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High-Pressure Stopped-Flow Study of Kinetics and Mechanism for Complex Formation Reactions of Tetraaquapalladium(II) and -platinum(II) with Thioethers in Aqueous Solution

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Complex formation between $Pd(H_2O)_4^{2+}$ and $Pt(H_2O)_4^{2+}$ and the thioethers Me_2S, Et_2S, 1,4-dithiane, and 1,4-thioxane has been studied as a function of temperature (278–308 K) and pressure (0.1–200 MPa) by use of stopped-flow and conventional spectrophotometry in an aqueous 1.00 M perchloric acid medium. The rate constants k_1 for complex formation are similar for the four thioethers, varying only between 1.02×10^4 and 3.78×10^4 M^{-1} s^{-1} for $Pd(H_2O)_4^{2+}$ and between 0.37 and 0.90 M^{-1} s^{-1} for $Pt(H_2O)_4^{2+}$ at 25 °C. This indicates that changes in size, bulkiness, and solvation of the thioethers have only little importance regarding their properties as entering ligands for these sterically unhindered tetraaqua complexes. The higher rate observed for Pd(II) is mainly an enthalpy effect, and $\Delta H^{\ddagger}$ is 38 ± 6 kJ mol^{-1} for the reactions with $Pd(H_2O)_4^{2+}$ and 56 ± 6 kJ mol^{-1} for those with $Pt(H_2O)_4^{2+}$. The reactivity ratio k_{1Pd}/k_{1Pt} is only ca. 4×10^4 for the thioethers compared to ca. 10^6 for hard ligands, indicating that the substitution rates of Pt(II) complexes are more sensitive to the nature of the entering ligand than those of Pd(II), as expected for a softer metal center. The rates of the complex formation reactions are similar to the exchange rates of thioethers on the corresponding tetrasolvated thioether cations in the case of Pt(II), in spite of the large trans effects present in the tetrasolvated thioether cations. For Pd(II), the complex formation reactions are even faster than the corresponding thioether-exchange reactions. The comparatively high rates of the complex formation reactions indicate that, in addition to steric factors, changes in relative trans effects as well as effects of bond breaking are important in the activation process for both the exchange and complex formation reactions. Activation volumes are -4.0 ± 0.2, -8.7 ± 0.1, -6.6 ± 0.2, and -10.1 ± 0.3 cm^3 mol^{-1} for reactions between Me_2S, Et_2S, $S(CH_2)_4O$, and $S(CH_2)_4S$ and $Pd(H_2O)_4^{2+}$, respectively, and -15.3 ± 0.4, -17.0 ± 0.3, -13.9 ± 0.3, and -20.1 ± 0.2 cm^3 mol^{-1} for the $Pt(H_2O)_4^{2+}$ reactions. These volumes are comparable in size to the activation volumes for thioether exchange on the tetracoordinated thioether cations. Thus, neither the size or the steric requirements of the ligand nor the steric hindrance of the first coordination sphere of the complex can be used to predict the values of $\Delta^{\ddagger}V$ in these systems.

Introduction

Since the first study of the exchange kinetics of a simple, tetrasolvated cation of platinum(II) in our laboratory in 1982,[2] a variety of such exchange reactions of both platinum(II) and palladium(II) complexes with oxygen-, nitrogen-, sulfur-, and carbon-bonding ligands have been investigated.[3-9] The exchange rates of these tetrasolvates vary largely. For instance, $Pd(MeNC)_4^{2+}$ exchanges its ligands ca. 10^5 times faster than $Pd(H_2O)_4^{2+}$, and for the corresponding platinum(II) complexes, the ratio of reactivity is even larger, ca. 10^{11}.[8] The increased sensitivity to the nature of the ligands in the case of platinum(II) results in very similar rates of exchange for platinum and palladium complexes with soft ligands, such as cyanide,[10] isonitriles,[8] and olefins.[11]

Attempts have been made to rationalize these large variations in rates in terms of, for instance, steric blocking and differences in nucleophilicity between the entering ligands.[8] However, in spite of the fact that these exchange processes are chemically simple, it is difficult to compare the reactivities of the various solvento complexes, since the influences of the nature of the entering and leaving groups and of the trans and cis ligands as well as the steric properties of both the substrate complex and the entering nucleophile are not separable.[9] Similar difficulties arise when trends in activation volumes for these processes are considered. In this case, differences in solvation for different tetrasolvates may also affect the observed volumes.[9,12]

An evaluation of the various parameters determining the reactivity and activation volumes requires a systematic variation of substrate complexes and entering ligands. That has been done previously for simpler systems.[13] The aim of the present work was to better elucidate the effect of the entering nucleophile on both the reaction rates and the activation volumes by keeping cis and trans effects constant and steric hindrance of the complex at a minimum. Therefore, the simple tetraaqua cations of platinum(II) and palladium(II) have been used as substrate complexes for reactions with some of the nucleophiles for which solvent exchange has already been studied. These include the noncharged thioethers Me_2S and Et_2S, the cyclic dithioether 1,4-dithiane, $S(CH_2)_4S$, and the structurally related 1,4-thioxane, $S(CH_2)_4O$.

Experimental Section

Chemicals and Solutions. Stock solutions of tetraaquapalladium(II) perchlorate (ca. 50 mM) and tetraaquaplatinum(II) perchlorate (ca. 10 mM) in 1.00 M perchloric acid (Baker, p.a.) were prepared from palladium sponge (Johnson and Matthey, Spec Pure) or K_2PtCl_4 (Johnson and

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Matthey) and $AgClO_4$ (G. F. Smith) as described previously.[14,15] The metal concentrations were determined spectrophotometrically from the absorbance either at 380 nm, where the molar absorptivity of $Pd(H_2O)_4^{2+}$ is 82.8 M^{-1} cm^{-1}, or at 275 nm, where the molar absorptivity of $Pt(H_2O)_4^{2+}$ is 56.5 M^{-1} cm^{-1}. For both complexes, the spectra were identical to those reported earlier.[14,15] The concentration of perchloric acid was determined potentiometrically. Ligand solutions were prepared from dimethyl sulfide (Merck, synthetic grade), diethyl sulfide (Merck, synthetic grade), 1,4-dithiane (Aldrich, 98%), and 1,4-thioxane (Lancaster, synthetic grade). All solutions were flushed with nitrogen to remove dissolved oxygen. The ionic strength was 1.00 M with perchloric acid (Baker, p.a.) as supporting electrolyte. At the low pH used, hydrolysis of the aqua complexes is negligible. The water was doubly distilled from quartz. The organic ligands were used as received.

Apparatus. A Varian Cary 2200 spectrophotometer with a water-thermostated cell holder was used for the slow kinetics. Faster reactions were monitored by use of a Hi-Tech SF-3L stopped-flow spectrophotometer. Variable-pressure measurements for both slow and fast reactions were performed by use of a Hi-Tech high-pressure stopped-flow spectrophotometer, HPSF-56,[16] connected to a Hi-Tech high-performance hydraulic pressurizing system (Hydratron) with a digital recording of the pressure. Water was used as the pressurizing medium and also as the thermostating liquid for the high-pressure bomb. All instruments were connected to IBM-AT compatible computers, VICTOR V286A, and kinetic data were collected and analyzed by use of the OLIS computer program "Model 4000 Data System Stopped-Flow", version 9.04.

Kinetic Measurements. The reactions between $Pt(H_2O)_4^{2+}$ and Me_2S and $S(CH_2)_4O$ were initiated by mixing equal volumes of metal and ligand solutions directly in the thermostated cell. These reactions were sufficiently slow to be monitored by the Cary spectrophotometer and could be followed by observing the increase in absorbance at 240 nm. The faster reactions between $Pt(H_2O)_4^{2+}$ and Et_2S and $S(CH_2)_4S$ were initiated by mixing equal volumes of metal and ligand solutions directly in the stopped-flow instrument and were followed by observing the increase in absorbance at 240 nm. Similarly, the reactions between $Pd(H_2O)_4^{2+}$ and all the nucleophiles were monitored by use of the stopped-flow instrument at 245 nm. To prevent formation of higher complexes, the complex formation reactions were followed under pseudo-first-order conditions with the concentration of metal complex in at least 10-fold excess over that of ligand. The variable-temperature measurements were performed between 278 and 308 K and are summarized in supplementary Tables SI–SVIII. Measurements at variable pressure were performed at 298 K in the interval 0.1–200 MPa. Pseudo-first-order conditions with excess metal complex were used, and the experiments were free of observable hysteresis due to decomposition of the reactants by pressure. The high-pressure results are given in supplementary Tables SIX–SXVI.

Calculations. All kinetic runs were best described by a single exponential. Observed pseudo-first-order rate constants were obtained from a least-squares fit of at least 3 half-lives of the reactions, and the values given represent the average of two to five experiments. The second-order rate constants were obtained by a fit of the observed rate constants vs the concentration of the excess free metal to a straight line by use of a least-squares routine; cf. Figures 1 and 2. Enthalpies and entropies of activation were determined by a fit of the natural logarithm of the second-order rate constants corrected for statistics, $k/4$, to the Eyring equation. Volumes of activation were obtained by a fit of the natural logarithm of the observed pseudo-first-order rate constants to eq 1, where k_0 denotes

$$\ln k_{\text{obsd}} = \ln k_0 - (\Delta^{\ddagger}V^{0})P/RT \qquad (1)$$

the rate constant at 0.1 MPa and 298 K; cf. Figure 3. Errors reported correspond to one standard deviation.

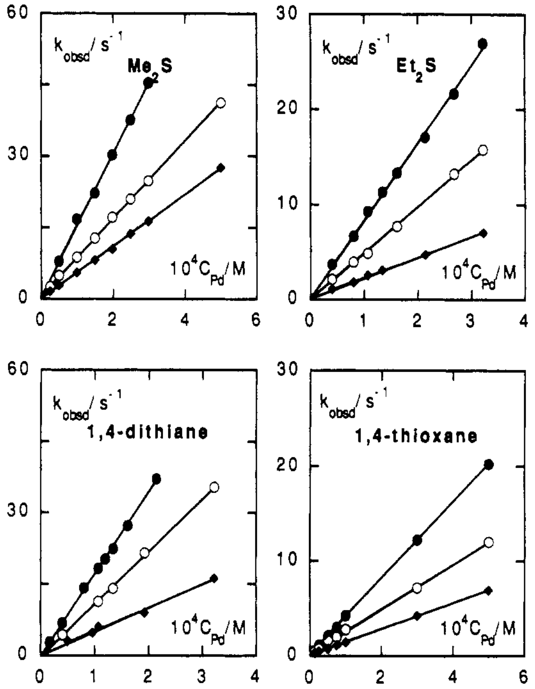

Figure 1. Observed pseudo-first-order rate constants for reactions of excess $Pd(H_2O)_4^{2+}$ with thioethers at 298.2 K (●), 288.2 K (○), and 278.2 K (◆) in 1.00 M aqueous perchloric acid medium. Experimental conditions are given in supplementary Tables SI–SIV.

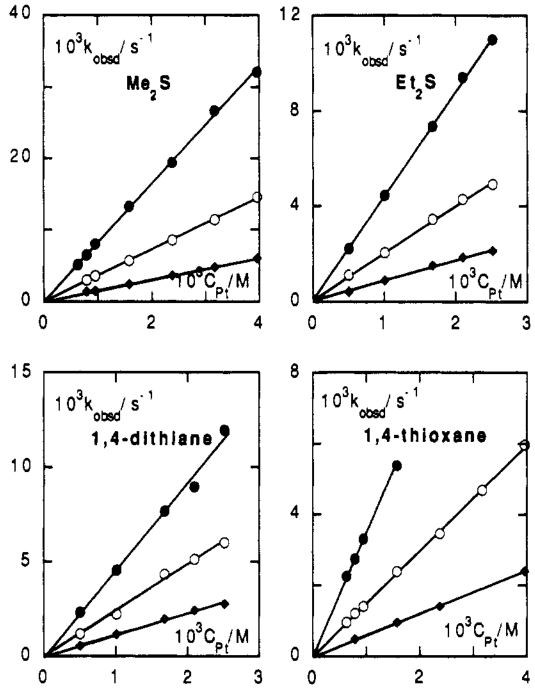

Figure 2. Observed pseudo-first-order rate constants for reactions of excess $Pt(H_2O)_4^{2+}$ with thioethers at 308.2 K (●), 298.2 K (○), and 288.2 K (◆) in 1.00 M aqueous perchloric acid medium. Experimental conditions are given in supplementary Tables SV–SVIII.

Results and Discussion

Reactions between the Tetraaqua Cations and Thioethers. The complexes between the S-bonding nucleophiles and palladium(II) and platinum(II) are strong, with stability constants β_1 between 4×10^5 and 6×10^5 M^{-1} for the Me_2S and 1,4-thioxane complexes.[17,24] Thus, for the excess metal concentrations used in the present work, the complex formation reaction is complete and the reverse of reaction 2 is negligible. The second-order rate constants k_1 were obtained directly from the plots of k_{obsd} vs

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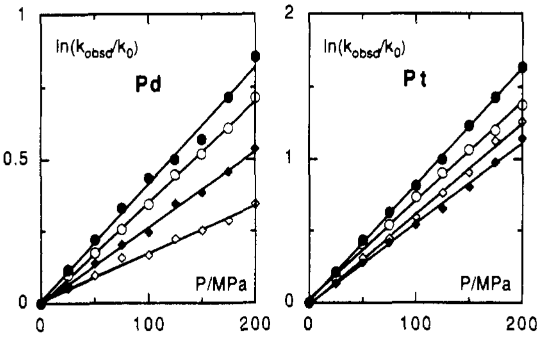

Figure 3. Normalized pseudo-first-order rate constants ln $(k_1{}^P/k_1{}^0)$ at 298.2 K as a function of pressure for reactions of 1,4-dithiane (●), Et_2S (○), 1,4-thioxane (◆) and Me_2S (◇) with $Pd(H_2O)_4^{2+}$ and $Pt(H_2O)_4^{2+}$. Experimental conditions are given in supplementary Tables SIX–SXV.

metal concentration. These plots had negligible intercepts; cf. Figures 1 and 2. Reaction 2 is first-order with respect to both metal complex and nucleophile. Statistically corrected rate

$$M(H_2O)_4^{2+} + L \xrightarrow{k_1} ML(H_2O)_3^{2+} + H_2O \qquad (2)$$

constants and activation parameters are given in Table I. Volumes and entropies of activation are negative, as expected for associatively activated processes.

Second-order rate constants k_1 for formation of complexes between the two metal centers and various ligands according to eq 2 are given in Table II. The ratios k_{1Pd}/k_{1Pt} are very similar for the thioethers studied, varying only from ca. 3 × 10^4 to 7 × 10^4. These are also very close to the ratios observed for other sulfur-bonding ligands like Me_2SO and thiourea.[21,22,24] The higher reactivity of $Pd(H_2O)_4^{2+}$ is mainly due to the much lower enthalpies of activation, 38 ± 6 kJ mol^{-1}, compared to 56 ± 6 kJ mol^{-1} for $Pt(H_2O)_4^{2+}$; cf. Table I. There is an obvious trend of k_{1Pd}/k_{1Pt} from ca. 10^6 for hard nucleophiles like water and chloride, via bromide, thiocyanate, and iodide, to ca. 5 × 10^4 for the much softer sulfur-bonding thioethers. This trend reflects a higher sensitivity of the platinum(II) center to the nature of the entering ligands, which agrees with the assumption that $Pt(H_2O)_4^{2+}$ is a softer metal center than $Pd(H_2O)_4^{2+}$. Differing sensitivities toward the nature of the entering ligands are also observed, when the relative entering ligand efficiencies are considered. For both cations, there is a trend in reactivity:

$$H_2O < Cl^- < Br^- \leq SCN^-, \text{thioethers} < I^-, \text{tu}$$

In the case of $Pt(H_2O)_4^{2+}$, the thioethers react ca. 10^5 times faster than water, whereas the corresponding ratio for $Pd(H_2O)_4^{2+}$ is only ca. 10^3.

A comparison of the four thioethers shows that the smallest molecule Me_2S exhibits a somewhat higher reactivity with both metal centers, if the values for the ambidentate dithiane are statistically corrected. However, the differences are very small, and the order of reactivity for Et_2S, $S(CH_2)_4O$, and $S(CH_2)_4S$ is not predictable on the basis of steric arguments. Thus, for reactions with these small and sterically nonhindered tetraaqua substrate complexes, the variations in size, bulkiness, and solvation of the ligands seem to be of only minor importance with regard to their properties as nucleophiles.

Reactivity Comparison between Tetraaqua and Tetrasolvento Complexes. Previous systematic investigations of substitution reactions involving square-planar complexes of Pt(II) and Pd(II) without steric hindrance show that the reactivity of these complexes is strongly influenced by both the trans and the entering ligands.[13,26] For complexes of both metal ions, the influences of the two cis ligands and the leaving ligand have been assumed to be of minor importance.

The estimations of the rates of the solvent-exchange reactions listed in Table I, based on the complex formation rates for $M(H_2O)_4^{2+}$ and assumed trans effects of the S-bonding thioethers of ca. 10^4–10^6 compared to that of water,[13] give rate constants for the solvent-exchange reactions exceeding the observed values by the same factor of 10^4–10^6. Inspection of the data in Table I for $Pt(H_2O)_4^{2+}$ shows that the ratio $k_{solv\ exch}/k_1$ is only ca. 2 for Me_2S and ca. 45 for dithiane. For the reactions with $Pd(H_2O)_4^{2+}$, the reactivity is reversed, solvent exchange being slower than complex formation by factors of 17 for Me_2S, 4 for dithiane, and as much as 4 × 10^3 for Et_2S. In the case of Et_2S, the very slow solvent exchange rate has been rationalized in terms of steric hindrance due to the four coordinated diethyl sulfide ligands.[8] The present finding that Et_2S reacts approximately as fast as the smaller thioethers with the unhindered substrate $Pd(H_2O)_4^{2+}$ supports this conclusion.

However, for exchange of Me_2S and 1,4-dithiane, steric blocking due to the ligands of the tetracoordinated thioether complex is probably much less important. It is known that the relative trans effects in particular, but also the relative efficacies of various leaving ligands, are affected when strong entering nucleophiles attack square-planar complexes.[22,25] This is natural, if there is a strong interaction between the entering, trans, and leaving ligands in the assumed trigonal-bipyramidal transition state.[22,25] For the present thioether nucleophiles, a lowering of the trans effect of the S-bonded thioether opposite to the leaving one in the exchange process is probably the main reason for the low exchange rate observed. Moreover, bond-breaking should also be important in the activation process for these reactions. Whereas only a weak metal–water molecule bond is broken in the case of the complex formation reaction, the exchange process involves breaking of a stronger metal–sulfur bond, which is likely to decrease the rate by increasing the free energy of activation. In the case of exchange in the sterically hindered $Pd(Et_2S)_4^{2+}$ complex, the effects of the trans and leaving ligands of course also influence the reactivity, in addition to the steric hindrance.

Volumes of Activation. For all the reactions studied, the volumes of activation are significantly negative; cf. Table I. This is in agreement with a net decrease of molar volume in the activation process, as expected for an I_a mechanism. For both complex formation and solvent-exchange reactions, the values of $\Delta^{\ddagger}V$ are much more negative in the case of Pt(II). Since structural studies show that tetracoordinated cations of Pd(II) and Pt(II) have very similar bond distances,[27–31] and probably also molar volumes, the differences observed in the values of $\Delta^{\ddagger}V$ can most probably be related to properties of the transition states. Less extensive orbital overlap in the five-coordinate transition state of Pd(II) should result in weaker and longer metal–ligand bonds, and a less compact structure, compared to those of isostructural Pt(II) complexes.

There is also a difference between the two metal centers when the volumes and entropies of activation for the respective complex formation reactions are compared. Whereas there is a good correlation between $\Delta^{\ddagger}S$ and $\Delta^{\ddagger}V$ for complex formation with $Pt(H_2O)_4^{2+}$, no similar relation can be observed for $Pd(H_2O)_4$. This fact may also originate from the stronger bonding in the case of Pt(II), also in the transition state. This means that loss of solvent molecules from the second coordination sphere in the activation process will be less extensive for Pt(II) than for Pd(II),

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Table I. Statistically Corrected Rate Constants and Activation Parameters for Reactions between Square-Planar Solvated Cations and Various Nucleophiles L

cation	L	$(k^{298}/4)$/M^{-1} s^{-1}	$\Delta^\ddagger H$/kJ mol^{-1}	$\Delta^\ddagger S$/J K^{-1} mol^{-1}	$\Delta^\ddagger V$/cm^3 mol^{-1}	ref
$Pd(H_2O)_4^{2+}$ [d]	H_2O	10.2 ± 0.7 [e]	49.5 ± 1.9	-60 ± 6	-2.2 ± 0.2	4
	Me_2S	$(3.78 \pm 0.02) \times 10^4$	31 ± 5	-54 ± 6	-4.0 ± 0.2	this work
	Et_2S	$(2.08 \pm 0.01) \times 10^4$	43 ± 5	-19 ± 2	-8.7 ± 0.1	this work
	$S(CH_2)_4O$	$(1.02 \pm 0.02) \times 10^4$	34 ± 2	-54 ± 2	-6.6 ± 0.2	this work
	$S(CH_2)_4S$	$(4.18 \pm 0.01) \times 10^4$ [a]	45 ± 6	-17 ± 2	-10.1 ± 0.3	this work
$Pd(Me_2S)_4^{2+}$ [c]	Me_2S	$(2.14 \pm 0.05) \times 10^3$	31.9 ± 0.6	-74.3 ± 1.9	-9.4 ± 0.4	8
$Pd(Et_2S)_4^{2+}$ [c]	Et_2S	5.0 ± 0.6	50.4 ± 2.4	-62.8 ± 6.9	-11.6 ± 0.4	8
$Pd(C_4H_8S_2)_2^{2+}$ [c]	$S(CH_2)_4S$	$(9.8 \pm 0.3) \times 10^3$	22.9 ± 0.6	-91.6 ± 2.1	-9.8 ± 0.4	9
$Pt(H_2O)_4^{2+}$ [d]	H_2O	$(7.1 \pm 0.5) \times 10^{-6}$ [e]	89.7 ± 2.4	-43 ± 8	-4.6 ± 0.2	3
	Me_2S	0.90 ± 0.02	61 ± 1	-40 ± 2	-15.3 ± 0.4	this work
	Et_2S	0.48 ± 0.02	57 ± 2	-60 ± 4	-17.0 ± 0.3	this work
	$S(CH_2)_4O$	0.368 ± 0.003	62 ± 2	-46 ± 6	-13.9 ± 0.3	this work
	$S(CH_2)_4S$	0.62 ± 0.03 [b]	50 ± 6	-84 ± 11	-20.1 ± 0.2	this work
$Pt(Me_2S)_4^{2+}$ [c]	Me_2S	1.54 ± 0.07	41.2 ± 0.7	-100.2 ± 2.2	-22.0 ± 1.3	9
$Pt(C_4H_8S_2)_2^{2+}$ [c]	$S(CH_2)_4S$	28.2 ± 4.8	32.9 ± 3.6	-106 ± 11	-12.6 ± 1.1	9

[a] Per S: 2.1×10^4 M^{-1} s^{-1}. [b] Per S: 0.31 M^{-1} s^{-1}. [c] In nitromethane solution. [d] In aqueous solution. [e] Estimations based on the observed first-order exchange rate constant divided by an assumed concentration of water 55 M.

Table II. Rate Constants, k_{1M}, for Formation of $ML(H_2O)_3^{(2-n)+}$ from $M(H_2O)_4^{2+}$ in Aqueous Solution at 298 K (M = Pd, Pt)

L^{n-}	k_{1Pd}/M^{-1} s^{-1}	k_{1Pt}/M^{-1} s^{-1}	k_{1Pd}/k_{1Pt}	ref
H_2O	41	2.8×10^{-5}	1.5×10^6	3, 4
Cl^-	1.8×10^4	2.66×10^{-2}	6.8×10^5	18, 19
Br^-	9.2×10^4	2.11×10^{-1}	4.4×10^5	18, 19
SCN^-	4.4×10^5	1.33	3.3×10^5	19, 24
I^-	1.14×10^6	7.7	1.4×10^5	20
Me_2SO	2.45	8.4×10^{-5}	2.9×10^4	21, 22
MeCN	3.09×10^2			23
Me_2S	1.51×10^5	3.6	4.2×10^4	this work
Et_2S	8.3×10^4	1.92	4.3×10^4	this work
$S(CH_2)_4O$	4.1×10^4	1.47	2.8×10^4	this work
$S(CH_2)_4S$	1.67×10^5	2.48	6.7×10^4	this work
$(NH_2)_2CS$	9.6×10^5	13.9	6.9×10^4	24

if the latter is assumed to have a more loosely bound transition state, with weaker solvation.

In spite of the small molecular dimensions of the tetraaqua cations used in the present work, the absolute values of the observed volumes of activation are large. For $Pd(H_2O)_4^{2+}$, the magnitudes are similar to those reported previously for reactions with both CH_3CN and Me_2SO.[21,23] As can be seen from Table I, the values of $\Delta^\ddagger V$ for corresponding complex formation and solvent-exchange reactions are comparable in magnitude. Thus, there seems to be no obvious correlation between the observed volumes of activation for these exchange and complex formation reactions and the size or steric requirements of the ligands, or the steric encumbrance of the first coordination sphere of the complex. This is in contrast to what has been suggested previously.[8,32]

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Supplementary Material Available: Observed pseudo-first-order rate constants for the reactions of $Pd(H_2O)_4^{2+}$ and $Pt(H_2O)_4^{2+}$ with Me_2S, Et_2S, 1,4-thioxane, and 1,4-dithiane as a function of temperature (Tables SI–SVIII) and as a function of pressure (Tables SIX–SXVI) (12 pages). Ordering information is given on any current masthead page.

Registry No. $Pd(H_2O)_4^{2+}$, 22573-07-5; $Pt(H_2O)_4^{2+}$, 60911-98-0; Me_2S, 75-18-3; Et_2S, 352-93-2; 1,4-dithiane, 505-29-3; 1,4-thioxane, 15980-15-1.

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