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Pyridine Derivatives as Complexing Agents.
XIII. The Stability of the Palladium(II) Complexes with Pyridine, 2,2'-Bipyridyl, and 1,10-Phenanthroline

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Abstract

The stability constants of the palladium(II) complexes with pyridine, 2,2'-bipyridyl, and 1,10-phenanthroline have been determined with potentiometric and spectrophotometric measurements. In the case of pyridine, the spectra of solutions of the components with different pH values are used. Otherwise, hydroxyl ion or a tetraamine are exchanged with the diamines in order to investigate equilibria from which the desired stability constants are also obtained. With pyridine, the values of K_1, K_2, K_3, and K_4 are of the expected magnitude. For the diamines, in contrast, a very strong drop from log K_1 to log K_2 is observed; this is due to the steric hindrance between the H atoms in α position with respect to the coordinated N atoms in the 1:2 complexes. Some complex salts of the different ligands have been prepared.

Introduction

We report here our investigations of the equilibria between palladium(II) and three aromatic amines containing one (pyridine: py) or two (2,2'-bipyridyl: bip and 1,10-phenanthroline: phen) nitrogen atoms. The formation of a 5-membered chelate ring by the bidentate ligands on coordination is characterized by a large increase in the stability of the corresponding complexes with respect to those with pyridine. For the 3d divalent cations, similar data were obtained more than 20 years ago [1, 2], but no data are available for the corresponding 4d cations.

Our interest in these ligands arose from the fact that we had already studied the complex formation of palladium(II) with different tetraamines as well as with ethylenediamine and diethylenetetraamine [3, 4]. The investigation of the equilibria between the title amines and the 4d cation is more complex than those with the above ligands because, in the presence of the normally used unidentate auxiliary ligands X^- (Br^-, SCN^-), the complexes give precipitates; *i.e.*, exchange reactions of type (I) and (II) cannot be used to obtain the stability constant of $[PdL_2]^{2+}$

$$[PdX_4]^{2-} + L \rightleftharpoons [PdLX_2] + 2X^- \qquad (I)$$

$$[PdLX_2] + L \rightleftharpoons [PdL_2]^{2+} + 2X^- \qquad (II)$$

and $[PdLX_2]$. For this reason, new possibilities had to be examined. The search for these new ways makes these investigations particularly interesting.

The reactions (I) and (II) are formulated for the case where L is a bidentate ligand. In the case of pyridine (py), the following mixed complexes are present: $[Pd(py)X_3]^-$, $[Pd(py)_2X_2]$ and $[Pd(py)_3X]^+$. However, they are insufficiently soluble to allow the determination of the required stability constants. In 1 M strong acid of a non-complexing anion, pyridine partially forms the 1:1 and the 1:2 complex with palladium(II); thus, the spectrophotometric method can be used. However, the choice of the acid is difficult because ClO_4^- forms the insoluble complex salt ($[Pd(py)_4](ClO_4)_2$) and NO_3^- shows a high optical absorbance in the same wavelength range, as do the species $[Pd(py)_4]^{2+}$ and $[Pd(py)_3]^{2+}$. We have determined the constants K_1 and K_2 in perchlorate, K_3 and K_4 in chlorate, and all four in methanesulfonate medium ($K_i = [Pd(py)_i]/([Pd(py)_{i-1}][py])$).

For the other two ligands, the constant K_2 can be obtained from the investigation of the hydrolysis of the complexes $[PdL]^{2+}$ and $[PdL_2]^{2+}$ by base addition because both complexes form $[PdL(OH)_2]$, and, in the case of the 1:2 complex, a ligand molecule is set free. Furthermore, the overall constant β_2 of $[PdL_2]^{2+}$ with both bidentate ligands can be obtained by exchange with triethylenetetraamine $H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$ (trien [3]), as its 1:1 complex is more stable with respect to $[Pd(bip)_2]^{2+}$ and $[Pd(phen)_2]^{2+}$ in basic solutions. The constant K_1 is then obtained from K_2, and $\beta_2 = K_1K_2$. The dimensions of the constants have been omitted.

Experimental

The measurements have been undertaken using salts prepared as follows.

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Pyridinium Perchlorate: pyHClO$_4$

Perchloric acid (11 ml, ~0.1 mol, Merck, 60%) was added dropwise in ice-bath to 8 ml pyridine (~0.1 mol, Fluka, puriss.). To the white gelatinous product formed were added 30 ml EtOH, and the suspension was filtered by suction. The solid was recrystallized after dissolution in 100 ml 90% EtOH. The white crystals were dried at 80 torr over P_2O_5. 14.4 g pyHClO$_4$ (yield 80%) were obtained. The molecular weight was controlled with four alkalimetric titrations giving a purity of at least 99%.

2,2′-Bipyridylpalladium(II) Nitrate Hemihydrate: Pd(bip)(NO$_3$)$_2$·0.5H$_2$O

Palladium(II) nitrate dihydrate (0.533 g, 2.0 mmol, Fluka, purum) was dissolved in 5 ml 65% nitric acid at 100 °C by reflux. A solution of 0.290 g 2,2′-bipyridyl (1.86 mmol, Fluka, puriss.) in 20 ml 0.1 M nitric acid was added to the hot solution. By slow cooling, orange–yellow needle-shaped crystals were formed. They were filtered off by suction, recrystallized from 20 ml 0.1 M nitric acid and dried over $CaCl_2$ in a dessicator. Yield: 0.407 g (55%). *Anal.* Calc. for $C_{10}H_8N_4O_6Pd \cdot 0.5H_2O$ (395.6): Pd, 26.90; C, 30.36; H, 2.29; N, 14.16. Found: Pd, 27.00; C, 30.70; H, 2.26; N, 13.94%.

Bis(2,2′-bipyridyl)palladium(II) Nitrate Monohydrate: [Pd(bip)$_2$](NO$_3$)$_2$·H$_2$O

Palladium(II) nitrate dihydrate (0.8 g, 3 mmol, Fluka, purum) was dissolved in 5 ml 65% nitric acid at 100 °C by reflux, and a solution of 1.09 g 2,2′-bipyridyl (7 mmol, Fluka, puriss.) in 10 ml 2 M nitric acid was added. After a few hours, long orange–yellow needles separated and the complete crystallization was accomplished in a refrigerator. The crystals were filtered off by suction and recrystallized from 28 ml of a solution of the following composition: 0.1 M HNO_3, 1 M KNO_3, and 0.05 M 2,2′-bipyridyl. 1.47 g (87%) product were obtained. *Anal.* Calc. for $C_{20}H_{16}N_6O_6Pd \cdot H_2O$ (560.8): Pd, 18.97; C, 42.83; H, 3.24; N, 14.99. Found: Pd, 18.73; C, 42.46; H, 2.88; N 14.93%.

1,10-Phenanthrolinepalladium(II) Nitrate: Pd(phen)(NO$_3$)$_2$

Palladium(II) nitrate dihydrate (0.7 g, 2.63 mmol, Fluka, purum) was dissolved in 5 ml 65% nitric acid at 100 °C by reflux, and to the warm solution 10 ml nitric acid solution containing 0.50 g 1,10-phenanthroline (2.52 mmol, Fluka, puriss.) were added. The yellow precipitate which immediately formed was filtered off by suction. It was dissolved in 230 ml 0.1 M nitric acid at 100 °C and after several hours the solution was filtered to separate the undissolved particles. After cooling, 30 ml 1 M KNO_3 were added. Small gold–yellow spheres formed during a period of several days. They were filtered by suction and dried over $CaCl_2$ in dessicator. Yield 0.872 g (84%). *Anal.* Calc. for $C_{12}H_6N_4O_6Pd$ (402.6): C, 35.10; H, 1.96; N, 13.64. Found: C, 34.98; H, 1.92; N 13.24%.

Bis(1,10-phenanthroline)palladium(II) Nitrate: [Pd(phen)$_2$](NO$_3$)$_2$

Palladium nitrate dihydrate (0.5 g, 1.88 mmol, Fluka, purum) was dissolved in 5 ml 65% nitric acid by reflux at 100 °C and to this hot solution a warm solution of 10 ml 0.1 M nitric acid containing 1 g 1,10-phenanthroline monohydrate (5.04 mmol, Fluka, puriss.) was added. Immediately an orange–yellow precipitate formed. To ensure complete complex formation, 35 ml 2 M potassium hydroxide were added, bringing the pH to 1.5. After cooling, the precipitate was filtered off by suction. It was recrystallized by dissolution at 100 °C in 150 ml 0.01 M nitric acid and 0.09 M potassium nitrate. The gold–yellow crystals were dried at 80 torr over P_2O_5 to constant weight. Yield 0.95 g (86%). *Anal.* Calc. for $C_{24}H_{12}N_6O_6Pd$ (546.7): C, 48.79; H, 2.73; N, 14.22. Found: C, 48.63; H, 2.80; N, 14.18%.

Tetrapyridinepalladium(II) Perchlorate: [Pd(py)$_4$](ClO$_4$)$_2$

Palladium(II) nitrate dihydrate (0.533 g, 2 mmol, Fluka purum) was dissolved in 2 ml 65% nitric acid and 3 ml water at 100 °C by reflux. Pyridine (3 ml, 37 mmol, Fluka, puriss.) was added to the cooled solution. This corresponds to the complete neutralization of the nitric acid. The yellow precipitate immediately formed was filtered off and dissolved in 10 ml water. To the resulting solution, heated at 80 °C, 1 ml pyridine and 10 ml water containing 1 g $NaClO_4$ were added. Immediately a yellow precipitate was formed, which was filtered off and recrystallized from 90 ml water after addition of 1 ml pyridine. The pale yellow crystals were dried over P_2O_5 at 80 torr. Yield 0.980 g (79%). *Anal.* Calc. for $C_{20}Cl_2H_{20}N_4O_8Pd$ (621.7): C, 38.64; H, 3.24; N, 9.01; Cl, 11.41. Found: C, 38.69; H, 3.29; N, 8.99; Cl, 11.50%.

The methanesulfonic acid (Fluka, puriss.) was not of the required purity for the measurements of the equilibria between palladium(II) and pyridine. The spectrum of Pd^{2+} in 1 M methanesulfonic acid was different from that obtained in 1 M perchloric acid. The acid was purified by isolating its barium salt and recrystallizing three times. The acid was then obtained by treatment of the salt solution with sulfuric acid. The Ba^{2+} determination by alkalimetric titrations of a mixture of EDTA with the barium methanesulfonate, dried at 0.1 torr, showed the presence of 2 mol H_2O per mol $Ba(CH_3SO_3)_2$. KNO_3, $NaClO_4$, NaOH, and KOH (Merck, p.a.) were used. The preparation of the palladium(II) solutions is given elsewhere [3].

Measurements

The spectra were measured with a Beckman ACTA CIII UV–Vis spectrophotometer. For the pH measurements, an Orion Research Digital Ionanalizer, Model 801 A and a Digital Burette Mettler DV 11 were used. The pH values of the solutions are defined using the concentration scale of the hydrogen ion [H] :pH = –log [H], used in the standard state given by the inert electrolyte in pure water.

The attainment of the equilibria was controlled by a series of measurements taken after constant time intervals. Constant pH values were normally obtained after 1 to 5 min for solutions of $[Pdbip(py)_2]^{2+}$, $[Pd\,phen(py)_2]^{2+}$, $[Pd\,bip]^{2+}$, and $[Pd(bip)_2]^{2+}$; after one hour for $[Pd\,phen]^{2+}$ and $[Pd(phen)_2]^{2+}$; after two hours for the exchange between $[Pd(bip)_2]^{2+}$ and protonated trien; and after 1 day for the same exchange but with $[Pd(phen)_2]^{2+}$. Batch measurements were therefore necessary for the last two systems.

The p*K* values of the three amines were determined in different inert salt solutions (*cf.* Table I), because in the preliminary studies it was not always known which medium to use to avoid precipitation of salts with components of the investigated equilibria.

TABLE 1. p*K* Values of HL^+ for L = Pyridine, 2,2′-Bipyridyl, and 1,10-Phenanthroline at 25 °C

L	Medium	p*K* of $HL^{+\,a}$	$\log \frac{[HL_2]^a}{[HL][L]}$
py	$0.1(KNO_3)$	5.25(1)	
	$0.1(KCH_3SO_3)$	5.23(1)	
	$1(NaClO_3)$	5.49(3)	
	$1(NaClO_4)$	5.67(2)	
	$1(NaCH_3SO_3)$	5.44(2)	
bip	$0.1(KNO_3)$	4.40(2)	
	$0.1(KCH_3SO_3)$	4.38(1)	
phen	$0.1(NaClO_3)$	4.93(2)	1.83(5)
	$0.1(KCH_3SO_3)$	4.89(2)	1.76(5)

[a] In parentheses, three times the standard deviation in the last figure.

Results

Alkalimetric Titrations of Solutions of the 1:1 Complex $[PdL]^{2+}$

Figures 1 and 2 show the titration curves (pH *vs.* $([OH]_a + [H] - [OH])/[PdL]_t = g$, where $[OH]_a$ is the total concentration of the added strong base and $[PdL]_t$ the total concentration of the complex) obtained for different concentrations of the complex $[PdL]^{2+}$ for L = 2,2′-bipyridyl and 1,10-phenanthroline respectively. The complex $[PdL(H_2O)_2]^{2+}$

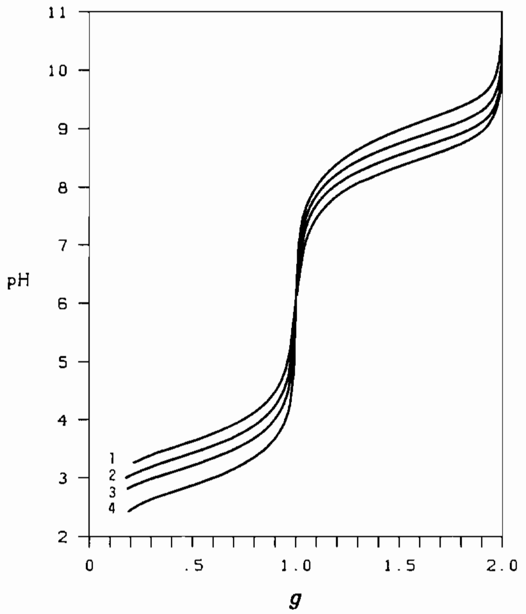

Fig. 1. Curves of the alkalimetric titrations of solutions containing different amounts of $[Pd(bip)]^{2+}$. For each titration pH *vs.* the true degree of neutralization is plotted. $g = ([OH]_a - [OH] + [H])/[PdL]_t$. $[OH]_a$ = concentration of the added strong base. 1. $[PdL]_t$ = 0.51 mM; 2. $[PdL]_t$ = 1.01 mM; 3. $[PdL]_t$ = 2.01 mM; 4. $[PdL]_t$ = 5.13 mM.

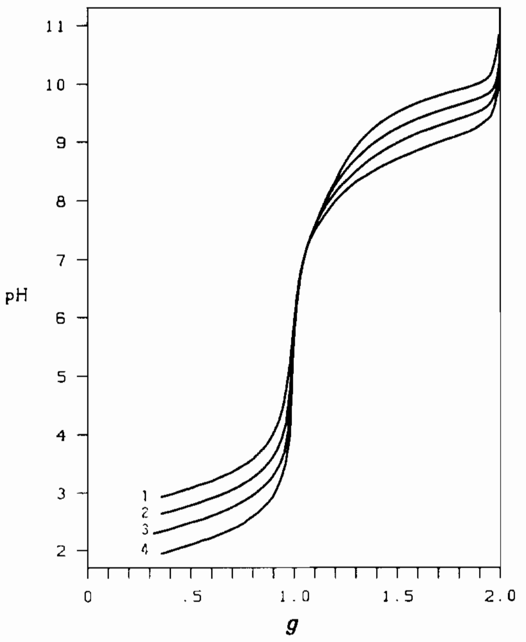

Fig. 2. Curves of the alkalimetric titrations of solutions containing different amounts of $[Pd(phen)]^{2+}$. For each titration pH *vs.* the true degree of neutralization is plotted. $g = ([OH]_a - [OH] + [H])/[PdL]_t$. $[OH]_a$ = concentration of the added strong base. 1. $[PdL]_t$ = 0.50 mM; 2. $[PdL]_t$ = 1.00 mM; 3. $[PdL]_t$ = 2.00 mM; 4. $[PdL]_t$ = 5.00 mM.

sets free two protons, one in acidic and the other in alkaline solution in two separate steps which, in the

$$[PdL(H_2O)_2]^{2+} \rightleftharpoons [PdL(H_2O)OH]^+ + H^+ \qquad \text{(III)}$$

$$[PdL(H_2O)OH]^+ \rightleftharpoons [PdL(OH)_2] + H^+ \qquad \text{(IV)}$$

simplest case, could be formulated as equilibria (III) and (IV). The solutions, before any base addition, show quite low pH values. Their values (see Figs. 1 and 2) show that 20% (bip) to 30% (phen) of the complex is already hydrolized according to reaction (III). For the simple deprotonation of eqn. (III), it was expected that for all curves of g, there would be pH overlap [5]. As this last condition was not fulfilled, a polymerization has to be considered. This also explains the observed pH dependence of the curves in Figs. 1 and 2 in acidic medium; *i.e.*, there is a decrease of the pH values with increasing concentration of the complex for a constant g value. In alkaline solution an opposite trend is observed; at each g value, the more concentrated solution corresponds to higher pH values, which may correspond to a depolymerization. Calculations and graphical representations show that the processes involved are not compatible with the simple 'core and links' hypothesis of Sillén [6]. Using that model, it is found that the degree of polymerization is between 3 and 5 for 2,2′-bipyridyl and between 6 and 10 for phenanthroline as ligand. The list of the species $[(PdL)_q(OH)_p]^{(2q-p)^+}$ included in our calculations is presented in Fig. 3, giving the pairs of values q, p. In each calculation, the following data are known: (i) the set of species and the pairs q, p; (ii) the corresponding estimated constants $\beta_{q,p}$; (iii) the total concentrations of the components and the experimental pH values. From all these quantities, considering all experimental points, the true degrees of neutralization $g_{i,calc}$ and the following sum $\Sigma(g_i - g_{i,calc})^2$ are calculated. The chosen $\beta_{q,p}$ are varied in order to minimize that sum. In Table II are given, for some sets of the species, the values of the obtained constants together with the standard deviation of g ($\sigma(g)$); these last values do not decrease by inclusion of more species. The values are of the expected magnitude, in consideration of the low ionic strength used; this also implies low concentrations of the involved components. Their values, in general, are larger for the complexes with phenanthroline because in this case the polymerization begins at lower pH values and the depolymerization begins at higher pH values with respect to the bipyridyl complex; under these conditions the errors of [H] and [OH] are larger. All possible combinations with three to six species of Fig. 3 have been computed. In the case of 2,2′-bipyridyl, the lowest $\sigma(g)$ is obtained for the set of the species with following q,p values: (2,2), (4,4), and (4,5). For 1,10-phenanthroline, because of the larger error, two pairs of species can be considered with nuclearity 5 and 6.

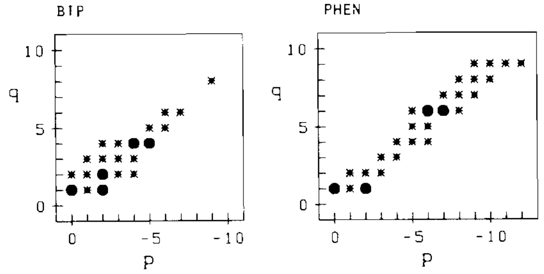

Fig. 3. Graphical representation of the p and q values for the species $[(PdL)_q(OH)_p]^{2q-p}$ considered in the polymerisation. Black circles are used for the species giving the lowest standard deviations of the true degree of neutralization g.

From such calculations it is also possible to calculate $K_{IV'}$ of eqn. (IV′), which corresponds to the overall equilibrium under consideration.

TABLE II. The Values of the Stability Constants $\beta_{qp} = [(PdL)_q(OH)_p][H]^p/[PdL]^q$ for Chosen Sets of Species Giving the Lowest Values for the Standard Deviation of the True Degree of Neutralization g ($\sigma(g)$)[a]

Complex	q	p	log β	q	p	log β	q	p	log β	q	p	log β	$\sigma(g)$
$[Pd\ bip]^{2+}$	1	2	−11.96	3	3	−4.06							0.0247
	1	2	−11.96	3	3	−4.07	3	4	−13.30				0.0198
	I	2	−11.96	3	3	−4.08	4	5	−13.55				0.0203
	1	2	−11.96	2	2	−4.08	4	4	−4.64				0.0225
	1	2	−11.96	2	2	−4.13	4	4	−4.60	4	5	13.48	0.0169
$[Pd\ phen]^{2+}$	1	2	−11.73	4	4	−1.97	4	5	−10.42				0.040
	1	2	−11.70	5	5	−1.64	5	6	−9.66				0.0375
	1	2	−11.70	6	6	−1.27	6	7	−9.04				0.0372
	1	2	−11.69	7	7	−0.88	7	8	−8.37				0.0399
	1	2	−11.70	8	8	−0.47	8	9	−7.82				0.0435

[a] For $[Pd\ bip]^{2+}$ 467 points from 12 curves and for $[Pd\ phen]^{2+}$ 689 points from 16 curves are used.

$$[PdL]^{2+} + 2OH^- \rightleftharpoons [PdL(OH)_2] \tag{IV'}$$

It appears that the values for $K_{IV'}$ are independent of the set of polynuclear species considered [7]. The mean value is included in Table III (and is used later for the calculation of K_2).

TABLE III. The Constants $K_{IV'}$, K_V, and K_{VI} of the Equilibria (IV'), (V), and (VI)[a]

L	Medium	$\log K_{IV'}$	$\log K_V$	$\log K_{VI}$
bip	$0.1(KNO_3)$		4.65(5)	1.89(5)
bip	$0.1(KCH_3SO_3)$	15.58(5)	4.79(5)	1.86(5)
phen	$0.1(KCH_3SO_3)$	15.84(8)	4.04(5)	1.42(5)

[a] In parentheses, three times the standard deviation in the least figure.

Alkalimetric Titrations of Solutions of the 1:2 Complex $[PdL_2]^{2+}$

In alkaline solutions the complex $[PdL_2]^{2+}$ reacts with a strong base as shown in reactions (V) and (VI) in two overlapping steps between pH 8 and 11,

$$[PdL_2]^{2+} + OH^- \rightleftharpoons [PdL_2OH]^+ \tag{V}$$

$$[PdL_2OH]^+ + OH^- \rightleftharpoons [PdL(OH)_2] + L \tag{VI}$$

in the case of both bidentate ligands. Systematic titrations with different amounts of complex show that, in all cases, polynuclear species can be neglected. The concentration of the intermediate species $[PdL_2OH]^+$ depends on the total concentration of the complex. For 5 mM solutions, its concentration reaches 40% in the case of bipyridyl and 30% in the case of phenanthroline. For 0.5 mM solutions, the corresponding concentrations are *ca.* 12% for both ligands. The inclusion of these species in the calculations is necessary in order to reduce the standard deviation of g from *ca.* 0.044 to 0.006. The results are presented in Table III.

Ligand Exchange in $[PdL_2]^{2+}$ in Solutions of the Protonated Triethylenetetraamine

The bound ligands in the two complexes $[PdL_2]^{2+}$ of the investigated diamines can be exchanged with other ligands if the latter form more stable complexes in a given pH range [3, 4]. In order to obtain a reliable exchange constant, this reaction should take place without precipitation; for this reason halogenide and thiocyanate ions are not suitable. A suitable ligand for exchange could be an aliphatic tetraamine giving much larger protonation and stability constants with respect to those of the diamines involved.

In fact, triethylenetetraamine; $H_2NCH_2CH_2$-NH-$CH_2CH_2NHCH_2CH_2NH_2$ shows the desired attributes. This can be seen for the case of $[Pd(bip)_2]^{2+}$, in Fig. 4, which shows the results of the alkalimetric titration of the protonated tetraamine H_4A^{4+} alone and in presence of the bipyridyl complex. In the latter case, because of the ligand exchange (VII),

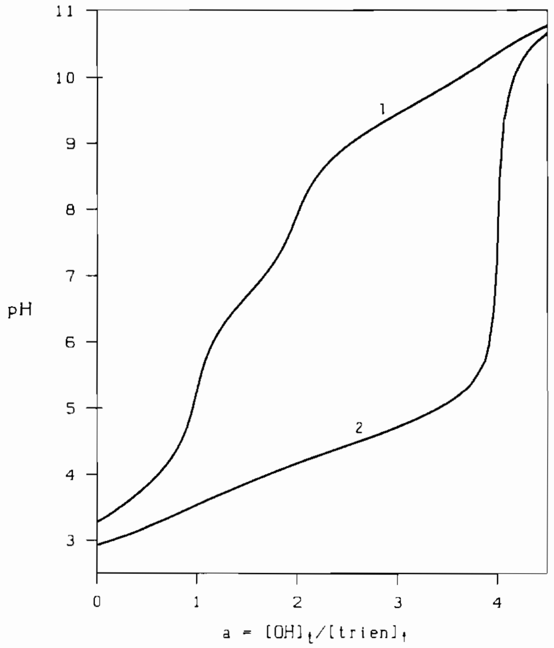

Fig. 4. Alkalimetric titrations of the protonated, 2,2,2-tet (H_4A^{4+}) alone (1) and in presence of $[Pd(bip)_2]^{2+}$ (2). $[H_4A]_t = [Pd(bip)_2]_t = 2$ mM; $I = 0.1$ (KNO_3) and 25 °C.

$$[PdL_2]^{2+} + H_4A^{4+} \rightleftharpoons [PdA]^{2+} + 2L + 4H^+ \tag{VII}$$

the protons of the amine are set free at much lower pH values with respect to the case of the amine alone. The calculation of the data allows the determination of the equilibrium concentration of L, A, $[H_4A]^{4+}$, $[PdL_2]^{2+}$, and $[PdA]^{2+}$ from the relations (eqns. (1–4)).

$$\begin{aligned}[L]_t = 2[Pd]_t &= 2[PdL_2] + [L] + [HL]\\ &= 2[PdL_2] + [L](1 + [H]K_{HL})\end{aligned} \tag{1}$$

$$[Pd]_t = [PdL_2] + [PdA] \tag{2}$$

$$\begin{aligned}[A]_t = [Pd]_t &= \Sigma[H_iA] + [PdA]\\ &= \sum_{i=1} \kappa_i[H]^i[A] + [PdA]\end{aligned} \tag{3}$$

$$\begin{aligned}[OH]_a &= \sum_{i=0}^{4} (4 - i)[H_iA] + K_{HL}[H][L] + [OH] - [H]\\ &= \sum_{i=0}^{4} (4 - i)\,\kappa_i[H]^i[A] + K_{HL}[H]\,[L]\\ &\quad + K_w[H]^{-1} - [H]\end{aligned} \tag{4}$$

For L = phen, the constancy of the values of the equilibrium constant (VII) can be increased by introducing a mixed complex $[PdL(HA)]^{3+}$. In this case for the calculations of the concentrations of the equilibrium species the above relations are not sufficient. We used the Haltafall program [8]: for given constant $\kappa_i = [H_iA]/([H]^i[A]$ ($\log \kappa_1 = 9.80$, $\log \kappa_2 = 18.29$; $\log \kappa_3 = 25.60$; $\log \kappa_4 = 29.29$) $\beta_1(PdA)$ ($\log \beta_1 = 39.4$ [3]), $\beta(PdL(HA))$ and $K_w = [H][OH]$ ($-\log K_w = 13.77$) and known total concentrations: $[L]_t$, $[Pd]_t$, $[A]_t$, and $[OH]_a$, the equilibrium concentrations are obtained. The constants $\beta_2(PdL_2)$ and $\beta(PdL(HA))$ are varied in order to minimize the sum of the square of the difference between the experimental and the calculated pH value for the different concentrations of the strong base added $[OH]_a$. In the case of bipyridyl, with data from six different titrations giving 71 experimental points, the result is $\log \beta_2 = 28.7 \pm 0.3$. For phenanthroline, from 5 batch titrations with 32 points, one obtains $\log \beta_2 = 31.2 \pm 0.1$ at $I = 0.1$ ($NaClO_4$) and $\log \beta_2 = 31 \pm 0.1$ ($0.1(KCK_3SO_3)$) with $\log([PdL(HA)]/[Pd][A][H][L]) = 47.7 \pm 0.2$.

Spectrophotometric Determination of the Consecutive Stability Constants K_1, K_2, K_3, and K_4 of the Complexes Formed by Palladium(II) with Pyridine

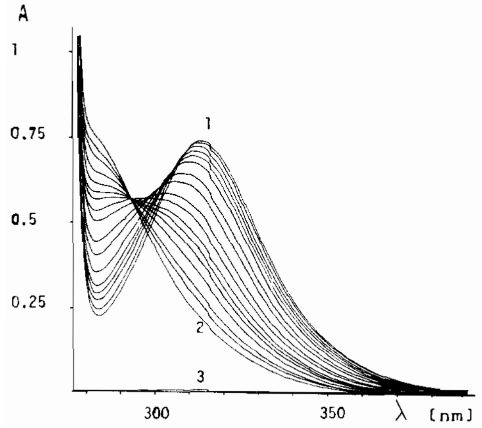

Fig. 5. Spectra of palladium solutions (1×10^{-3} M) in presence of pyridine (4×10^{-3} M) at different pH values: 1.41 (curve 1), 1.51, 1.641, 1.734, 1.827, 1.961, 2.170, 2.318, 2.536, 2.654, 2.811, 2.918, 3.048, 3.216, 3.486, 3.655, and 3.939 (curve 2). Curve 3: 1 M $NaClO_4$. 2 cm cells.

By successive additions of pyridine to a strongly acidic solution of palladium(II), the spectrum of that cation is displaced towards shorter wavelengths (Fig. 5). The maximum for the aqua ion is found at 380 nm. For the 1:4 complex $[Pd(py)_4]^{2+}$, the maximum lies below 300 nm and cannot be detected because of the strong self-absorption due to pyridine. These are the only two species for which the spectra can be obtained from their solutions. Because of the equilibria established and the strong overlap of the species present in solutions, the spectra of the other pure species cannot be obtained separately. In general, for each wavelength the measured optical absorbance A, with cells of path length l, is due to the contributions of the different species in eqn. (5). Thus, in this system the unknowns are the four stability constants K_1, K_2, K_3, and K_4 and the molar absorptivities

$$A = \sum_{i=0}^{4} \epsilon(Pd(py)_i)[Pd(py)_i] \cdot l \qquad (5)$$

ϵ of the three complexes $[Pd(py)]^{2+}$, $[Pd(py)_2]^{2+}$, and $[Pd(py)_3]^{2+}$ at the different wavelengths. If the constants are known, from the total concentrations of the components and the pH value using the stoichiometric relations (eqns. (6–8)), it is possible to calculate the equilibrium concentrations of all species present. From the measured A values, at each

$$[Pd]_t = [Pd] + \sum_{i=1}^{4} [Pd(py)_i] = [Pd](1 + \sum_{i=1}^{4} \beta_i[py]^i) \qquad (6)$$

$$[py]_t = [py] + [Hpy] + \sum_{i=1}^{4} i[Pd(py)_i]$$

$$= [py](1 + K_{Hpy}[H]) + \sum_{i=1}^{4} i\beta_i[Pd][py]^i \qquad (7)$$

$$[H]_t = [H] + [Hpy] - [OH]$$

$$= [H] + K_{Hpy}[H][py] - K_w[H]^{-1} \qquad (8)$$

given wavelength, using N solutions of different compositions, a system of N linear equations in the three unknowns is obtained. Because $N > 40$, using a least square method, not only the unknowns are obtained but also their standard deviations and that of A. The values obtained in this way depend on the constants

$$A = (\epsilon(Pd)[Pd] + \epsilon(Pd(py)_4)[Pd(py)_4]$$

$$+ \epsilon(Pd(py))[Pd(py)] + \epsilon(Pd(py)_2)$$

$$\times [Pd(py)_2] + \epsilon(Pd(py)_3)[Pd(py)_3])l \qquad (5')$$

used in the calculations. The best constants are those which minimize the standard deviation of A, *i.e.*, $\sigma(A)$. The constants $K_1 - K_4$ can be varied with a procedure which takes into consideration the standard deviation $\sigma(A)$ in order to find its minimum more rapidly. The results in the different media are summarized in Table IV. The calculated spectra are given in Fig. 6, and the values of the wavelengths and the molar absorptivities for the maxima are collected in Table V, together with the corresponding values for the ammonia complexes.

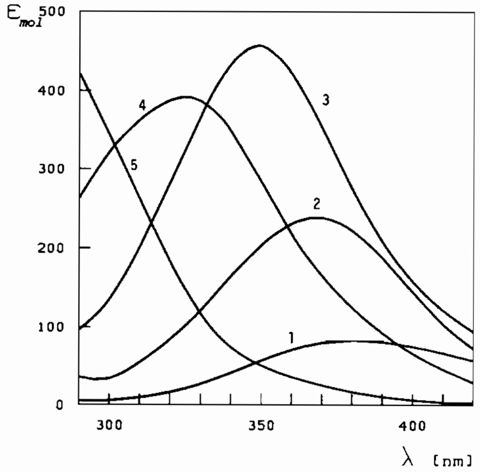

Fig. 6. Spectra of the palladium pyridine complexes from the data at I = 1($NaCH_3SO_3$) and 25 °C. 1. $[Pd(H_2O)_4]^{2+}$; 2. $[Pd(py)]^{2+}$; 3. $[Pd(py)_2]^{2+}$; 4. $[Pd(py)_3]^{2+}$; 5. $[Pd(py)_4]^{2+}$.

TABLE IV. The Stability Constants[a] of $[Pd(py)_i]^{2+}$ (i = 1–4) at 25 °C and I = 1 M

	$NaClO_4$	$NaClO_3$	$NaCH_3SO_3$
$\log K_1$	8.4 ± 0.2		8.5 ± 0.2
$\log K_2$	7.7 ± 0.2		7.5 ± 0.2
$\log K_3$		6.6 ± 0.2	6.3 ± 0.1
$\log K_4$		5.9 ± 0.2	5.7 ± 0.1

[a] The errors given represent three times the standard deviation.

The Formation of Mixed Complexes between the 1:1 Complexes $[PdL]^{2+}$ of the Two Diamines and Pyridine

During the alkalimetric titrations of solutions of the 1:1 complex $[PdL]^{2+}$ with protonated pyridine, the reactions (VIII) and (IX) take place. These are followed by decomposition reactions with formation

$$[PdL]^{2+} + Hpy^+ \rightleftharpoons [PdL(py)]^{2+} \qquad (VIII)$$

$$[PdL(py)]^{2+} + Hpy^+ \rightleftharpoons [PdL(py)_2]^{2+} \qquad (IX)$$

$$[PdL(py)_2]^{2+} + OH^- \rightleftharpoons [PdL(py)OH]^+ + py \qquad (X)$$

$$[PdL(py)OH]^+ + OH^- \rightleftharpoons [PdL(OH)_2] + py \qquad (XI)$$

of $[PdL(py)OH]^+$ and $[PdL(OH)_2]$ in the two steps X and XI. For both ligands, the constant K_2 (= $[PdL(py)_2]/([PdL(py)][py])$) can be obtained directly, since the 1:1 complex $[PdL(py)]^{2+}$ is already formed in the mixture to be titrated. The constant K_1 is then obtained from β_2 (= K_1K_2), which is involved in the evaluation of the decomposition of $[PdL(py)_2]^{2+}$ according to (X) and (XI). The calculation is done by fitting the calculated curve into the experimental one, varying the involved constants and minimizing the true degree of neutralization using the program KVARI. The values obtained are summarized in Table VI.

TABLE V. Spectral Data for the Pyridine and Ammonia [9] Complexes of Palladium(II)

Complex	L = py		L = NH_3	
	λ_{max} (nm)	ε_{mol} (M^{-1} cm^{-1})	λ_{max} (nm)	ε_{mol} (M^{-1} cm^{-1})
$[PdL]^{2+}$	368	240	360	130
$[PdL_2]^{2+}$	348	450	341	215
$[PdL_3]^{2+}$	323	380	317	–
$[PdL_4]^{2+}$			295	200

TABLE VI. The Stability Constants K_1 and β_2 of the Mixed Complexes between $[PdL]^{2+}$ (L = 2,2′-Bipyridyl or 1,10-phenanthroline) and Pyridine at 25 °C and I = 0.1 (KCH_3SO_3)[a]

Complex	$\log K_1$	$\log \beta_2$	$\log \frac{[PdLpyOH][H]}{[PdLpy]}$
$[Pdbip]^{2+}$	6.25(5)	11.80(10)	−5.32(7)
$[Pdphen]^{2+}$	6.44(5)	12.26(10)	−5.20(7)

[a] In parentheses, three times the standard deviation in the least group.

Discussion

Only the spectra of the palladium(II) complexes (Table V) with one, two, and three pyridine ligands are of interest because for $[Pd(py)_4]^{2+}$ the self-absorption due to the ligand with $\varepsilon_{mol} \simeq 10^5$ M^{-1} cm^{-1} does not allow the separation of the spectrum due to the interaction between the coordinated atoms and palladium(II). In comparison to the analogous ammonia complexes, the first three pyridine complexes show similar wavelength maxima, but the corresponding molar absorptivities are twice as high. It is a general trend that for the same cation the pyridine complexes are weaker than the ammonia complexes, although the change in the stability constant is lower in magnitude compared to that observed in their protonation constant [10]. The differences in $\log K_i$ (i = 1–4) for Pd^{2+} (1.2) are more similar to those for Ni^{2+} (1) than those for Cu^{2+} (1.8).

As can be seen from Table VII, the stability constants with the aromatic amines are lower than those of the corresponding aliphatic amines: in general the trends and the chelate effect correspond to those found with copper(II) [2]. The only excep-

TABLE VII. Stability Constants of Palladium(II) Complexes at 25 °C

Ligand	Medium	log K_1	log K_2	log K_3	log K_4	log β_2	log β_4
py	1(KCH$_3$SO$_3$)	8.5	7.5	6.3	5.7	16.0	28.0
NH$_3$ [9]	1(NaClO$_4$)	9.6	8.9	7.5	6.8	18.5	32.8
bip	0.1(KCH$_3$SO$_3$)	19.8	8.9			28.7	
phen	0.1(KCH$_3$SO$_3$)	20.7	10.4			31.1	
en	1(NaClO$_4$)	23.6	18.6			42.2	

tions are the much lower K_2 values for both aromatic diamines. This is explained by the special structures of the ligands which do not allow the favored square planar arrangement of the N atoms in [PdL$_2$]$^{2+}$ to be reached, because of the strong repulsion between the H atoms in α-position with respect to the donor atoms. This is in agreement with the X-ray structure of the solid complex salts of the 1:2 complexes [11, 12]. The planes of the two ligand molecules are tetrahedrally twisted in such a way that the angle between them is equal to 24° in the case of bipyridyl and to 18.7° for phenanthroline. The values of K_2 are lower by a factor of from 100 to 1000 with respect to the product of the constants $K_1K_2 = \beta_2$ of the mixed complexes [PdL(py)$_2$]$^{2+}$; this shows that, because of the discussed steric hindrance for both aromatic diamines, the complex [PdL]$^{2+}$ prefers to coordinate two pyridine molecules instead of a second equal ligand molecule, this last step being characterized by a negative chelate effect [13].

The hydrolysis products of the 1:1 complexes with the aromatic diamines are different from those obtained with ethylenediamine. Instead of the dimeric product [4] alone, as obtained in the latter case, at least two or three polymeric products are formed; their exact compositions cannot be established because, in such situations, different sets of species give an almost equal fit of the experimental results, and the crystalline products obtained from the equilibrated solutions are not of the suitable dimensions for X-ray structural analysis. The coordination number of palladium(II) for all mononuclear complexes is four. The only exception is [PdL$_2$(OH)]$^+$ (L = bip or phen), which is analogous to the known [Pt(bip)$_2$OH)]$^+$ [14], both having a coordination number of five. Another possibility for such complexes is a nucleophilic attack of H$_2$O to a coordinate ligand molecule with corresponding deprotonation, thus maintaining the coordination number equal to four [15]. The ^{13}C NMR spectrum of the palladium bipyridyl complex shows that this cannot be the case, because the measurements in solutions of that complex show no signals at the location of the sp^3 carbons [7]. A coordination number of 5 has already been postulated for the complex [PdL(OH)$_3$]$^-$ obtained by base addition from the 1:1 complex [16]. Our measurements have shown the formation of [PdL(OH)$_2$] only, without any further hydroxyl ion addition in strong alkaline solution (pH = 9–13).

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