The Reaction of Hydroxo-species of Palladium(II) with Bidentate Nucleophiles *

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The species present in solutions of $[Pd(bipy)(H_2O)_2]^{2+}$ (bipy = 2,2′-bipyridine) and $[Pd(en)(H_2O)_2]^{2+}$ in the $[OH^-]$ range 0.01—0.1 mol dm^{-3} react with the nucleophiles (L–L) ethylenediamine (en), *NNN′N′*-tetramethylethylenediamine, or glycylglycinate to give respectively $[Pd(L\text{–}L)_2]^{n+}$ (n = 0 or 2) and $[Pd(en)(L\text{–}L)]^{n+}$ (n = 1 or 2). The $k_{obs.}$ values for the entry of the first L–L, which occurs in one observable step, depend both on [L–L] and $[OH^-]$ and the observed rate law, under pseudo-first-order conditions, is $k_{obs.} = \{a + b/[OH^-]\}$ [L–L]. The kinetic data have been interpreted assuming that both a monohydroxo- and a dihydroxo-complex, in fast equilibrium, are the reacting species. The reactivity of the dihydroxo-complex could be evaluated only in the case of the bipy species.

The kinetic reactivity of hydroxide co-ordinated to platinum(II) or palladium(II) with respect to nucleophilic substitution has been little studied. Hydroxo-species of platinum(II) and palladium(II) which are present in aqueous solutions of aqua complexes as a result of their acidity predominate at high pH. Hydroxide may either be co-ordinated to the metal as a terminal group or bridge metal atoms in dimeric or oligomeric species.[1–5] Very little is known about the rate of hydroxide substitution in these compounds. Terminal hydroxide is, however, expected to be rather inert and hydroxo-complexes seem to be almost unreactive even with strong nucleophiles.[6] On the basis of such indications our experimental observation of a relatively fast reaction between $[Pd(bipy)(H_2O)_2]^{2+}$ (bipy = 2,2′-bipyridine) and ethylenediamine (en) in strong alkaline medium, where both water molecules should be deprotonated, was unexpected. This prompted us to perform a kinetic investigation of the reaction between $[Pd(L\text{–}L)(H_2O)_2]^{2+}$ (L–L = bipy or en) and ethylenediamine, *NNN′N′*-tetramethylethylenediamine (tmen), or glycylglycinate (glyglyO) in the presence of OH^- (0.01—0.1 mol dm^{-3}) at I = 0.1 mol dm^{-3}.

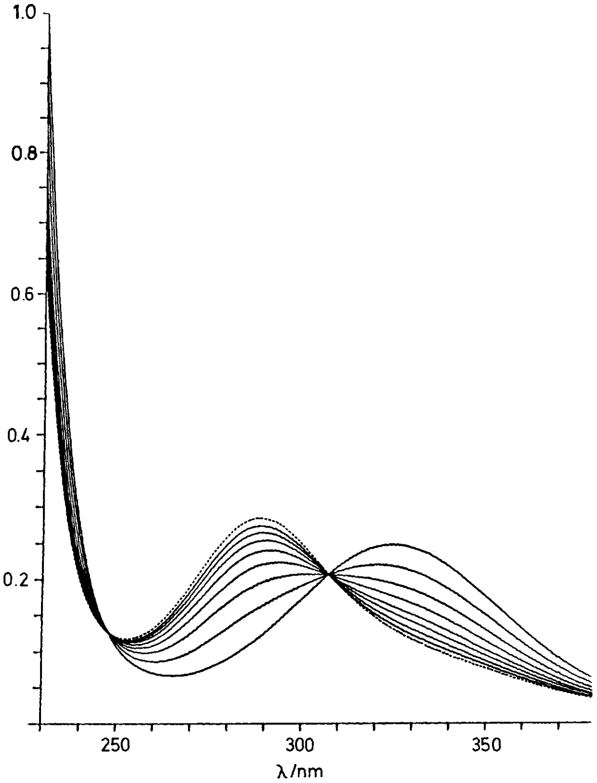

Figure 1. Spectral variation with time for the reaction of [Pd(en)] with en. [Complex] = 6×10^{-4} and $[OH^-]$ = 0.01 mol dm^{-3}; T = 25 °C

Experimental

Ethylenediamine and *NNN′N′*-tetramethylethylenediamine were distilled over KOH pellets. Sodium glycylglycinate was obtained by mixing glycylglycine with the appropriate amount of NaOH in water; the solid residue, obtained by removing the solvent under reduced pressure, was stored over P_4O_{10}. Water was doubly distilled.

The complexes $[Pd(bipy)Cl_2]$ and $[Pd(en)Cl_2]$ were prepared according to the methods reported in the literature.[7,8] $[Pd(bipy)(H_2O)_2]^{2+}$ and $[Pd(en)(H_2O)_2]^{2+}$ were prepared by treating the respective dichloro-derivatives with $AgClO_4$ in a 1:2 ratio. After removing the AgCl precipitate, appropriate amounts of NaOH and $NaClO_4$ were added in order to reach the desired hydroxide concentration and a final ionic strength of 0.1 mol dm^{-3}. The total palladium concentration used for the kinetic runs usually ranged from 8×10^{-5} to 4×10^{-4} mol dm^{-3}. The nucleophilic solutions had the same hydroxide concentration and ionic strength as the complexes. The pH measurements were performed with a PHM 62 Radiometer pH meter.

The kinetics were followed spectrophotometrically using a Perkin-Elmer Lamba 5 spectrophotometer. In all cases a large excess of reagent was used to provide pseudo-first-order conditions and to force the reaction to completion. Pseudo-first-order rate constants $k_{obs.}$ (s^{-1}) were obtained either from the gradients of the plots $\log(A_t - A_\infty)$ *vs.* time or from non-linear least-squares fit of the experimental data to $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obs.}t)$, where A_0, A_∞, and $k_{obs.}$ were the parameters to be optimized (A_0 = absorbance after mixing of the reagents,

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* *Supplementary data available* (No. SUP 56731, 7 pp.): values of observed rate constants. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

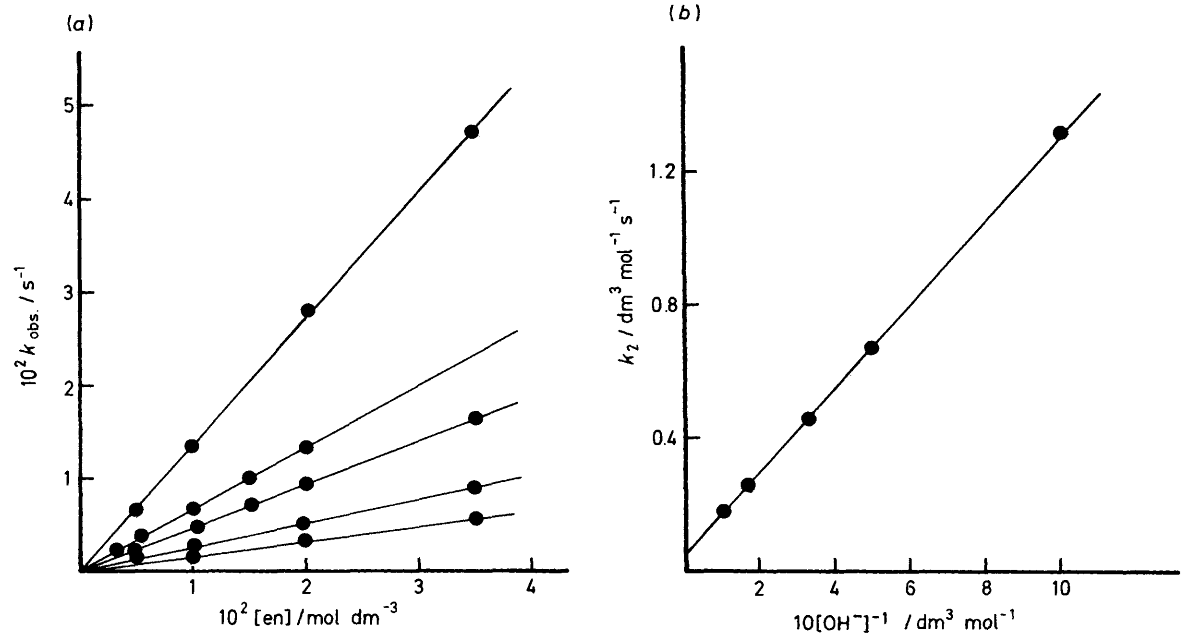


Figure 2. Plots of (*a*) $k_{obs.}$ *vs.* [en] and (*b*) k_2 *vs.* $1/[OH^-]$ for the reaction of [Pd(bipy)] with en; $I = 0.1$ mol dm^{-3}, $T = 25$ °C

A_∞ = absorbance at completion of reaction). The $k_{obs.}$ values were reproducible to better than ±5%.

Results and Discussion

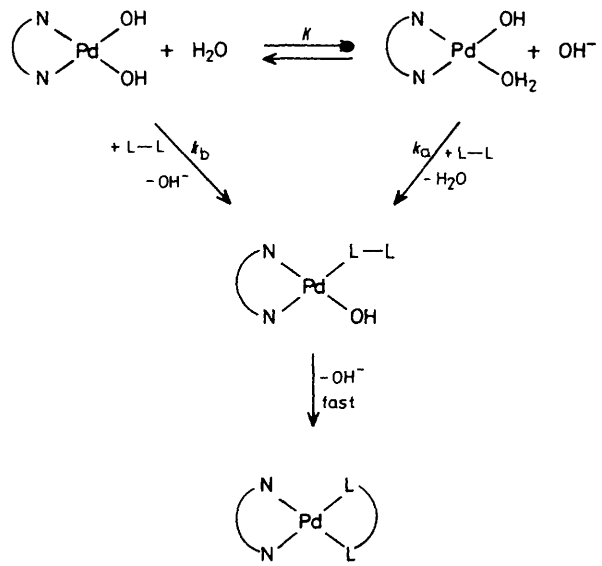
When the nucleophile L–L was added to a solution of [Pd(en)] {[Pd(en)] and [Pd(bipy)] represent all species, deprotonated and not} at basic pH a single-step reaction occurred as shown by the spectrophotometric analysis of the reaction mixture with time in the u.v.–visible region (Figure 1). The reaction product, isolated in the case of en and glyglyO, was respectively $[Pd(en)_2]^{2+}$ and $[Pd(en)(glyglyO)]^+$. Glycylglycinate is potentially a multidentate ligand; it has been suggested,[9–11] by analogy with some complexes of Cu^{II} and Ni^{II}, which have a known structure, that in $[Pd(en)(glyglyO)]^+$ this ligand is bidentate, co-ordinating to palladium(II) through the terminal amino nitrogen and the oxygen atom of the carboxylate group. In the case of the species [Pd(bipy)], reaction with all the nucleophiles L–L proceeded in two observable steps. Again isolation of the final reaction product yielded $[Pd(L\text{–}L)_2]^{2+}$. In addition, during the second step, the typical spectrum of free bipy appeared in the range 220—290 nm (neither en nor $[Pd(L\text{–}L)_2]^{2+}$ have a significant absorption in this range). This suggests that this step refers to the process shown in equation (1). Kinetic analysis confirmed this assumption. The rate law for

$$[Pd(bipy)(en)]^{2+} + en \longrightarrow [Pd(en)_2]^{2+} + bipy \qquad (1)$$

this reaction, under pseudo-first-order conditions with respect to the complex, is the usual two-term rate law shown by equation (2). The value of k_2 (0.115 ± 0.004 $dm^3 mol^{-1} s^{-1}$),

$$k_{obs.} = k_1 + k_2[en] \qquad (2)$$

obtained for the second step of the reaction of [Pd(bipy)] with en, is comparable to that determined for the reaction of $[Pd(bipy)(en)]^{2+}$ with en under the same experimental conditions (0.106 ± 0.005 $dm^3 mol^{-1} s^{-1}$).



Scheme.

The kinetics referring to the reaction of [Pd(en)] with L–L and to the first step of reaction between [Pd(bipy)] and the same nucleophiles were studied spectrophotometrically under pseudo-first-order conditions in the presence of large amounts of OH^- (0.01 mol dm^{-3}—0.1 mol dm^{-3}) at $I = 0.1$ mol dm^{-3}. The kinetics follow a first-order course and at fixed $[OH^-]$ the $k_{obs.}$ values are linearly correlated [equation (3)] to the

$$k_{obs.} = k_2[L\text{–}L] \qquad (3)$$

nucleophile concentration (Figure 2). In addition, the $k_{obs.}$ values are dependent on $[OH^-]$, decreasing at fixed [L–L] on increasing hydroxide concentration. Plots of $k_{obs.}/[L\text{–}L]$, or k_2,

Table. Values of *a* and *b* for the reaction of [Pd(en)] or [Pd(bipy)] with ethylenediamine (en), *NNN'N'*-tetramethylethylenediamine (tmen), or glycylglycinate (glyglyO) at 25 °C and $I = 0.1$ mol dm^{-3}

	[Pd(en)]	[Pd(bipy)]	
L–L	*b*	*a*	*b*
en	$1.42 \pm 0.01 \times 10^{-2}$	$4.3 \pm 0.3 \times 10^{-2}$	$1.26 \pm 0.1 \times 10^{-2}$
tmen	$1.70 \pm 0.05 \times 10^{-4}$		
glyglyO	$1.39 \pm 0.01 \times 10^{-2}$	$2.59 \pm 0.4 \times 10^{-2}$	$8.35 \pm 0.1 \times 10^{-3}$

against 1/[OH$^-$] are linear with, in the case of [Pd(bipy)], a small but significant intercept (Figure 2). These results indicate an overall rate law of the form (4). This law can be accounted for

$$k_{\text{obs.}} = \{a + b/[\text{OH}^-]\}[\text{L–L}] \qquad (4)$$

in terms of a mechanism in which two species in fast protonic equilibrium both lead to the product by reaction with L–L.

The species present in solution of the aqua complexes $[\text{Pd(bipy)(H}_2\text{O)}_2]^{2+}$ and $[\text{Pd(en)(H}_2\text{O)}_2]^{2+}$ as a function of pH, and the relating equilibria, have been studied by Lim and Martin[1] and more recently by Anderegg and Wanner.[2] For both complexes the titration curves with bases could not be interpreted by these authors in terms of a simple deprotonation and a polymerization had to be considered. In particular, while in the case of [Pd(en)] a simple dimerization [equation (5)]

$$2[\text{Pd(en)(H}_2\text{O)}_2]^{2+} \rightleftharpoons [\text{Pd}_2\text{(en)}_2\text{(OH)}_2] + 2\text{H}_3\text{O}^+ \qquad (5)$$

accounted for the titration data, for [Pd(bipy)] the presence of several polymeric products had to be assumed.

An equilibrium between a monomeric aqua complex and an oligomeric hydroxo-bridged complex as in equation (5) does not account for our experimental data. We do not observe, in fact, any dependence of $k_{\text{obs.}}$ on [complex] in a large range of complex concentration (5×10^{-5}—5×10^{-3} mol dm^{-3}). Furthermore, the strict analogy of the kinetic behaviour of the two systems contrasts with the diversity of species present in the case of [Pd(en)] and [Pd(bipy)]. Finally at the high experimental values of pH depolymerization [equation (6)] is expected to occur.

$$[\text{Pd}_2\text{(en)}_2\text{(OH)}_2]^{2+} + 2\text{OH}^- \rightleftharpoons 2[\text{Pd(en)(OH)}_2] \qquad (6)$$

We propose alternatively that the product forms by reaction of L–L with a dihydroxo- and a monohydroxo-species in equilibrium (Scheme; charges are omitted for clarity). Although at the high $[\text{Pd}]_{\text{total}}$ used for the titrations the presence of the latter species has not been considered,[1] under the experimental conditions used in the present investigation it may well be in equilibrium with $[\text{Pd(L–L)(H}_2\text{O)(OH)}]^+$. The rate law for such a reaction, under pseudo-first-order conditions, is in fact given by equation (7) which, for [OH$^-$] ≫ *K* reduces to the observed

$$k_{\text{obs.}} = \{(k_\text{a}K + k_\text{b}[\text{OH}^-])/(K + [\text{OH}^-])\}[\text{L–L}] \qquad (7)$$

rate law. According to such a hypothesis plots of $k_{\text{obs.}}$/[L–L], or k_2, *vs.* 1/[OH$^-$] yield the values of k_b and $k_\text{a}K$ respectively as intercept and slope.

The values of $a\ (= k_\text{b})$ and $b\ (= k_\text{a}K)$ are reported in the Table. The salient feature of the data is the similarity of the values of *b* for the two systems. This is, at first sight, surprising, as usually [Pd(bipy)] and [Pd(en)] complexes exhibit a large difference in reactivity. In [Pd(bipy)], in fact, the presence of the aromatic ring, by way of extensive π interaction, increases the electrophilicity of palladium, relative to [Pd(en)], easing the entry of the nucleophile. Thus, for instance, replacement of the first chloride co-ordinated to palladium(II) in $[\text{Pd(bipy)Cl}_2]$ by en, in dimethylformamide at 25 °C, is about 20 times faster[12] than the analogous reaction in $[\text{Pd(en)Cl}_2]$ (266 ± 13 *versus* 14 ± 0 dm^3 mol^{-1} s^{-1} respectively). Nonetheless it must be borne in mind that *b* has a composite nature; while the values of k_a, which refer to the reactivity of the monoaqua-species, should increase on going from $[\text{Pd(en)(H}_2\text{O)(OH)}]^+$ to $[\text{Pd(bipy)(H}_2\text{O)(OH)}]^+$, the values of the equilibrium *K*, relative to the protonation of the substrates $[\text{Pd(L–L)(OH)}_2]$, should vary in the opposite direction compensating the increase of k_a. The values of *K* are not available, but nonetheless an indication of the relative magnitude of the two constants for [Pd(en)] and [Pd(bipy)] can come from acidity measurements of the respective diaqua complexes. Significantly the pH of solutions of $[\text{Pd(bipy)(H}_2\text{O)}_2]^{2+}$ and $[\text{Pd(en)(H}_2\text{O)}_2]^{2+}$ (6×10^{-3} mol dm^{-3}) at $I = 0.1$ mol dm^{-3} are respectively 2.8 and 4.1.

The values of $a\ (= k_\text{b})$ represent the reactivity of the hydroxo-complexes $[\text{Pd(L–L)(OH)}_2]$. The contribution of such species to the overall reactivity of the systems under study is very small and can be appreciated only in the case of [Pd(bipy)]. The values of *a*, $4.3 \pm 0.3 \times 10^{-2}$ and $2.58 \pm 0.4 \times 10^{-2}$ dm^3 mol^{-1} s^{-1} respectively for the nucleophiles en and glyglyO, show that this complex is much more inert than other bipy palladium(II) complexes but not unreactive. It is interesting, in this respect, that the reaction of [Pd(bipy)] with en proceeds also in the presence of a very large hydroxide concentration, when the substrate should be present entirely in the dihydroxo form. Increasing [OH$^-$] beyond 0.1 mol dm^{-3}, at constant [L–L], does not cause any major change in $k_{\text{obs.}}$. On increasing [OH$^-$] by 40 times (0.1 to 4 mol dm^{-3}) the $k_{\text{obs.}}$ value referring to the reaction of [Pd(bipy)] with en decreases only by 23% (1.75×10^{-3} to 1.34×10^{-3} s^{-1}).

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