on results obtained by the NBO analysis. Partial charges for the Pd, N, O, and Cl atoms of individual complexes are summarized in Table 2.

The table shows that the different total charge of the whole complex influences the partial charge of the Pd atom only slightly (in contrast to the Mulliken analysis where the partial charge varied from −0.08 e ($PdCl_2(H_2O)_2$) up to 4.19 e ($[Pd(NH_3)_4]^{2+}$). Also, the charge of the nitrogen and oxygen atoms remains practically constant. Mild influence can only be observed in the case of chlorines. From these values, it can be seen that the basis of the metal bonding consists of the coordination−covalent (dative) character of the Pd−ligand interaction. Some amount of additional Coulombic stabilization can be observed, too. For example, compare the substitution of either the hydroxyl group or water for chlorine in the DDPd complex. In the case of the OH group, a relatively large partial charge of oxygen, which is only partially compensated with a hydrogen atom, helps to increase the bonding energy of Pd−O and to stabilize this complex.

Comparison of Pd and Pt Complexes. The computational model used for the hydration of chosen palladium complexes allows a straightforward comparison with previously published results on analogous platinum complexes.

Figure 4 depicts a scheme with the differences between corresponding Pd and Pt reaction energies. For the sake of simplicity, the general label Px was used for the naming of the complexes. Figure 4 underlines the striking extent of the similarity between the energetics of both metals, at least in the reactions presently investigated. The largest difference for the reaction energies is 10 kcal/mol. Some of the final complexes of the solvation process, the hydrated $Px(NH_3)_2(OH)_2$ species (Px = Pd, Pt), are slightly less stabilized in the case of Pd. Also, the energy difference between the cis and trans conformer is slightly increased in the case of the Pd compound.

In other cases, not only qualitative but also quantitative agreements for all the considered reactions can be observed. When the markedly different biochemical roles of Pt- and Pd-based compounds are considered, the really very high degree of similarity between the calculated hydration surfaces of the Pd and Pt compounds is unexpected. The differences are

TABLE 2: Partial Charges (in e) Based on NBO Analysis of MP2 Corrected Wave Functions

complex	Pd	N	Cl	O[a]
$[Pd(NH_3)_4]^{2+}$	0.749	−1.076		
$[Pd(NH_3)_3(H_2O)]^{2+}$	0.827	−1.040		−0.993
		−1.082		
		−1.071		
$[Pd(NH_3)_3(OH)]^{+}$	0.713	−1.114		−0.971
		−1.078		
		−1.078		
cis-DDPd	0.537	−1.094	−0.484	
cis-$[PdCl(NH_3)_2(H_2O)]^{+}$	0.675	−1.111	−0.432	−0.946
		−1.031		
cis-$PdCl(NH_3)_2(OH)$	0.652	−1.094	−0.565	−1.009
		−1.103		
cis-$[Pd(NH_3)_2(H_2O)_2]^{2+}$	0.889	−1.030		−0.989
cis-$[Pd(NH_3)_2(H_2O)(OH)]^{+}$	0.785	−1.119		−0.950
		−1.052		−0.975
cis-$Pd(NH_3)_2(OH)_2$	0.737	−1.105		−1.061
cis-$PdCl_2(NH_3)(H_2O)$	0.563	−1.086	−0.421	−0.960
			−0.506	
cis-$[PdCl_2(NH_3)(OH)]^{-}$	0.646	−1.066	−0.678	−1.077
			−0.613	
cis-$PdCl_2(H_2O)_2$	0.620		−0.433	−0.958
cis-$[PdCl_2(H_2O)(OH)]^{-}$	0.694		−0.661	−1.091
			−0.555	−0.956
cis-$[PdCl_2(OH)_2]^{2-}$	0.738		−0.736	−1.129
			−0.766	−1.056
cis-$[PdCl(NH_3)(H_2O)_2]^{+}$	0.705	−1.021	−0.363	−0.984
				−0.949
cis-$PdCl(NH_3)(H_2O)(OH)$	0.701	−1.100	−0.515	−0.966
				−1.028
cis-$[PdCl(NH_3)(OH)_2]^{-}$	0.720	−1.084	−0.716	1.021
trans-DDPd	0.569	−1.042	−0.574	
trans-$[PdCl(NH_3)_2(H_2O)]^{+}$	0.649	−1.055	−0.364	−0.991
		−1.072		
trans-$PdCl(NH_3)_2(OH)$	0.658	−1.051	−0.621	−1.061
trans-$[Pd(NH_3)_2(H_2O)_2]^{2+}$	0.946	−1.070		−0.971
trans-$[Pd(NH_3)_2(H_2O)(OH)]^{+}$	0.752	−1.072		−0.985
		−1.085		−0.912
trans-$Pd(NH_3)_2(OH)_2$	0.731	−1.054		−1.101
trans-$PdCl_2(NH_3)(H_2O)$	0.642	−1.012	−0.571	−0.928
trans-$[PdCl_2(NH_3)(OH)]^{-}$	0.637	−1.091	−0.645	−0.982
			−0.669	
trans-$PdCl_2(H_2O)_2$	0.751		−0.565	−0.913
trans-$[PdCl_2(H_2O)(OH)]^{-}$	0.674		−0.653	−0.966
			−0.660	−0.916
trans-$[PdCl_2(OH)_2]^{2-}$	0.758		−0.720	−1.119
trans-$[PdCl(NH_3)(H_2O)_2]^{+}$	0.776	−1.104	−0.434	−0.927
trans-$PdCl(NH_3)(H_2O)(OH)$	0.731	−1.021	−0.632	−0.940
				−1.052
trans-$[PdCl(NH_3)(OH)_2]^{-}$	0.735	−1.059	−0.663	−1.14
				−1.13
$[PdCl_2(HCl)(H_2O)]$	0.499		−0.408	−0.973
			−0.158	
			−0.364	
$[PdCl_3(H_2O)]^{-}$	0.571		−0.609	−0.949
			−0.609	
			−0.466	
$[PdCl_3(OH)]^{2-}$	0.657		−0.703	−1.033
			−0.720	
			−0.665	
$[PdCl_4]^{2-}$	0.537		−0.631	

[a] In complexes with both H_2O and OH ligands present, charges from the water oxygens are first.

considerably smaller compared to those we have recently noticed when comparing Zn^{2+} and Mg^{2+} cations.[35] This defers the understanding of the basic principles of the Pd vs Pt differences to further studies, and additional calculations are currently underway in our laboratories.

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