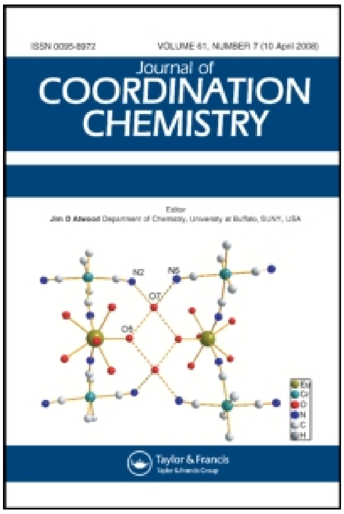

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

A quantum chemical consideration of ligand exchange in palladium(ii) aqueous and chloride complexes

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To cite this Article Pankratov, Alexei N. , Borodulin, Vladimir B. and Chaplygina, Olga A.(2004) 'A quantum chemical consideration of ligand exchange in palladium(ii) aqueous and chloride complexes', Journal of Coordination Chemistry, 57: 10, 833 — 842

To link to this Article: DOI: 10.1080/00958904100017209999

URL: http://dx.doi.org/10.1080/0095890410001720999

J. Coord. Chem., Vol. 57, No. 10, 10 July 2004, pp. 833–842

A QUANTUM CHEMICAL CONSIDERATION OF LIGAND EXCHANGE IN PALLADIUM(II) AQUEOUS AND CHLORIDE COMPLEXES

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(Received 25 August 2003; In final form 4 May 2004)

The behavior of potassium tetrachloropalladate(II) in media simulating biological fluids has been studied. In aqueous solutions of NaCl, the aquation rate is higher than the rate of chloro ligand introduction into the internal coordination sphere of palladium. In HCl solutions, on the contrary, the process of palladium chloro complex formation predominates. The latter is apparently due to protonation of water molecules composing aqua complexes. By means of the ZINDO/1 method, the substitution of ligands – water molecules and hydronium ion – in planar complexes of palladium(II) by chloride ion has been investigated. All complexes containing H_2O and H_3O^+ ligands, other than $[Pd(H_2O)_4]^{2+}$, have intramolecular hydrogen bonds. In $[Pd(H_2O)_3(H_3O)]^{3+}$ and *trans*-$[Pd(H_2O)_2(H_3O)Cl]^{2+}$, a "non-classic" symmetric hydrogen bond $O\cdots H\cdots O$ is established (ZINDO/1, RHF/STO-6G*). By the first three steps the substitution of hydronium ion in the internal sphere of palladium atom is more favorable thermodynamically, compared to water molecules. Logarithms of stepwise stability constants of palladium(II) chloride complexes correlate linearly to enthalpies (ZINDO/1, PM3) of water substitution by chloride ion.

Keywords: Palladium(II) complexes; Ligand exchange; Quantum chemical consideration; Theory–experiment correlation

INTRODUCTION

Palladium is an abiogenous, xenobiotic element. Nevertheless, it is capable of taking part in important cycles of human vital activity. Palladium-containing substances exhibit biological activity. The variety of biological functions of ions of palladium and other platinum metals is based on peculiar chemical and stereochemical properties of these metals' coordination compounds with biologically active ligands (DNA, amino acids, peptides, etc.), and, in particular, the structure of coordination centers of the metal–ligand (fragment or functional group of biological system) [1]. Palladium(II) complexes with organic ligands are promising as drugs [2].

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ISSN 0095-8972 print: ISSN 1029-0389 online © 2004 Taylor & Francis Ltd
DOI: 10.1080/0095890410001720999

When studying the reactions of palladium ion with bioligands, it is necessary to take into account the interaction between this ion and inorganic compounds entering the composition of an organism's fluids. Inorganic ligands (H_2O, Cl^- and others) competing with biologically active substances for metal ion could diminish the latter's toxicity. On the other hand, the metal cation's binding with inorganic ligands can decrease the efficiency of drugs based on palladium compounds. Palladium(II) chloro complexes bind with DNA molecules, resulting in disruption of the replication process (transcription and translation) [1].

The systems Pd(II)–NaCl–H_2O and Pd(II)–HCl–H_2O simulate the behavior of palladium(II) compounds in biological fluids. Thus, blood plasma is imitated by a 0.86% (0.147 M) solution of sodium chloride, and gastric juice by a 0.1 M solution of hydrochloric acid [3].

The purpose of the present work is to study ligand exchange reactions in chloride and hydrochloric acidic solutions of palladium(II).

EXPERIMENTAL AND COMPUTATIONAL METHODS

Potassium tetrachloropalladate(II) was synthesized using the procedures [4] with metallic palladium and palladium(II) chloride. Solutions of $K_2[PdCl_4]$ (0.03067 M) and NaCl (0.1 M) were prepared using the exactly weighed samples. A 0.1 M solution of HCl was prepared from the commercial standard.

Kinetic studies were performed spectrophotometrically using a SPECORD UV-vis spectrophotometer. Working solutions of $K_2[PdCl_4]$ with a concentration of 8.496×10^{-5} M were prepared by dilution. Into a cuvette of 10-mm path length, 3.610 cm^3 of $K_2[PdCl_4]$ solution and 20×10^{-3} cm^3 of 0.1 M NaCl or HCl solution were added by a dosator. Electron absorption spectra of the reactive mixtures were then recorded.

Quantum chemical computations were performed by means of the ZINDO/1 [5], PM3 [6] and RHF/STO-6G* [7] methods using software from the *HyperChem* package (HyperChem™, Hypercube, Inc., 1115 NW 4th Street, Gainesville, FL 32601, USA) with the complete geometry optimization (Polak–Ribiere function minimizer) [8]. The condition of the gradient norm not exceeding 0.02 kcal/(mol Å) was preset.

The linear regression analysis was performed with the confidence level of 0.95 taking into account the Student coefficient.

RESULTS AND DISCUSSION

Kinetic studies were undertaken from electronic spectra of reactive systems obtained by mixing aqueous solutions of potassium tetrachloropalladate(II) and NaCl (HCl).

In aqueous solutions, tetrachloropalladate undergoes aquation, and complexes of various composition occur: $[Pd(H_2O)_3Cl]^+$, $[Pd(H_2O)_2Cl_2]$, $[Pd(H_2O)Cl_3]^-$, $[PdCl_4]^{2-}$. Addition of sodium chloride or hydrochloric acid reduces the concentrations of the aqua complexes.

Aqua chloride ($[Pd(H_2O)_3Cl]^+$, $[Pd(H_2O)_2Cl_2]$, $[Pd(H_2O)Cl_3]^-$) and chloride ($[PdCl_4]^{2-}$) complexes of palladium(II) have similar spectrophotometric characteristics [9,10]. Thus the absorbance at wavelength maxima of electronic spectra of reaction mixtures (222, 234.5, 279 nm) may be regarded as assigned to the overall absorption of Pd(II) chloro complexes and approximately proportional to the total concentration of species with Pd–Cl bonds.

We have established that the absorbance of potassium tetrachloropalladate(II)–sodium chloride–water at a wavelength of 222 nm decreases with time. Conversely, in the system potassium tetrachloropalladate(II)–hydrochloric acid–water the absorbance increases with time. Consequently, in aqueous solutions of NaCl the aquation rate exceeds the rate of chloro ligand introduction into the internal coordination sphere of palladium. In hydrochloric acid solutions, on the contrary, palladium chloro complex formation prevails. The latter is apparently due to the protonation of water molecules of the aqua complexes.

The dependences of ln *A* upon *t* (*A* is absorbance, *t* is time) are almost linear (Table I; Figs. 1 and 2), characteristic of first-order reactions. Let us underline once again that in both chloride and hydrochloride acid solutions the mutually reverse reactions occur, namely aquation and chloro complexes formulation, either of the two being multistep process. Therefore the perfectly linear interrelations of InA *vs* t can't exist. Even if a conclusion on the first-order reactions is far too vigorous, of importance is similarity between the kinetic regularities (to an accuracy of a sign of the dependences InA *vs* t slope) we found for the reactions of aquation and substitution of aqua ligand by chloride ion, that provides a possibility of comparing correctly two reactive series: Pd(II)–NaCl–H_2O and Pd(II)–HCl–H_2O, which differ solely by the occurrence of sodium and hydronium ions. The distinct kinetic behavior suggests aqua ligand protonation in the presence of HCl. Such supposition is in agreement with the results of quantum chemical considerations.

TABLE I Dependences $\ln A = a + bt$ and values of correlation coefficient *r* for reaction systems Pd(II)–NaCl–H_2O and Pd(II)–HCl–H_2O

System	*a*	*b*	*r*
Pd(II)–NaCl–H_2O	−0.6280 ± 0.0351	−0.001817 ± 0.000282	−0.9596
Pd(II)–HCl–H_2O	−0.1304 ± 0.0079	0.0008128 ± 0.0001725	0.9525

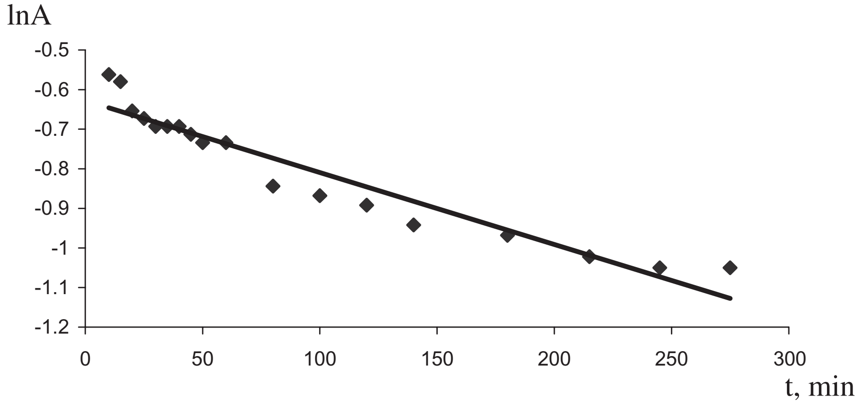

FIGURE 1 Dependence of *A* on *t* for reaction system Pd(II)–NaCl–H_2O.

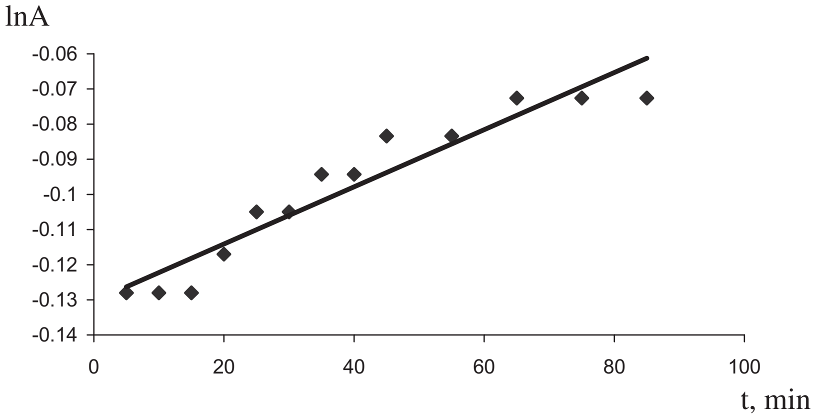

FIGURE 2 Dependence of *A* on *t* for reaction system Pd(II)–HCl–H_2O.

Using ZINDO/1, we have carried out a quantum chemical study of substitution of water molecules and hydronium ion in palladium(II) planar complexes by chloride ion. One aqua ligand in any complex was assumed to be protonated in acidic media. Single protonation of an aqua complex results in formation of positively charged complex ions which inhibits further protonation (especially for triple-charged $[Pd(H_2O)_3(H_3O)]^{3+}$ and double-charged $[Pd(H_2O)_2(H_3O)Cl]^{2+}$ cations).

Given below are point groups of the molecular systems of the complexes: $[Pd(H_2O)_4]^{2+}$ (C_1), $[Pd(H_2O)_3(H_3O)]^{3+}$ (C_2), $[Pd(H_2O)_3Cl]^{+}$ (C_1), *cis*-$[Pd(H_2O)_2(H_3O)Cl]^{2+}$ (C_1), *trans*-$[Pd(H_2O)_2(H_3O)Cl]^{2+}$ (C_1), *cis*-$[Pd(H_2O)_2Cl_2]^{2+}$ (C_2), *cis*-$[Pd(H_2O)(H_3O)Cl_2]^{+}$ (C_1), *trans*-$[Pd(H_2O)_2Cl_2]^{2+}$ (C_1), *trans*-$[Pd(H_2O)(H_3O)Cl_2]^{+}$ (C_1), $[Pd(H_2O)Cl_3]^{-}$ (C_1), $[Pd(H_3O)Cl_3]$ (C_s), $[PdCl_4]^{2-}$ (D_{4h}). In the first pair of cases, designations *cis* and *trans* are assumed for characterizing the relative positions of H_2O molecules. For the complexes with three types of ligands, mutual localization of chloride ions is implied. Quantum chemical computations reproduce adequately the known [11,12] data on a planar configuration of tetracoordinated compounds of palladium(II). *Trans* isomers of the complexes $[Pd(H_2O)_2Cl_2]$ and $[Pd(H_2O)(H_3O)Cl_2]^{+}$ are favored over *cis* forms by 10.3 and 12.4 kcal/mol, respectively. However, for the cation $[Pd(H_2O)_2(H_3O)Cl]^{2+}$ the *cis* isomer is more thermodynamically stable by 17.0 kcal/mol.

We note the mutual influence of ligands arranged *cis* with respect to each other, observed for all oxygen-containing complexes under study, except for $[Pd(H_2O)_4]^{2+}$. The above effect is exhibited by: (1) shielded conformations of planar or near-planar Cl–Pd–O–H and O–Pd–O–H fragments, with distorted bond distances and valence angles; (2) shortened contacts between atoms having no valence bonds with each other: on one hand, hydrogen atoms included in water molecules or hydronium ion, and, on the other hand, chlorine atoms or oxygen atoms from water (Table II).

The structural guidelines in deciding whether or not a hydrogen bond exists have been discussed on the basis of van der Waals radii [13–18]. A hydrogen bond in a crystal occurs provided that the O···H and Cl···H distances do not exceed 2.1 and 2.6 Å, respectively [13]; threshold interatomic distances at the interfaces between van der Waals and specific interactions are: R (O···H) = 2.15 Å, R (Cl···H) = 2.67 Å [18]. Interatomic distances serve as arguments in support of the occurrence of O–H···Cl and O–H···O

TABLE II Selected intramolecular contacts in palladium(II) complexes

Complex	*n*[a]	*Fragment of shielded conformation*	*Shortened intramolecular contact*	*Interatomic distance* (Å)
$[Pd(H_2O)_3(H_3O)]^{3+}$	1	O–Pd–O–H	O···H[b]	1.21
$[Pd(H_2O)_3Cl]^{+}$	1	Cl–Pd–O–H	Cl···H	2.00
cis-$[Pd(H_2O)_2(H_3O)Cl]^{2+}$	1	Cl–Pd–O–H	Cl···H[b]	1.46
trans-$[Pd(H_2O)_2(H_3O)Cl]^{2+}$	1	O–Pd–O–H	O···H[b]	1.21
cis-$[Pd(H_2O)_2Cl_2]$	2	Cl–Pd–O–H	Cl···H	1.85
cis-$[Pd(H_2O)(H_3O)Cl_2)]^{+}$	2	Cl–Pd–O–H	Cl···H[b]	1.44
			Cl···H[c]	1.92
trans-$[Pd(H_2O)_2Cl_2]$	2	Cl–Pd–O–H	Cl···H	1.91
trans-$[Pd(H_2O)(H_3O)Cl_2]^{+}$	2	Cl–Pd–O–H	Cl···H[b]	1.45
			Cl···H[c]	2.18
$[Pd(H_2O)Cl_3]^{-}$	1	Cl–Pd–O–H	Cl···H	1.81
$[Pd(H_3O)Cl_3]$	2	Cl–Pd–O–H	Cl···H	1.57

[a] *n* is a quantity of shielded fragments with shortened intramolecular contacts.
[b] Hydrogen atom in hydronium ion.
[c] Hydrogen atom in water molecule.

TABLE III O–H bond distances in selected palladium(II) complexes

Complex	*Type of hydrogen bond*	*Distance of separate O–H bond* (Å)
$[Pd(H_2O)_3(H_3O)]^{3+}$	H_2O–H···O	1.21
cis-$[Pd(H_2O)_2(H_3O)Cl]^{2+}$	H_2O–H···Cl	1.29
trans-$[Pd(H_2O)_2(H_3O)Cl]^{2+}$	H_2O–H···O	1.19
cis-$[Pd(H_2O)(H_3O)Cl_2)]^{+}$	H_2O–H···Cl	1.29
trans-$[Pd(H_2O)(H_3O)Cl_2]^{+}$	H_2O–H···Cl	1.29
$[Pd(H_3O)Cl_3]$	H_2O–H···Cl	1.16

hydrogen bonds in all complexes involving H_2O and H_3O^+ ligands, exclusive of $[Pd(H_2O)_4]^{2+}$ (Table III).

When hydrogen-bond strength is judged from a decrease in the Cl···H distance compared to the threshold value, one can conclude that stronger hydrogen bonding exists for a proton of hydronium ion, rather than a proton of water, conforming to the dominating role of electrostatic forces in hydrogen-bond stability [19] and on its energy correlation to the acidic properties of a proton donor [20].

For a number of molecular systems (Table III) computations show stretching of an O–H bond compared to typical covalent bonds (1.01 Å in a water molecule and 1.03 Å in hydronium ion by the data of the ZINDO/1 method). In the complexes $[Pd(H_2O)_3(H_3O)]^{3+}$ and *trans*-$[Pd(H_2O)_2(H_3O)Cl]^{2+}$, a "non-classic" symmetric hydrogen bond O···H···O is established. We have not found any analogs in the literature for such binding in metal complexes with monodentate ligands. However, existence of symmetric intramolecular O···H···O hydrogen bonds in metals chelates with 1,2-dioximes and related compounds [12], as well as in organic molecules [21–23], has been proved. For the enolic form of dipivaloyl methane, the structure has been elucidated using gas electron diffraction [22,23]. For $[Pd(H_2O)_3(H_3O)]^{3+}$ the presence of a symmetric hydrogen bond is confirmed by *ab initio* (RHF/STO-6G*) computations, according to which the O···H bond distance is 1.186 Å.

Interaction between *cis* ligands of complexes involving formation of intramolecular hydrogen bonds could serve as a prerequisite to the occurrence of static and dynamic

TABLE IV Standard enthalpies (ΔH^0) of reactions of H_2O and H_3O^+ ligands substitution by Cl^- in palladium(II) complexes

Reaction	ΔH^0 *(*kcal/mol*)*
First step	
$Cl^- + [Pd(H_2O)_4]^{2+} \rightarrow [Pd(H_2O)_3Cl]^+ + H_2O$	−216.67
$Cl^- + [Pd(H_2O)_4(H_3O)]^{3+} \rightarrow [Pd(H_2O)_3Cl]^+ + H_3O^+$	−470.82
Second step	
$Cl^- + [Pd(H_2O)_3Cl]^+ \rightarrow cis\text{-}[Pd(H_2O)_2Cl_2] + H_2O$	−114.01
$Cl^- + [Pd(H_2O)_3Cl]^+ \rightarrow trans\text{-}[Pd(H_2O)_2Cl_2] + H_2O$	−124.34
$Cl^- + cis\text{-}[Pd(H_2O)_2(H_3O)Cl]^{2+} \rightarrow cis\text{-}[Pd(H_2O)_2Cl_2] + H_3O^+$	−243.86
$Cl^- + cis\text{-}[Pd(H_2O)_2(H_3O)Cl]^{2+} \rightarrow trans\text{-}[Pd(H_2O)_2Cl_2] + H_3O^+$	−254.19
$Cl^- + trans\text{-}[Pd(H_2O)_2(H_3O)Cl]^{2+} \rightarrow cis\text{-}[Pd(H_2O)_2Cl_2] + H_3O^+$	−260.84
$Cl^- + trans\text{-}[Pd(H_2O)_2(H_3O)Cl]^{2+} \rightarrow trans\text{-}[Pd(H_2O)_2Cl_2] + H_3O^+$	−271.34
Third step	
$Cl^- + cis\text{-}[Pd(H_2O)_2Cl_2] \rightarrow [Pd(H_2O)Cl_3]^- + H_2O$	−13.83
$Cl^- + trans\text{-}[Pd(H_2O)_2Cl_2] \rightarrow [Pd(H_2O)Cl_3]^- + H_2O$	−3.50
$Cl^- + cis\text{-}[Pd(H_2O)(H_3O)Cl_2]^+ \rightarrow [Pd(H_2O)Cl_3]^- + H_3O^+$	−37.72
$Cl^- + trans\text{-}[Pd(H_2O)(H_3O)Cl_2]^+ \rightarrow [Pd(H_2O)Cl_3]^- + H_3O^+$	−25.38
Fourth step	
$Cl^- + [Pd(H_2O)Cl_3]^- \rightarrow [PdCl_4]^{2-} + H_2O$	92.81
$Cl^- + [Pd(H_3O)Cl_3] \rightarrow [PdCl_4]^{2-} + H_3O^+$	185.84

cis influence (*cis*-effect) and *trans* influence (*trans*-effect) in the reactions of palladium(II) complexes.

Ligand–ligand interactions occur through *s* and $d_{x^2-y^2}$-orbitals and direct donor-acceptor interaction [11]. CO, and $^-$CN, as well as ligands involving atoms of sulfur, phosphorus and other elements with vacant *d* orbitals are effective acceptors [11]. The formation of direct bonds between ligands can change the *cis* influence over a series of ligands [12].

The interligand interaction we observed is an example of ligand mutual influence as a special case of mobile proton with a partially vacant 1s orbital being a ligand-acceptor.

The quantum chemical computations allowed analysis of the thermodynamic characteristics of substitution of H_2O and H_3O^+ ligands in palladium(II) complexes by chloride ion (Table IV).

Complexes with one to three chloro ligands containing water molecules in the internal coordination sphere provide a measure for hydration; coordination hydration is described explicitly.

The initial three steps for substitution of hydronium ion in the internal sphere of palladium (Table IV) is more favorable thermodynamically than for water molecules.

For a great number of reactions, linear free energy relationships (LFER) are valid [20]

$$\lg(k/k_0) = A + B\Delta W, \tag{1}$$

where k and k_0 are rate constants of a particular reaction mediated by the compound under study and a reference compound, respectively; ΔW is a change in a certain quantity characterizing the thermodynamic stability of these two substances or their reactive complexes.

Provided that ligand substitution in palladium(II) complexes obey the LFER principle, for the exchange of H_2O (H_3O^+) ligand for Cl^- a more negative value of enthalpy

TABLE V Pd–O bond distances in palladium(II) complexes from ZINDO/1 computations

	Bond length (Å)	
Complex	*Pd–OH$_2$*	*Pd–OH$_3$*
$[Pd(H_2O)]^{2+}$	1.76	–
$[Pd(H_2O)_3Cl]^{+}$	1.75[a]; 1.78[b]	–
cis-$[Pd(H_2O)_2(H_3O)Cl]^{2+}$	1.74[a]; 1.77[b]	1.81
cis-$[Pd(H_2O)_2Cl_2]$	1.77	–
cis-$[Pd(H_2O)(H_3O)Cl_2)]^{+}$	1.75	1.83
trans-$[Pd(H_2O)_2Cl_2]$	1.75	–
trans-$[Pd(H_2O)(H_3O)Cl_2]^{+}$	1.73	1.80
$[Pd(H_2O)Cl_3]^{-}$	1.76	–
$[Pd(H_3O)Cl_3]$	–	1.80

[a] Water molecule in *cis* position with respect to chloro ligand.
[b] Water molecule in *trans* position with respect to chloro ligand.

(free energy) corresponds to lesser enthalpy (free energy) of activation. Water molecule protonation in the internal coordination sphere of palladium atom weakens a Pd–O bond (Table V) increasing the kinetic and thermodynamic lability of the reactive complex. Thus, the kinetic behavior agrees with the data from theoretical consideration of the ligand exchange thermodynamics for the systems $K_2[PdCl_4]$–NaCl–H_2O and $K_2[PdCl_4]$–HCl–H_2O.

The equilibrium constant (K_p) is related to the standard free energy (ΔG^0) of a chemical reaction by the equation [24]:

$$\Delta G^0 = -RT \ln K_p.$$

Dewar points out [25] that the general contributions to the free energy of chemical processes are enthalpy, not entropy, terms. Entropy is often almost unchanged over a series of structurally similar isomeric compounds, and changes in entropy are essentially constant for similar chemical reactions between compounds with close molecular geometry (*e.g.*, refs 20, 26–39). Thus one can expect the occurrence of linear antibate dependence between logarithms of stepwise stability constants of palladium(II) chloride complexes and standard enthalpies of complexation reactions for the corresponding steps. Indeed, we have found that the $\lg K_{stab}$ values determined experimentally by three independent research groups [40–44] are related linearly to the ΔH^0 values for substitution of water molecules by chloride ion computed using the ZINDO/1 and PM3 methods (Table VI). The existence of quantitive $\lg K_{stab}$ *vs.* ΔH^0 relationships confirms the correctness of quantum chemical computations carried out and the constant aqueous medium contribution to ΔH^0 at all steps of substitution. The correlation coefficients are high, in spite of the fact that non-uniform quantities are compared: the experimental values of stability constants for aqueous solutions and standard enthalpies of the reactions estimated on the basis of gaseous-phase quantum chemical computations. This underlines the reliability and predicting significance of the correlations.

Use of correlation equations for other central atoms and ligands enables one to evaluate *a priori* the stepwise constants of complexation and to synthesize complexes using the interrelationship of stability constants.

The results obtained are important for studying Pd(II) complexation with organic ligands. As shown in the present work, the rate of exchange of hydronium ion by chlo-

TABLE VI Logarithms of stepwise stability constants for palladium(II) chloride complexes, c and d coefficients in equations $\lg K_{\mathrm{stab}} = c + d\Delta H^0$, and values of correlation coefficient r

$\lg K_1$	$\lg K_2$	$\lg K_3$	$\lg K_4$	*Ref.*	c	d	r
From ZINDO/1 data							
4.34	3.54	2.68	1.68	40[a]	2.519 ± 0.144	-0.008597 ± 0.001097[c]	-0.9991[c]
					2.531 ± 0.249	-0.008403 ± 0.001867[d]	-0.9973[d]
3.98	3.24	2.30	2.00	41[a]	2.460 ± 0.534	-0.006672 ± 0.004075[c]	-0.9804[c]
					2.467 ± 0.445	-0.006572 ± 0.003337[d]	-0.9864[d]
3.88	3.06	2.14	1.34	42–44[b]	2.083 ± 0.123	-0.008299 ± 0.000938[c]	-0.9993[c]
					2.094 ± 0.093	-0.008128 ± 0.000699[d]	-0.9996[d]
From PM3 data							
4.34	3.54	2.68	1.68	40[a]	2.295 ± 0.370	-0.009484 ± 0.002814[c]	-0.9953[c]
					2.299 ± 0.371	-0.009431 ± 0.002809[d]	-0.9952[d]
3.98	3.24	2.30	2.00	41[a]	2.280 ± 0.494	-0.007435 ± 0.003758[c]	-0.9865[c]
					2.282 ± 0.453	-0.007409 ± 0.003434[d]	-0.9886[d]
3.88	3.06	2.14	1.34	42–44[b]	1.864 ± 0.211	-0.009182 ± 0.001603[c]	-0.9984[c]
					1.868 ± 0.172	-0.009136 ± 0.001304[d]	-0.9989[d]

[a] $\lg K_{\mathrm{stab}}$ values are determined by the spectrophotometric method.

[b] $\lg K_{\mathrm{stab}}$ values are determined by solubility, potentiometric and spectrophotometric methods.

[c] Correlations are found assuming *cis*-[Pd(H_2O)$_2$Cl$_2$] participation in reactions by second and third steps.

[d] Correlations are found assuming *trans*-[Pd(H_2O)$_2$Cl$_2$] participation in reactions by second and third steps.

ride ion in palladium(II) complexes exceeds the rate of substitution of water. Using an organic reagent instead of a chloride ion, the reaction would be expected to proceed more readily in an acidic medium. The reaction should be conducted at optimal acidity, with protonation of the water molecule in the internal coordination sphere of the metal atom, even though the reagent molecule is protonated, so not to the reaction center of the complexation.

CONCLUSION

A comparative study of the kinetics of the substitution of H_2O and H_3O^+ ligands in aqua and aqua-chloride complexes of palladium(II) has been performed thorough quantum chemical analysis. Peculiarities of the mutual influence of ligands in complexes have been elucidated. The substitution of hydronium ion in the internal sphere of a palladium atom has been shown to be more favorable thermodynamically than that of a water molecule. Quantitative relationships between the stepwise stability constants for palladium(II) chloride complexes and the enthalpies of substitution reactions of water molecules by chloride ion have been found.

Consequently, we have established the dependence between the substitutional reactivity of aqua and aqua-chloride complexes of palladium(II) in reactions of aqua ligand substitution by chloride ion, and the electron structure of molecular systems.

Acknowledgments

The authors would like to thank Dr. Asya D. Shebaldova, Senior Researcher of Scientific-Research Institute of Chemistry Attached to the N. G. Chernyshevskii Saratov State University, for valuable advice and discussion, and Dr. Olga M. Tsivileva, Senior Researcher of the Institute of Biochemistry of Plants and

Microorganisms, Russian Academy of Sciences, Saratov, Russia, for technical assistance.

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