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# Acid Dissociation and Dimerisation Constants of Some *cis*-Diaqua Complexes of Palladium(II) with Chelating N, N′ and N, C′ Ligands[1]

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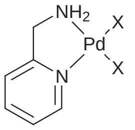
The acidity and dimerisation constants are determined for $[Pd(L)(H_2O)_2]^{2+}$ [L=2-(aminomethyl)pyridine and *N*′-methyl-2,4′-bipyridin-3-ylium

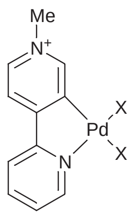
The coordination of a water molecule to a metal ion usually renders the aqua ligand more acidic than the bulk solvent molecule.[2] A complication in the determination of the acidity constants of polyaqua complexes for labile metal ions such as palladium(II)[3] is that condensation to hydroxo-bridged oligomers, generally dimers occurs during the titration.[2]

The nature of the ligand L in $[Pd(L)(H_2O)_2]^{2+}$ has a profound influence on its acid properties. Thus, at low pH when L is ethylenediamine, the diaqua complex is stable,[3,4] whereas for L = 2, 2′-bipyridine, the dimer $[Pd(bpy)(\mu\text{-}OH)]_2^{2+}$ is the stable species[5–7] *i.e.* under the conditions where $[Pd(bpy)(H_2O)_2]^{2+}$ has been assumed to exist.[8]

We report the acidity and dimerisation of $[Pd(AMP)(H_2O)_2]^{2+}$ [**1b**, AMP = 2-(aminomethyl)pyridine] and $[Pd(2,4'\text{-}bpyMe\text{-}H)(H_2O)_2]^{2+}$ [**2b**, 2,4′-bpyMe-H = N-methyl-2,4′-bipyridin-3-ylium].



**1a** X = $ONO_2$
**1b** X = $OH_2$



**2a** X = $ONO_2$
**2b** X = $OH_2$

The complexes $[Pd(L)(ONO_2)_2]$ (L = AMP, 2,4′-bpyMe-H; **1a** and **2a**) were prepared from the corresponding dichloro complexes[9,10] using silver nitrate in dilute nitric acid. The nitrato complexes were isolated by evaporating the resulting pale yellow solutions to dryness and were then recrystallised from dilute nitric acid. The IR spectra of **1a** and **2a** indicate coordinated nitrate;[11,12] there is no evidence for hydroxy-bridged dimer formation.

Aqueous solutions of the diaqua complexes were prepared by redissolving the dinitrato complexes. The solutions (ionic strength = 0.1 M $NaNO_3$) were titrated with NaOH (0.1 M) using a Radiometer ABU8O autoburette with a PHM82 pH meter and a REC80 chart recorder at 25 °C under an atmosphere of argon. The titration curves were fitted with the TOT programme.[13]

Titration of $[Pd(AMP)(H_2O)_2]^{2+}$ **1b** consumes two equivalents of hydroxide with two end points (Fig. 1). Fitting the titration curve using the equations shown in the Scheme gives the two acidity constants. These together with the dimerisation constants are summarised in the Table. The values are comparable to those reported for similar palladium(II) complexes. The distribution of the species as a function of pH is illustrated in Fig. 2.

The spectrophotometric titration of $[Pd(2,4'\text{-}bpyMe\text{-}H)(H_2O)_2]^{2+}$ **2b** in water with NaOH shows only one end point after one mole of NaOH has been added. The $pK_{A1}$ is calculated to be 7.13 ± 0.05. The isosbestic points at 350, 285, 260 and 240 nm suggest there are only two species in equilibrium. The titration curve of **2b** also shows only one titratable proton. The fitted dimerisation constants are given in the Table.

In summary, the ligands en, AMP and (bpyMe-H) give rise to weakly acidic *cis*-diaqua complexes; these remain in the diaqua form at low pH. Bpy yields a much more acidic diaqua complex (approx $pK_A < 2$) and in solution it exists solely as the hydroxo-bridged dimer.

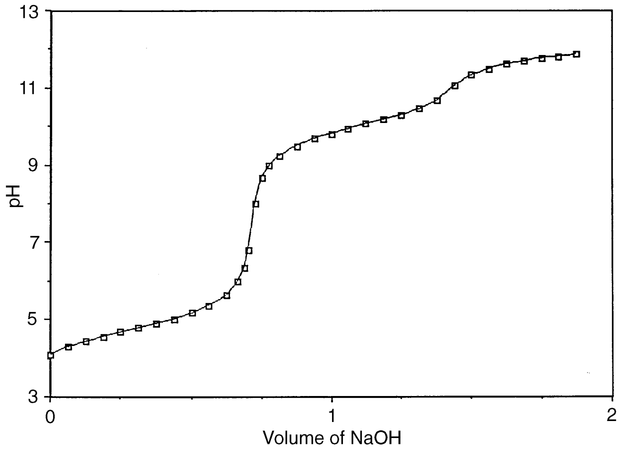


**Fig. 1** pH titration of $[Pd(AMP)(H_2O)_2]^{2+}$; [Pd(II)] = $6.34 \times 10^{-3}$ M, volume = 11 ml; [NaOH] = 0.100 M; ionic strength = 0.1 M.

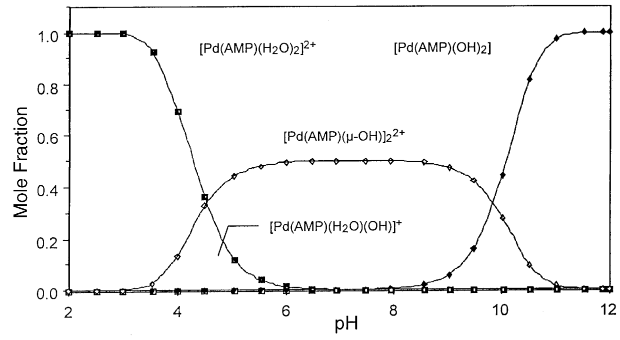


**Fig. 2** Mole fraction of the various species in the Pd–AMP system as a function of pH.

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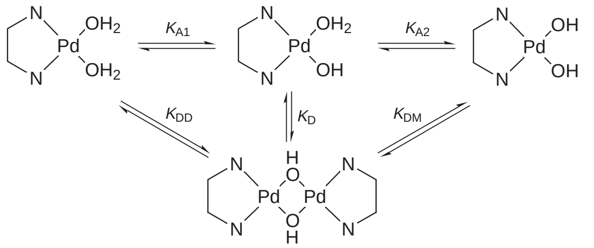
**Table 1** Dissociation and dimerisation constants for palladium(II) aqua complexes

| Complex | p$K_{A1}$ | log $K_D$[b] | log $K_{DD}$[c] | Ionic strength | Ref. |
|---|---|---|---|---|---|
| $[Pd(AMP)(H_2O)_2]^{2+,a}$ | 6.80 | 7.0 | −6.6 | 0.1 M $NaNO_3$ | This work |
| $[Pd(en)(H_2O)_2]^{2+}$ | 6.2 | 3.7 | −8.33 | 0.2 M $KNO_3$ | 3, [d] |
| $[Pd(dien)(H_2O)]^{2+}$ | 7.74 | 2.12 | −5.62 | 0.5 M $KNO_3$ | [d,e] |
|  | 7.38 | — | — | 0.1 M $NaClO_4$ | [f] |
|  | 6.13 | — | — | 0.1 M $NaClO_4$ | [g] |
| $[Pd(en)Cl(H_2O)]^+$ | 7.3 | — | — | 0.1 M $NaClO_4$ | 4 |
| $[Pd(2,4'\text{-bpyMe-H})(H_2O)_2]^{2+}$ | 7.1 | 5.4 | −8.7 | 0.1 M $NaNO_3$ | This work |

[a] p$K_{A2}$ = 7.60; all the other complexes only have one dissociation constant. [b] Dimerisation of the aqua/hydroxo complex. [c] Dimerisation with concomitant deprotonation of the diaqua complex. [d] R. B. Martin, in *Platinum, Gold and Other Metal Chemotherapeutic Reagents,* ACS Symp. Ser., ACS, Washington DC, 1983. [e] K. S. Scheller, V. Scheller-Kratinger and R. B. Martin, *J. Am. Chem. Soc.,* 1978, **103**, 6833. [f] E. L. J. Breet, R. van Eldick and H. Kelm, *Polyhedron,* 1983, **2**, 118. [g] R. M. Alcock, F. R. Hartley and D. E. Rogers, *J. Chem. Soc., Dalton Trans.,* 1973, 1070.

Even if rapid dimer formation takes place (Scheme), a labile metal such as palladium(II), will still display two end points on titration with hydroxide. Both the en and the bpyMe-H complexes once dimerised show no tendency to be cleaved with hydroxide. This may well be a kinetic effect and the reaction with hydroxide may be slow. Thus, although $[Pd(phen)(\mu\text{-}OH)]_2^{2+}$ reacts with hydroxide on mixing, methyl substituents on the aromatic ligand dramatically increase the half-life of the reaction to several hours.[14]



**Scheme** Equilibria in aqueous solution for *cis*-diaqua palladium(II) complexes. Charges have been omitted for clarity.

The acidity of a proton depends on the strength of the metal–oxygen bond which in turn is affected by the ligand in the *trans*-position. The strong σ-donor ability of the cyclometallated ring should decrease the acidity of the *trans*-water molecule, whereas Pd-ligand π-bonding would have the opposite effect.

In $[Pd(2,4'\text{-bpyMe-H})(H_2O)_2]^{2+}$ it would appear that the Pd–ligand π-bonding[1] and the ligand–Pd σ-bonding are more or less balanced so that the net effect is a ligand similar to en. On the other hand, bpy is less of a σ-donor than en and a better π-acceptor resulting in a distinctly acidic aqua complex.

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Fig. 3: Change of absorption of an aqueous solution of $[Pd(2,4'\text{-bpyMe-H})(H_2O)_2]^{2+}$ at 305 nm as a function of pH; [Pd(II)] = 1.57 × $10^{-3}$ M; [NaOH] = 0.0785 M; ionic strength = 0.1 M.

Fig. 4: Mole fraction of the various species in the Pd–2,4′-bpyMe-H system as a function of pH (L = 2,4′-bpyMe-H). Total [Pd(II)] = 6.8 × $10^{-3}$ M.

Techniques used: IR, NMR, spectrophotometric titration

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