Ammine Ligand Exchange in Tetraamminepalladium(II) in Aqueous Solution

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The rate of exchange of ammonia between tetraamminepalladium(II) and ammonia solution in aqueous ammonium perchlorate of unit ionic strength has been determined for the pH range 6–11 using nitrogen-15 labelling. The rate of exchange increases with increasing pH, and the pH-dependence can be accounted for in terms of two parallel reactions: (i) a direct exchange between NH_3 and $Pd(NH_3)_4^{2+}$ predominant in alkaline solution (statistically corrected second-order rate constant k_{NH_3} = $1.6(2)\times10^{-2}$ l mol^{-1} s^{-1}m, $\Delta H^{\ddagger}$ = 67(3) kJ mol^{-1}, $\Delta S^{\ddagger}$ = −54(12) J mol^{-1} K^{-1} at 25.0 °C); (ii) an indirect exchange predominant in neutral solution, which involves transient formation of $Pd(NH_3)_3H_2O^{2+}$ (k_{H_2O} = $3.0(2)\times10^{-4}$ s^{-1}, $\Delta H^{\ddagger}$ = 80(2) kJ mol^{-1}, $\Delta S^{\ddagger}$ = −38(6) J mol^{-1} K^{-1}). The moderately negative entropy of activation for both reactions is in accordance with a transition state in which both bond formation and bond breaking are of importance, as also confirmed by a linear free energy relationship for ligand substitutions in the tetraamminepalladium(II) ion. The direct exchange in the tetraamminepalladium(II) is an order of magnitude slower than the exchange in the isoelectronic tetraamminegold(III) as a result of a larger enthalpy of activation.

Ammine ligand exchange rates and activation parameters for the exchange process provide the most fundamental characterization of the inertness and intrinsic reactivity of metal ammine complexes.[1] However, few metal ammine complexes have been subjected to detailed kinetic investigations affording mechanistic classifications of the ammine ligand exchange processes.[2–4] Examples are the investigations of the ligand exchange in cobalt(III) ammine complexes[4–6] and gold(III) ammine complexes,[7] both in aqueous ammonia solution, from which important differences between the exchange behaviour of octahedral d^6 complexes and square-planar d^8 complexes were inferred.[7] The introduction of a π-donor ligand at the cobalt(III) centre thus accelerates the exchange considerably, whereas the opposite effect was seen for the gold(III) complex.[5–7] Moreover, the tetraamminegold(III) complex was found to exchange ammine ligands in aqueous ammonium solution as a result of at least three different reaction paths.[6] This latter indication of a complex mechanism for ammine exchange reactions, which from a more cursory examination could be believed to be elementary reactions, has provided a strong incentive to include other metal ammine complexes in these studies. The square-planar tetraamminepalladium(II) ion was chosen for the present kinetic study, since this d^8 ion combines a high thermodynamic stability[8,9] with a moderate reactivity with respect to ligand exchange.[9–12]

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Experimental

pH measurement. A Metrohm 605 pH meter and an Ingold type 405 combination glass electrode with 1.0 M NaCl in the reference part were used for pH measurement. The kinetic studies were all made in a 1.0 M perchlorate medium, and the definition pH = −log [H^+] was employed throughout, with solutions of standardized perchloric acid in 1.0 M NH_4ClO_4 used as pH standards. The pK_a value of NH_4^+ in 1.0 M NH_4ClO_4 at the required temperatures was interpolated from available thermodynamic data.[12]

Chemicals. Palladium(II) chloride was obtained from Johnson Matthey Chemicals, [15]NH_4Cl (99 % nitrogen-15) from Amersham Int.; Na(tos), sodium *p*-toluenesulfonate (reagent grade) from BDH; and other commercial chemicals were of analytical grade.

Labelling procedure. Nitrogen-15 labelled [$Pd(NH_3)_4$]$Cl_2 \cdot H_2O$[9] was prepared by dissolution of $PdCl_2$ (1.0 g) in an enriched ammonia/ammonium buffer (1.0 g [15]NH_4Cl in 10.0 ml of 12 M NH_3) and subsequent heating to 50 °C for 5 min. The hot pale-yellow solution was filtered through a fine-porosity sintered-glass funnel and kept in an ice bath for 10 min. The desired product was isolated by filtration and washed with ice-cold ethanol, subsequently with ether, and then air-dried [yield 680 mg (46 %)]. The UV spectrum (λ_{max} = 296 nm, ε_{max} = 196 l mol^{-1} cm^{-1}; Cary 219 spectrophotometer) agreed with the spectrum reported for the

tetraamminepalladium(II) ion.[8] Calculated ^{15}N enrichment 13%, found 12.7%.

Isotopic analysis. The ^{15}N isotopic abundance in the labelled compound and in the [Pd(NH$_3$)$_4$](tos)$_2$ precipitated in the exchange experiments was determined by optical emission spectroscopy. The analytical procedure involved a Dumas destruction at 400°C of the material [copper plus copper(II) oxide].[13]

Exchange experiments. An aqueous 1.0 M (Na, NH$_4$)ClO$_4$ reaction medium was employed throughout. In the neutral region, 3-morpholinopropanesulfonate was used to buffer the medium (0.050 M buffer), whereas standardized sodium hydroxide was used to adjust the pH in the alkaline region (formation of NH$_4^+$/NH$_3$ buffer). The pH was measured in each of the reaction media after the addition of [Pd(NH$_3$)$_4$]Cl$_2\cdot$H$_2$O at the temperature of the experiment. The labelled compound (weighed amounts corresponding to a complex concentration between 0.011 and 0.043 M) was dissolved in the actual reaction medium (thermostatted to within 0.1°C) to initiate the exchange reaction. Dissolution was virtually instantaneous, and 300 μl aliquots were removed at known times and poured into 100 μl of an ice-cold 2.3 M sodium p-toluensulfonate solution. A white precipitate of [Pd(NH$_3$)$_4$](tos)$_2$ was immediately formed (cf. Ref. 8). The mixture was cooled in ice for 2 min, and the precipitate was filtered off in a fine-porosity sintered-glass funnel, washed twice with 0.1 ml of ice-cold water, and air-dried on the filter. The precipitate was subsequently dissolved in 0.1 ml of 1 M HBr (ca. 50°C), and ca. 10 μl of the resulting yellow solution was *immediately* transferred to a 1 cm long glass capillary by capillary attraction. The solution was evaporated to dryness in the capillary (ca. 50°C in vacuum), and the residue was subjected to Dumas destruction and subsequent isotopic analysis.

Results

Tetraamminepalladium(II), labelled with ^{15}N, was found to lose ^{15}N enrichment when dissolved in aqueous ammonium perchlorate solutions. The fast and almost quantitative precipitation of the p-toluenesulfonate salt, [Pd(NH$_3$)$_4$](tos)$_2$,[8] provides a convenient method for removing Pd(NH$_3$)$_4^{2+}$ from the reaction mixture and thereby for quenching the exchange reaction.

At a fixed temperature, the exchange rate was strongly dependent on the pH of the ammonium perchlorate solution. However, for conditions of fixed pH and a large excess of ammonium ($c_{NH_4^+}$ >> c_{Pd}), the exchange was found to follow first-order kinetics, as shown in eqn. (1), where % ^{15}N(t) denotes the decreasing ^{15}N enrichment in the precipitated [Pd(NH$_3$)$_4$](tos)$_2$, as illustrated in Fig. 1.

$$\ln\left(\frac{\%\ ^{15}N(t) - \%\ ^{15}N(t=\infty)}{\%\ ^{15}N(t=0) - \%\ ^{15}N(t=\infty)}\right) = -k_{obs}\ t \qquad (1)$$

For the exchange reaction between Pd(*NH$_3$)$_4^{2+}$ and NH$_3$/NH$_4^+$, the McKay equation[14] yields eqn. (2) from

$$\ln\left(\frac{\%\ ^{15}N(t) - \%\ ^{15}N(t=\infty)}{\%\ ^{15}N(t=0) - \%\ ^{15}N(t=\infty)}\right) = -R_{ex}\left(\frac{c_{Pd} + c_{NH_4}}{4c_{Pd}c_{NH_4}}\right) t \qquad (2)$$

which it is seen that the exchange rate, R_{ex}, is related to the observed first-order rate constant by eqn. (3), in which c_{Pd} and c_{NH_4} denote the total concentration of complex and ammonium/ammonia, respectively.

$$R_{ex} = 4k_{obs}\left(\frac{c_{Pd}\ c_{NH_4}}{c_{Pd} + c_{NH_4}}\right) \qquad (3)$$

For the experimental conditions employed in the present study [c_{NH_4} >> c_{Pd}, and exchange at pH for which Pd(NH$_3$)$_4^{2+}$ is thermodynamically stable], eqn. (3) is approximated by eqn. (4).

$$R_{ex} = 4k_{obs}\ [Pd(NH_3)_4^{2+}] \qquad (4)$$

The observed first-order rate constant, k_{obs}, depends both on c_{NH_4} and on the solution pH. The pH dependence for k_{obs}, shown in Fig. 2 for c_{NH_4} = 1.00 M at four different temperatures, could be accounted for in terms of two parallel reactions according to Scheme 1: (i) a direct exchange between NH$_3$ and Pd(NH$_3$)$_4^{2+}$, and (ii) an indirect exchange involving transient formation of Pd(NH$_3$)$_3$H$_2$O^{2+}. Accord-
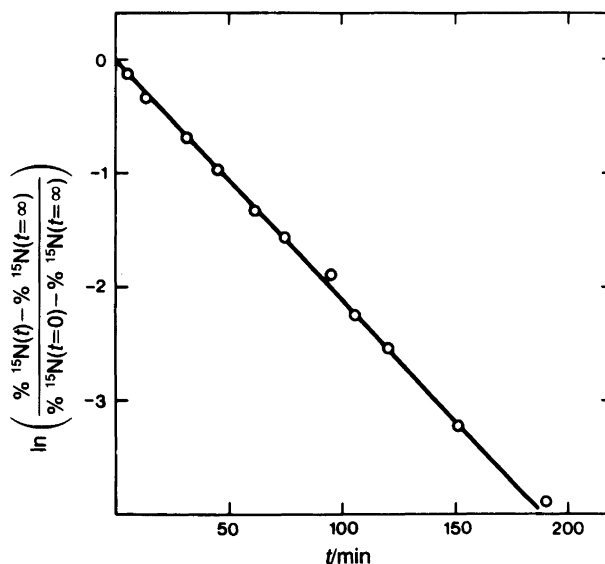

Fig. 1. Decreasing ^{15}N-enrichment in Pd(NH$_3$)$_4^{2+}$ plotted according to the McKay equation. The initial enrichment of Pd(*NH$_3$)$_4^{2+}$, % ^{15}N(t=0) = 12.7, decreases during exchange with solution ammonia/ammonium to % ^{15}N(t=∞) = 1.48. Experimental conditions: 25.0°C, c_{Pd} = 0.0219 M in 1.00 M NH$_4$ClO$_4$ with pH 6.18. The exchange has a half-life of 33 min under these experimental conditions and the reaction was followed for more than 5 half-lives.

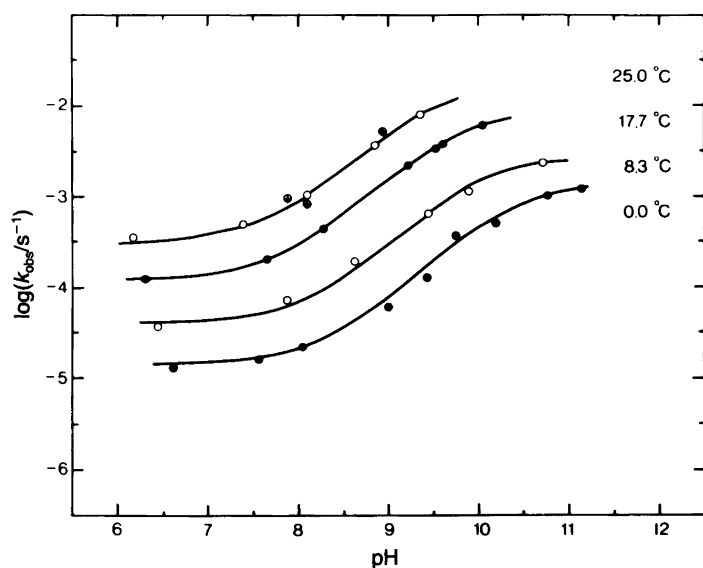**Fig. 2.** Observed first-order rate constant for ammine ligand exchange in $Pd(NH_3)_4^{2+}$ as a function of pH. Experimental points were determined for solutions with $c_{Pd} = 0.020$ M in 1.00 M NH_4ClO_4 (except $c_{Pd} = 0.043$ M for ⊕), as outlined in Fig. 1. The solid lines were calculated by regression analysis (χ^2 goodness-of-fit test) according to eqns. (6) and (7) for each temperature, incorporating the pK_a values of Table 1.

ing to the model of Scheme 1, the rate of exchange for the two parallel reactions is given by eqn. (5)[15] with k_{Pd,H_2O} and k_{Pd,NH_3} being the pseudo-first-order and second-order rate

$$R_{ex} = (k_{Pd,H_2O} + k_{Pd,NH_3}[NH_3])[Pd(NH_3)_4^{2+}] \quad (5)$$

constants for indirect and direct exchange, respectively, both based on complex concentration. However, since the observed rate constant is based on ligand concentration and

thus inherently statistically corrected [the factor of 4 in eqns. (2)–(4)], the relation between the observed rate constant and k_{H_2O} and k_{NH_3}, the statistically corrected rate constants for the parallel exchange reactions, is given by eqn. (6).

$$k_{obs} = k_{H_2O} + k_{NH_3}[NH_3] \quad (6)$$

The pH dependence of k_{obs} was analyzed by a general regression procedure according to eqn. (6), including the independently determined $K_a(NH_4^+)$[12] [eqn. (7)], and the

$$[NH_3] = \frac{K_a(NH_4^+)}{K_a(NH_4^+) + [H^+]} \cdot c_{NH_4} \quad (7)$$

rate constants k_{H_2O} and k_{NH_3} at each of the four temperatures are presented in Table 1.

The observed rate constant for the exchange process was independent of the ammonium-ion concentration (0.13 <

Scheme 1.

Table 1. Acid dissociation of ammonium and rate constants[a] for exchange of ammonia coordinated in tetraamminepalladium(II) with ammonia/ammonium in aqueous 1.0 M ammonium perchlorate.

$t/°C$	$pK_a(NH_4^+)$[b]	k_{H_2O}/s^{-1} [c]	$k_{NH_3}/l\ mol^{-1}\ s^{-1}$ [d]
0.0	10.29	$1.4(1)\times10^{-5}$	$1.32(5)\times10^{-3}$
8.3	9.98	$4.0(4)\times10^{-5}$	$2.69(5)\times10^{-3}$
17.7	9.67	$1.23(7)\times10^{-4}$	$8.1(2)\times10^{-3}$
25.0	9.43	$3.1(3)\times10^{-4}$	$1.64(2)\times10^{-2}$

[a]Calculated by regression analysis from the observed rate constants presented in Fig. 1 and the pK_a for ammonium. [b]$pK_a = -\log(K_a/mol\ l^{-1})$, from Ref. 12. [c]Pseudo-first-order rate constant based on ligand concentration for solvent path for ammine ligand exchange. [d]Second-order rate constant based on ligand concentration for direct exchange of ammine ligand with solvent ammonia.
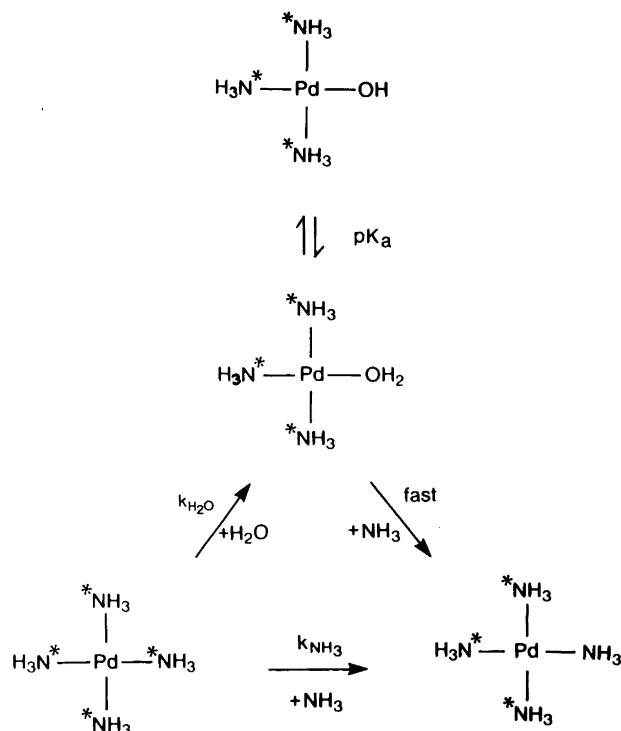
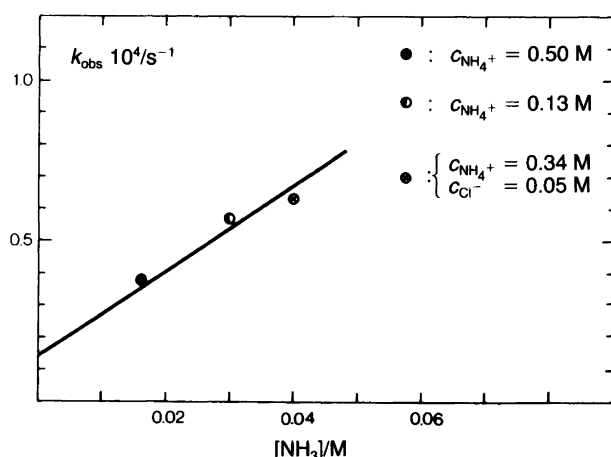Fig. 3. Test of influence of ammonium-ion concentration and of chloride concentration on ammine exchange rate in $Pd(NH_3)_4^{2+}$. The observed pseudo-first-order rate constants were determined at 0.0 °C in (Na, NH_4)(ClO_4, Cl) solutions of unit ionic strength and compared with the solid line calculated from the parameters given in Table 1, which were determined for 1.00 M NH_4ClO_4.

$[NH_4^+] < 1.00$ M, at constant ionic strength 1.0) at fixed ammonia concentration, as shown in Fig. 3, and a direct exchange between the tetraamminepalladium(II) ion and the ammonium ion could not be detected. The exchange rate was likewise independent of the presence of chloride ions (Fig. 3), excluding catalysis via transient formation of chloro complexes.

The temperature dependence of the rate constants for the two significant exchange reactions is well described by the Arrhenius equation (Fig. 4) leading to the activation parameters given in Table 2.

Discussion

The activation parameters for the direct and the indirect ammine-ligand exchange reactions, both of significance to the tetraamminepalladium(II) ion, are compared in Table 2 with the activation parameters for exchange reactions in the likewise square-planar tetraamminegold(III). As for the weak acid, $Au(NH_3)_4^{3+}$, ammine-ligand exchange is the

result of at least three reaction paths,[7] one of which is the direct exchange shown in eqn. (8).

$$Au(^*NH_3)_4^{3+} + NH_3 \rightleftharpoons Au(^*NH_3)_3NH_3^{3+} + NH_3 \qquad (8)$$
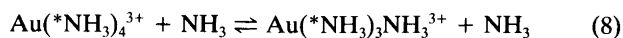
At ambient temperature, the rate of exchange for $Au(NH_3)_4^{3+}$ according to eqn. (8) is an order of magnitude faster than the similar reaction for $Pd(NH_3)_4^{2+}$, eqn. (9).

$$Pd(^*NH_3)_4^{2+} + NH_3 \rightleftharpoons Pd(^*NH_3)_3NH_3^{2+} + {}^*NH_3 \qquad (9)$$

The entropy of activation is negative for both of the reactions of eqns. (8) and (9), which is in agreement with a transition state of increased coordination number.[16] The net increase in bonding in the transition state seems very
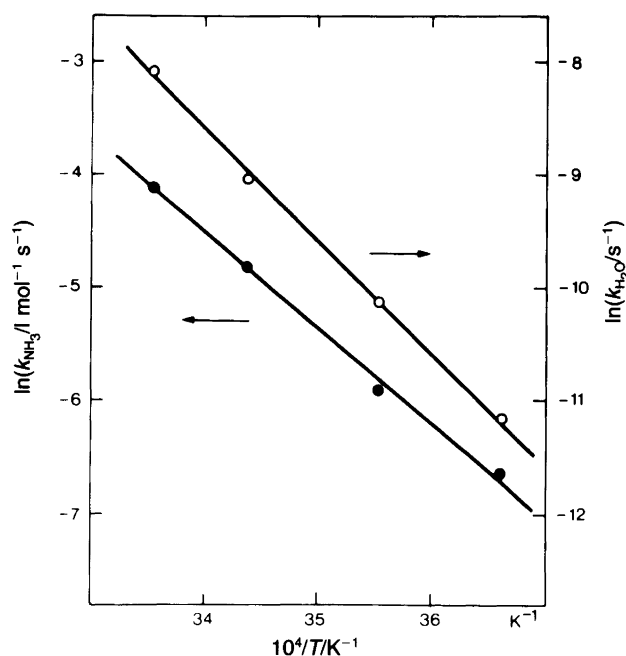

Fig. 4. Temperature dependence of the rate constant for the two parallel reaction paths for ammine exchange in tetraamminepalladium(II) plotted according to the Arrhenius equation.

Table 2. Activation parameters and rate constants at 25.0 °C for exchange of ammonia coordinated in tetraamminepalladium(III) and tetraamminegold(III) with ammonia/ammonium in aqueous 1.0 M ammonium perchlorate solution.

Reactants[a]	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}	k	Ref.
$Pd(NH_3)_4^{2+}/H_2O$[b]	80(2)	−38(6)	$3.0(2) \times 10^{-4}$ s^{-1}[c]	This work
$Pd(NH_3)_4^{2+}/NH_3$[b]	67(3)	−54(12)	$1.6(2) \times 10^{-2}$ l mol^{-1} s^{-1}	This work
$Au(NH_3)_4^{3+}/NH_4^+$	84(2)	−42(5)	$6.0(3) \times 10^{-5}$ l mol^{-1} s^{-1}	7
$Au(NH_3)_4^{3+}/NH_3$	61(2)	−55(6)	$1.69(6) \times 10^{-1}$ l mol^{-1} s^{-1}	7
$Au(NH_3)_3NH_2^{2+}/NH_3$	68(2)	−44(8)	$3.9(2) \times 10^{-2}$ l mol^{-1} s^{-1}	7

[a]Reactants in rate-determining step for ammine exchange. [b]Calculated from rate constants of Table 1. [c]Determined spectrophotometrically for hydrolysis of $Pd(NH_3)_4^{2+}$ in 1.0 M $HClO_4$ at 25.0 °C to have the value 2.8×10^{-4} s^{-1},[11] when corrected statistically for the four equivalent leaving groups.

similar for the two metal centres, as judged from the entropies of activation, and the difference in rate is mainly an enthalpy effect. The smaller enthalpy of activation for the gold(III) complex shows that the fifth ammonia ligand binds more easily to $Au(NH_3)_4^{3+}$ than to $Pd(NH_3)_4^{2+}$, forming the transition state leading to exchange. This is in contrast to the cyanide-ligand exchange in $Au(CN)_4^-$ and $Pd(CN)_4^{2-}$, for which the enthalpy of activation is larger for the gold(III) complex than for the palladium(II) complex.[17] Notably, at ambient temperature, the $Au(CN)_4^-/CN^-$ exchange is faster than the $Pd(CN)_4^{2-}/CN^-$ exchange as a result of a less negative, and more favourable, entropy of activation. Charge repulsion seems to be important in controlling the cyanide exchange rate, whereas the bond formation determines the differences in ammine-ligand exchange rate for these square-planar complexes.

The indirect exchange involves rate-determining formation of the reactive $Pd(NH_3)_3H_2O^{2+}$ complex (Scheme 1). Accordingly, the rate of indirect exchange should be identical with the rate of hydrolysis for $Pd(NH_3)_4^{2+}$, which has been found to have a first-order rate constant of $k_{Pd,H_2O} = 1.1 \times 10^{-3}$ s^{-1} at 25 °C in 1 M $HClO_4$.[11] This rate constant was determined spectrophotometrically,[11] and should be divided by a statistical factor of 4 to be comparable with the rate of indirect exchange (see footnote to Table 2). The noted agreement adds strong support to the interpretation (Scheme 1) of the dependence on pH for the rate of ammine exchange (Fig. 2). The pK_a of $Pd(NH_3)_3H_2O^{2+}$ is not known, but for the pH region in the 1.0 M NH_4ClO_4 medium with a significant contribution to the total exchange rate from the indirect exchange, hydroxo-complex formation is not expected to influence the kinetics, as judged from the equilibrium studies of Rasmussen and Jørgensen.[8]

The complex formation between ammonia and palladium(II) is extensive, even in acidic ammonium-salt solution, and the determination by Rasmussen and Jørgensen[8] of the four consecutive stability constants by pH measurements according to Bjerrum's original method,[18] represents the limit of that method for ammine complex formation in aqueous solution. According to the reported stability constants $(Pd(NH_3)_4^{2+}: \beta_4 = 10^{32.8}$ l^4 mol^{-4}, $K_4 = 10^{6.8}$ l mol^{-1}, at 25 °C and unit ionic strength[8]), more than 99.95 % of the total palladium(II), c_{Pd}, is present as $Pd(NH_3)_4^{2+}$ in 1.0 M NH_4ClO_4, even at pH 6. The tetraamminepalladium(II) ion is thus thermodynamically stable under all the experimental conditions used, and no spectral changes could be detected during the exchange experiments. Moreover, the thermodynamic characterization of the tetraamminepalladium(II) ion, which also includes a direct determination of the equilibrium constant for the exchange of one ammonia with a chloride in $Pd(NH_3)_4^{2+}$ $(K_4' = 10^{-4.2}$, at 25.0 °C and unit strength[9]), allows a comparison between the kinetics and the thermodynamics of ligand exchange in the tetraamminepalladium(II) ion. The free energy of activation for the substitution of NH_3 by NH_3, Cl^- and H_2O, calculated from the rate constants,[10,11] in combination with the reaction free energy, calculated
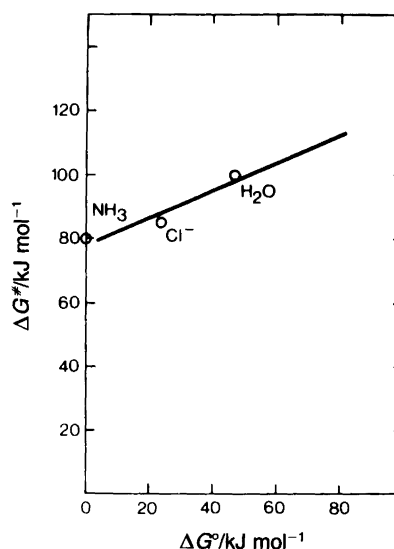

Fig. 5. Relationship between free energy of reaction and free energy of activation for substitution of ammonia in tetraamminepalladium(II) in aqueous solution at 25.0 °C. For details of calculation, see Ref. 16.

from the equilibrium constants,[9,8] establishes a slope of 0.43 ± 0.12 in the linear free energy relationship of Fig. 5. Admittedly, the available rate and equilibrium data are very limited. However, the slope is beyond doubt smaller than the slope of the similar free energy relationship for the tetraamminegold(III) ion, for which a value of 0.96 ± 0.16 has been found.[19] The role of the incoming ligand is thus less important in determining the rate of ligand substitution in $Pd(NH_3)_4^{2+}$ as compared to $Au(NH_3)_4^{2+}$. Moreover, a slope close to 0.5 is indicative of a transition state in which bond formation and bond breaking are equally important. The moderately negative entropies of activation for ligand exchange in $Pd(NH_3)_4^{2+}$ (Table 2, and $\Delta S^{\ddagger} = -30$ J mol^{-1} K^{-1} for chloride anation[10]) are also in agreement with a transition state in which both bond formation and bond breaking are of importance.

In conclusion, the ammine-ligand exchange in tetraamminepalladium(II) is an order of magnitude slower than the exchange in the isoelectronic tetraamminegold(III) as a result of a larger enthalpy of activation. The exchange rate, together with the rate of hydrolysis and chloride anation, shows that the nature of the incoming ligand is less important to substitution in tetraamminepalladium(II) than in tetraamminegold(III), and a comparison of linear free energy relationships for the two metal centres shows that bond-breaking in the transition state plays a larger role in tetraamminepalladium(II).

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