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On the Stability of Palladium(II) Aquo Complexes with 2,2′-Bipyridyl and 1,10-Phenanthroline

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The method generally used to prepare aquo complexes* such as $[Pd(en)(OH_2)_2]^{2+}$ and $[Pd(dien)(OH_2)]^{2+}$ involves halide abstraction from the corresponding halo complexes with a silver(I) salt [1–4]. The reactions of these aquo species, often prepared *in situ*, with various inorganic ligands [2, 3, 5] and nucleosides and nucleotides [6–8] have been studied.

Recently, Anderegg and Wanner [9] described the alkalimetric titrations of palladium(II) complexes of 2,2′-bipyridyl and 1,10-phenanthroline. The nitrato complexes $[Pd(L)(ONO_2)_2]$ (L = bpy, phen) were synthesised from $Pd(NO_3)_2 \cdot 2H_2O$ in concentrated nitric acid and these were used to prepare solutions of $[Pd(L)(OH_2)_2]^{2+}$ in water. The following reaction was assumed

$$[Pd(L)(ONO_2)_2] \xrightarrow{H_2O} [Pd(L)(OH_2)_2]^{2+} + 2NO_3^- \qquad (1)$$

since nitrato ligands are known [10] to be rapidly substituted.

The alkalimetric titrations in turn presuppose the following equilibria

$$[Pd(L)(OH_2)_2]^{2+} \rightleftharpoons [Pd(L)(OH_2)(OH)]^+ + H^+ \qquad (2)$$

$$[Pd(L)(OH_2)(OH)]^+ \rightleftharpoons [Pd(L)(OH)_2] + H^+ \qquad (3)$$

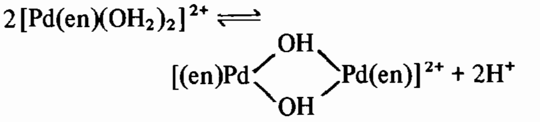
The salient points in their results are

(i) Solutions of $[Pd(L)(ONO_2)_2]$ show quite low pH values (≈2–3) which depend on the concentration of the complex (the range examined was 0.5–5.0 mM), thus indicating hydrolysis (eqn. (2)). The authors suggested 20% hydrolysis for the bpy complex and 30% for the phen complex.

(ii) Their titration curves show a well-defined end point after addition of one mole of hydroxide and a further end point at two moles of hydroxide. The first end point for L = bpy is symmetric while that for L = phen shows a deviation at 1.1 moles of added hydroxide.

(iii) When the titration curves are plotted *versus* the true degree of neutralisation for four different concentrations of the complex, these curves do not overlap. This suggests that the ionisation shown in eqn. (2) is not applicable and that a polymerisation has to be considered. Calculations using the model of Sillén give the degree of polymerisation as being between 3 and 5 for the bpy system and between 6 and 10 for the phen system.

Lim and Martin [1] found that a solution of the platinum complex $[Pt(en)(OH_2)_2]^{2+}$ reversibly titrates two moles of base to reach an end point by pH 9.5. Analysis of the titration curve yields for the two acidity constants, $pK_1 = 5.8$ and $pK_2 = 7.6$. In contrast, one equivalent of protons is removed reversibly from $[Pd(en)(OH_2)_2]^{2+}$ upon addition of base to reach an end point by pH 7, but the titration curve is flattened on the pH axis and cannot be fitted with the equilibrium expression for a simple deprotonation. The result may be accounted for by an ionisation and dimerisation to give a hydroxy-bridged dimer



$$2[Pd(en)(OH_2)_2]^{2+} \rightleftharpoons [(en)Pd\begin{smallmatrix}OH\\OH\end{smallmatrix}Pd(en)]^{2+} + 2H^+ \qquad (4)$$

Thus, Lim and Martin conclude that neither the mononuclear aquo-hydroxy or the dihydroxy complexes of Pd(en) occur in significant amounts at 10 mM concentration and that the titration reaction is represented by eqn. (4) which occurs rapidly for Pd(II). Nakayama *et al.* [11] in a qualitative study of the S-pn system obtained similar results.

We have isolated [12] the products obtained on dissolution of $[Pd(L)(ONO_2)_2]$ in water. Thus, $[Pd(L)(ONO_2)_2]$ dissolves in water at 30 °C to give a pale yellow solution which on cooling to 25 °C yields a pale yellow precipitate of the dimer $[(L)Pd(\mu\text{-}OH)_2Pd(L)](NO_3)_2$ (L = bpy, **1**; L = phen, **2**) in 80% yield. The pH of the solution is 1.0–1.5 since the other product is nitric acid

$$[Pd(L)(ONO_2)_2] \xrightarrow{H_2O} \tfrac{1}{2}[(L)Pd(\mu\text{-}OH)_2Pd(L)]^{2+} + H^+ + 2NO_3^- \qquad (5)$$

Addition of $NaClO_4$ to a solution of $[Pd(L)(ONO_2)_2]$ at 30 °C results in an immediate precipitate of $[(L)Pd(\mu\text{-}OH)_2Pd(L)](ClO_4)_2$.

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*The following abbreviations are used in this paper: en = 1,2-diaminoethane, dien = diethylenetriamine, S-pn = S-propylenediamine, bpy = 2,2′-bipyridyl, phen = 1,10-phenanthroline.

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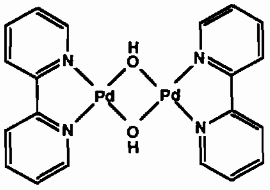

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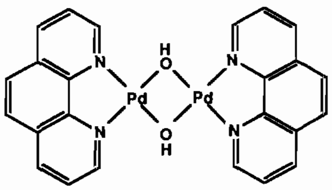

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Result (i) of Anderegg and Wanner [9] follows as a consequence, *viz.* solutions of [Pd(L)(ONO_2)$_2$] are acidic with a pH dependent on the concentration of the complex. Apparently, Anderegg and Wanner carried out their titrations in a medium of either 0.1 M KNO_3 or 0.1 M KSO_3CH_3. Under these conditions the dimers **1** and **2** will precipitate, although no mention was made of this. Secondly, titration with NaOH will give a sharp end point after the addition of one mole of base corresponding to the neutralisation of the nitric acid. There are no UV spectral changes during this process.

Kinetic studies with amine complexes of platinum(II) indicate that the dimerisation shown in eqn. (4) requires the prior formation of the aquo-hydroxy complex (eqn. (2)), which is the intermediate for dimerisation [13, 14]. In acidic solutions the complexes $[Pd(en)(OH_2)_2]^{2+}$ and $[Pd(S\text{-}pn)(OH_2)_2]^{2+}$ are stable [13, 15], since both aquo ligands are protonated. The rate and extent of dimer formation increases as the pH of the solution approaches neutrality [13]. This corresponds to increasing formation of the aquo-hydroxy species.

If a similar mechanism of dimerisation operates for complexes with N-heterocyclic ligands, then the aquo ligands in $[Pd(L)(OH_2)_2]^{2+}$ (L = bpy, phen) are considerably more acidic than those of $[Pd(en)(OH_2)_2]^{2+}$ so that in acidic solution the first acid dissociation is already complete and this in turn leads to complete formation of the dimer. This is consistent with the relative donor properties of the ligands (e.g. pK_a bpy $<$ phen $\ll$ en).

The dimer $[(L)Pd(\mu\text{-}OH)_2Pd(L)]^{2+}$ itself adds one mole of hydroxide to give a deep yellow intermediate $[Pd_2(L)_2(OH)_3]^+$ which rapidly decays in alkaline solution to colourless $[Pd(L)(OH)_2]$

$$[(L)Pd(\mu\text{-}OH)_2Pd(L)]^{2+} + OH^- \rightleftharpoons [Pd_2(L)_2(OH)_3]^+ \qquad (6)$$

$$[Pd_2(L)_2(OH)_3]^+ + OH^- \rightleftharpoons 2[Pd(L)(OH)_2] \qquad (7)$$

The overall stoichiometry of the reaction is one mole of hydroxide for each mole of palladium. $[Pd_2(bpy)_2(OH)_3]^+$ is more reactive than $[Pd_2(phen)_2(OH)_3]^+$ so that at ambient temperature the former complex is rapidly cleaved according to eqn. (7) while the latter complex persists for some time. This difference probably accounts for the deviation in the titration curve for the phen system (*i.e.* result (ii) of Anderegg and Wanner [9].)

Rasmussen and Jørgensen [16] reported that treatment of 5 mM $[Pd(H_2O)_4]^{2+}$ in 1 M $HClO_4$ with 5 mM phenH^+ yields exclusively $[Pd(phen)(OH_2)_2]^{2+}$ which can be precipitated as a pale yellow material (no analyses given). Our experience and that of others [17] indicates that diaquo complexes of palladium(II) and platinum(II) are very soluble in water. They cannot be salted out of solution by addition of acids such as $HClO_4$ and the only means of isolation is evaporation to dryness. We suggest that the solid obtained by Rasmussen and Jørgensen is $[Pd(phen)(\mu\text{-}OH)]_2(ClO_4)_2$ which is pale yellow and sparingly soluble even in hot water. We confirm their report that heating $[Pd(phen)Cl_2]$ with sodium hydroxide gives a yellow compound, which in our hands analyses for $[Pd(phen)(OH)_2]\cdot 2H_2O$.

In conclusion, the diaquo complex, $[Pd(L)(OH_2)_2]^{2+}$ (L = bpy, phen), does not exist in aqueous solution under normal pH conditions. For physicochemical studies it is necessary to know the identity of the species in solution. The assumption that a complex dissolves in a solvent unchanged can, for labile systems, sometimes lead to errors.

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