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The Stability of the Palladium(II) Complexes with Linear Tetraamines

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Abstract

The formation of complexes of Pd^{2+} with tetraamines of type $R-CH_2-NH-(CH_2)_n-NH-CH_2-R$, for $R = CH_2NH_2$, and 2-pyridyl, and n = 2, 3, 4, 5 and 6 was investigated at 25 °C and I = 1 using pH and UV-measurements. The 1:1 complexes of all tetraamines involved are completely formed in 1 M $HClO_4$, so that the usual direct pH method cannot be used. Exchange equilibria with auxiliary ligands (such as bromide or thiocyanate ions) as well as 2,2′-bipyridyl were applied. The values obtained for the stability constants of the 1:1 complexes are between 10^{34} and 10^{47} M^{-1}. Some of the values were checked using different methods. Pd^{2+} forms the strongest complexes of the divalent cations investigated hitherto.

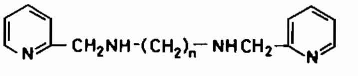
Introduction

The linear tetraamines of type **A**, abbreviated as 2,n,2-tet, contain four aliphatic N atoms capable of forming three chelate rings and stable complexes

$H_2NCH_2CH_2NH-(CH_2)_n-NHCH_2CH_2NH_2$ 2,n,2-tet

A

with 3d divalent cations [1]. Another series of tetraamines which have similar properties are those of type **B** [2]. They are analogous to those of type **A**



2,n,2-dpa

B

but the two terminal N atoms are part of pyridine rings.

The four N atoms of all these ligands are also in a favourable position to coordinate to palladium(II), which prefers a square planar geometry. However, their stability constants are not known, except for that with 2,2,2-tet which was investigated using a metal indicator method. From the equilibrium with the coloured palladium(II) complex of arsenazo I [3] at pH = 4 a 1:2 complex, $[Pd(2,2,2\text{-tet})_2]^{2+}$ was postulated. However, as encountered in other investigations of Pd(II) complexes [4], it is difficult to obtain such data because the aqua ion undergoes hydrolysis even at pH = 1, and its 1:1 complexes $[PdL]^{2+}$ are too stable to be investigated using the customary pH method. Fortunately, in acidic medium, the highly coloured $[PdX_4]^{2-}$ (X = Br, SCN) is in equilibrium with the palladium(II)–tetraamine complexes.

Using the anion X^- as auxiliary ligand, exchange equilibria can be followed both by spectrophotometry and by alkalimetric titrations. In this way it is possible to obtain the equilibrium constants between the complexes of the two ligands in question. These can be used to calculate the constants for the palladium(II) complexes $[PdL]^{2+}$ with the different tetraamines. Furthermore, the eventual changes in the coordination sphere of the 1:1 complexes $[PdL]^{2+}$ can be studied using their solutions at different pH values, mainly using spectrophotometric measurements. The involved equilibria are not usual for such purposes, thus each one is briefly described in relation to a chosen example.

Experimental

The pure salts of the tetraamines were used [1, 2]. Palladium perchlorate solutions were prepared starting from the pure metal or from palladium nitrate [5]. Other salts were from Merck or Fluka. HBr (40%, Siegfried, Zofingen) was distilled over red phosphor under 11 Torr pressure at 80 °C. The complexes with 2,n,2-dpa (n = 2–6) were isolated from solutions of the ligands and $Pd(NO_3)_2$ in 1 M nitric acid, after filtration, by addition of saturated $NaClO_4$ solutions until precipitation occurred. The products were filtered off and recrystallized from water and dried under vacuum over P_2O_5†.

The spectra were measured with a Beckman ACTA III UV-Vis spectrophotometer. For pH measurements

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†The Elemental Analysis Data Table is obtainable from G.A. on request.

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an Orion Research Digital Ionanalizer Model 801 A and a Digital Burette Mettler DV III were used. The pH values of the solutions were defined using the concentration of the hydrogen ions [H]:pH = −log[H], in the standard state used, given by the supporting electrolyte in pure water. For solutions with [H] = 0.02–1 M, the pH values cannot be measured exactly, but they can be calculated from solution compositions taking into consideration the equilibria involved. Since the concentrations of the palladium(II) complexes are very low (1×10^{-5}–1×10^{-3} M) with respect to those of H^+, the corrections due to the protonation of the ligand species present in solution are very small and often negligible. In some cases the protonation constants of the amines were checked in different inert salt solutions (Table I).

Measurements on all the palladium-containing solutions were carried out until equilibrium was reached. The time needed for equilibration varied between some hours ($[PdBr_4]^{2-}$ with 2,n,2-dpa, pH = 0–2) and several days (Pd^{2+} with 3,2-tet, pH = 0–2) or weeks ($[Pd(bip)_2]^{2+}$ with 2,6,2-tet, pH = 3–7). Sometimes the sequence of addition of the different components was changed or inverted in order to check the attainment of the same composition in the equilibrated solutions. In the cases where there was separation of solid products, the concentrations of the components were decreased or different supporting electrolytes were used. For the determination of some spectra sodium methylsulphonate was used instead of the usual inert salt ($NaClO_4$), because of the higher solubilities of the complexes in the former medium.

TABLE I. Protonation Constants ($k_i = [H_iL]/([H][H_{i-1}L])$) of the Tetraamines in Solutions of Different Supporting Electrolytes at 25 °C.

	Medium	log k_1	log k_2	log k_3	log k_4
2,2,2-tet	1 M KNO_3	10.05	9.39	7.19	4.08
	1 M $NaClO_4$	10.03	9.59	7.23	3.92
	1 M KBr	10.00	9.42	7.07	3.93
	1 M NaBr	10.03	9.47	7.11	3.94
2,3,2-tet	1 M $NaClO_4$	10.28	9.64	7.43	6.09
	0.1 M KNO_3	10.02	9.24	6.89	5.53
2,4,2-tet	1 M $NaClO_4$	10.48	9.74	7.67	6.86
2,5,2-tet	1 M $NaClO_4$	10.70	10.00	7.79	7.05
2,6,2-tet	0.1 M KNO_3	10.38	9.64	7.35	6.69
	1 M $NaClO_4$	10.69	10.02	7.80	7.21
2,2,2-dpa	1 M NaBr	8.44	5.78	1.8	
	1 M KNO_3	8.33	5.71	1.74	
2,3,2-dpa	1 M NaBr	9.03	7.30	2.39	
	1 M KNO_3	8.94	7.26	2.28	1.3
2,4,2-dpa	1 M NaBr	9.41	8.06	2.1	
	1 M KNO_3	9.26	8.02	2.4	1.5
2,5,2-dpa	1 M NaBr	9.385	8.64	2.57	0.6
	0.1 M KNO_3	9.15	8.17	2.05	
	1 M KNO_3	9.28	8.53	2.66	1.0
2,6,2-dpa	1 M KNO_3	9.34	8.73	2.43	1.3

Description of the Equilibria

Protonation of the 1:1 Complex $[PdL]^{2+}$*, for* $L = 2,2,2\text{-tet}$

Equimolar solutions of palladium(II) and 2,2,2-tet at ionic strength 1, using $NaClO_4$ and $HClO_4$ as supporting electrolytes in the pH range from 0 to 7, show an isosbestic point and, therefore, an equilibrium between two species occurs (Fig. 1). As the wavelength of the maxima λ_{max} of the palladium(II) complexes with N donors depends on their number [6], the observed bands are assigned to the following species: (1) $\lambda_{max} = 296$ nm to $[PdL]^{2+}$ with four coordinated N atoms and (2) $\lambda_{max} = 320$ nm to $[Pd(HL)]^{3+}$ with three coordinated N atoms. In agreement with expectations, $[PdL]^{2+}$ is stable at a higher pH value. However, on acidification of the neutral solution of $[PdL]^{2+}$, the wavelength of the maximum increases. At pH = 0, the protonated complex $[Pd(HL)]^{3+}$ is not completely formed but a further lowering of the pH is not possible at ionic strength 1. Because only the spectrum of $[PdL]^{2+}$ is known, the constant of

$$[PdL]^{2+} + H^+ \rightleftharpoons [Pd(HL)]^{3+} \qquad \text{(I)}$$

equilibrium (I) cannot be calculated directly using eqn. (1). (A(PdL)) and A(Pd(HL)) are the optical absorbancies of the solutions containing only the

$$\frac{[Pd(HL)]}{[H][PdL]} = \frac{A(PdL) - A}{[H](A - A(Pd(HL)))} \qquad (1)$$

species given in parentheses; A is that of the equilibrated solution, at given [H], containing both species for the same total concentration of the complex and the same wavelengths.

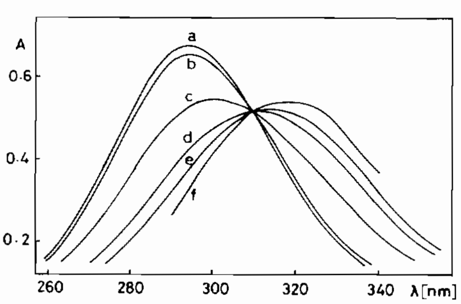

Fig. 1. Spectra of $[Pd(2,2,2\text{-tet})]^{2+}$ in acidic solutions with $NaClO_4$ as supporting electrolyte. (a) pH = 5–3, (b) pH = 2, (c) pH = 1, (d) pH = 0.4, (e) pH = 0.09, (f) $[Pd(HL)]^{3+}$; $[Pd]_t = [trien]_t = 8 \times 10^{-4}$ M, 1 cm cells.

Equation (1) can be transformed into eqn. (2): for $x = A$ and $y = (A(\mathrm{PdL}) - A)/[\mathrm{H}]$ it gives a straight

$$A = A(\mathrm{Pd(HL)}) + \frac{A(\mathrm{PdL}) - A}{K_{\mathrm{I}}[\mathrm{H}]} \qquad (2)$$

line with an intersection for $y = 0$ at $x = A(\mathrm{Pd(HL)})$ and slope $1/K_{\mathrm{I}}$. Because the number of values of the pairs A, [H] being large, a least squares method was used. The calculated spectrum of $[\mathrm{Pd(HL)}]^{3+}$ is shown in Fig. 1 and the pK value of $[\mathrm{PdHL}]^{3+}$ ($=\log K_{\mathrm{I}}$) from the data for seven wavelengths is 0.84 ± 0.04.

Formation of a Mixed Complex $[PdBr(HL)]^{2+}$ from $[PdL]^{2+}$, for L = 2,2,2-tet

The species $[\mathrm{Pd(HL)}]^{3+}$, for L = 2,2,2-tet, has a protonated N atom, thus a palladium coordination site, occupied by H_2O, is readily available for other donors. In bromide medium, H_2O can be replaced by that anion. The spectra of solutions containing equimolar quantities of metal ion and tetraamine with bromide concentration ranging from 0.01 to 0.1 M and at constant pH = 2.1 are shown in Fig. 2. Also these spectra are characterized by the presence of an isosbestic point indicating that $[\mathrm{PdL}]^{2+}$ reacts to form only one bromo complex with $\lambda_{\mathrm{max}} = 346$ nm.

Another series of measurements were carried out on solutions with a constant 0.01 M bromide concentration and a variable pH value. The spectra (see Fig. 3) show an isosbestic point and correspond to solutions containing the complexes $[\mathrm{PdL}]^{2+}$ and $[\mathrm{PdBr(HL)}]^{2+}$. At pH = 1 disruption of these complexes with formation of $[\mathrm{PdBr_4}]^{2-}$ occurs. The spectra change with increasing pH while the wavelength λ_{max} decreases from 342 to 296 nm as expected if $[\mathrm{PdBr(HL)}]^{2+}$ goes into $[\mathrm{PdL}]^{2+}$. In this case, the spectrum of the former species is considered as unknown but, using eqn. (3) and a least square procedure, the constant K_{II} for equilibrium

$$A = A(\mathrm{PdBr(HL)}) + \frac{A(\mathrm{PdL}) - A}{[\mathrm{H}]\,[\mathrm{Br}]K_{\mathrm{II}}} \qquad (3)$$

(II) and $A(\mathrm{PdBr(HL)})$ are obtained. From the data for ten different wavelengths and eight pH values one obtains $\log K_{\mathrm{II}} = 4.34 \pm 0.08$.

$$[\mathrm{PdL}]^{2+} + \mathrm{H}^+ + \mathrm{Br}^- \rightleftharpoons [\mathrm{PdBr(HL)}]^{2+} \qquad (\mathrm{II})$$

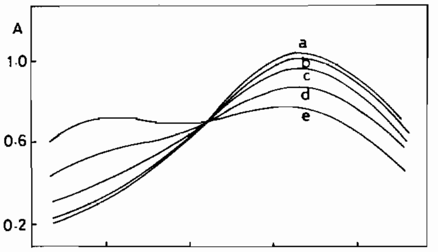

Fig. 2. Spectra of $[\mathrm{Pd(2,2,2\text{-}tet)}]^{2+}$ in bromide solutions at pH = 2.1. $[\mathrm{Br}]_t$: a = 0.1 M, b = 0.08 M, c = 0.04 M, d = 0.02 M, e = 0.01 M; $[\mathrm{Pd}]_t = [\mathrm{trien}]_t = 0.002$ M, 1 cm cells.

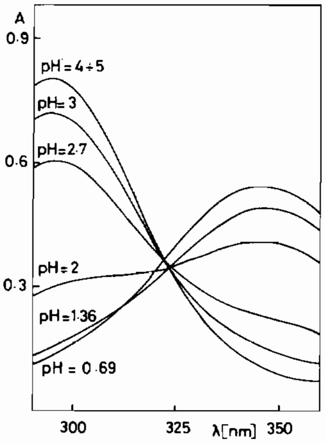

Fig. 3. Spectra of $[\mathrm{Pd(2,2,2\text{-}tet)}]^{2+}$ at different pH values. $[\mathrm{PdL}]_t = 1 \times 10^{-3}$ M 1 cm cells.

Formation of a Mixed Complex $[PdBr(HL)]^{2+}$ from $[PdBr_4]^{2-}$, for L = 2,2,2-tet

Solutions containing equimolar quantities of palladium(II) and 2,2,2-tet, in the presence of a large excess of bromide ions (1 M), show a strong decrease of the absorptivity at the λ_{max} of $[\mathrm{PdBr_4}]^{2-}$ (332 nm) on increasing the pH value from 1 to 2. This is due to the decrease in concentration of $[\mathrm{PdBr_4}]^{2-}$ with formation of $[\mathrm{PdBr(HL)}]^{2+}$ according to equilibrium (III). The concentration of

$$[\mathrm{PdBr_4}]^{2-} + \mathrm{H_4L}^{4+} \rightleftharpoons [\mathrm{PdBr(HL)}]^{2+} + 3\mathrm{H}^+ + 3\mathrm{Br}^- \qquad (\mathrm{III})$$

$[\mathrm{PdL}]^{2+}$ is less than 1% of the total palladium(II) concentration, as can be shown using the value of the constant $K_{\mathrm{II}} = [\mathrm{PdBr(HL)}]/([\mathrm{PdL}][\mathrm{H}][\mathrm{Br}])$ and the known concentrations of Br^- and H^+. The absorbance A at 332 nm with the molar absorptivities of $[\mathrm{PdBr_4}]^{2-}$ and $[\mathrm{PdBr(HL)}]^{2+}$ allows the determination of the concentrations of both species using eqns. (4) and (5). Finally the concentration of

$$A = \epsilon_{\mathrm{mol}}(\mathrm{PdBr_4})[\mathrm{PdBr_4}] + \epsilon_{\mathrm{mol}}(\mathrm{PdBr(HL)}[\mathrm{PdBr(HL)}] \qquad (4)$$

(1 cm cells)

$$[\mathrm{Pd}]_t = [\mathrm{PdBr_4}] + [\mathrm{PdBr(HL)}] \qquad (5)$$

$$[\mathrm{L}]_t = [\mathrm{H_4L}] + [\mathrm{PdBr(HL)}] \qquad (6)$$

$\mathrm{H_4L}^{4+}$ is calculated using eqn. (6). The equilibrium constant $K_{\mathrm{III}} = [\mathrm{PdBr(HL)}]\,[\mathrm{Br}]^3[\mathrm{H}]^3/([\mathrm{PdBr_4}][\mathrm{H_4L}])$ can be calculated as it contains known equilibrium concentrations. Its value is combined with the stability constant β_4 of $[\mathrm{PdBr_4}]^{2-}$ (=[Pd-

TABLE II. Overall Stability Constant of $[PdBr(HL)]^{2+}$ for L = 2,2,2-tet, from Spectrophotometric Measurements. $[Pd]_t = [2,2,2\text{-tet}]_t = 8 \times 10^{-5}$ M; [Br] = 1 M (1 cm cells).

pH	A at 323 nm	$\log K_{IV}$	pH	A at 323 nm	$\log K_{IV}$
1.00	0.865	44.85	1.98	0.224	44.71
	0.877	44.44		0.238	44.64
1.25	0.806	44.77	1.01	0.869	44.68
	0.814	44.72	1.26	0.815	44.66
1.50	0.637	44.72	1.50	0.648	44.6?
	0.658	44.65	1.76	0.404	44.66
1.73	0.401	44.74	1.99	0.230	44.61
	0.432	44.68			

$Br_4]/([Pd][Br]^4) = 10^{14.94}$ [4, 5]) and the overall protonation constant K_4 $(=[H_4L]/([H]^4[L]))$ of 2,2,2-tet ($10^{30.42}$ for I = 1(KBr)) to obtain the constant K_{IV} (Table II) for the equilibrium (IV).

$$Pd^{2+} + Br^- + H^+ + L \rightleftharpoons [PdBr(HL)]^{2+} \qquad (IV)$$

Direct Formation of $[PdL]^{2+}$ from $[PdX_4]^{2-}$ with L = 2,n,2-dpa (n = 2, 3, and 4)

Solutions containing equimolar amounts of palladium(II) and 2,n,2-dpa in the presence of 1 M bromide ion, at different pH values, give spectra which correspond to the presence of $[PdL]^{2+}$ and $[PdX_4]^{2-}$ only. The exchange equilibrium (V) takes place and from the measured absorbancy A,

$$[PdX_4]^{2-} + H_4L^{4+} \rightleftharpoons [PdL]^{2+} + 4H^+ + 4X^- \qquad (V)$$

through the molar absorptivities of $[PdX_4]^{2-}$ and $[PdL]^{2+}$, it is possible to calculate the unknown concentrations of the species in equilibrium and their relative constant $K_V = [PdL][H]^4[X]^4/([PdX_4][H_4L])$ using eqns. (7), (8), and (9) for each wavelength. Table III summarizes the values of the stability constants K_1 obtained from this constant and the overall constants β_4 or $[PdX_4]^{2-}$ and K_4 of H_4L^{4+} for the three ligands 2,n,2-dpa (n = 2, 3 and 4).

$$A = \epsilon_{mol}(PdX_4)][PdX_4] + \epsilon_{mol}(PdL)[PdL] \qquad (7)$$

(1 cm cells)

$$[Pd]_t = [PdX_4] + [PdL] \qquad (8)$$

$$[L]_t = [H_4L] + [PdL] \qquad (9)$$

Exchange of X^- with L in $[PdX_4]^{2-}$ Using Alkalimetric Titrations

Solutions containing equimolar amounts of $[PdX_4]^{2-}$ and protonated ligand H_4L^{4+}, in the presence of a known concentration of the anion X^-, give titration curves of a different shape, depending on the ligands L and X^- and on their relative concentrations. Thus, in the case of the three amines 2,n,2-dpa (n = 2, 3 and 4) the formation of $[PdL]^{2+}$ occurs below pH 1 even in 1 M bromide. Therefore, a mixture of the above composition (millimolar solution of $[PdBr_4]^{2-}$ and H_4L^{4+} in 1 M NaBr with pH = 2.4) already contains the final product and on addition of a strong base "free" hydrogen ions are neutralized (see Fig. 4). As no exchange occurs, in this case equilbrium (V) cannot be studied using this method. The same behaviour is observed in the case of the aliphatic tetraamine 2,3,2-tet, because of the very high stability of the corresponding $[PdL]^{2+}$ complex.

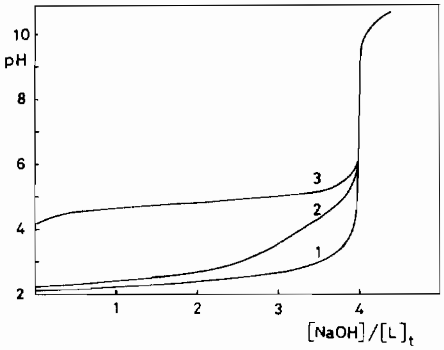

Fig. 4. Titration curve of protonated tetraamine H_4L^{4+} in presence of $[PdX_4]^{2-}$ and an excess of NaX by addition of an NaOH solution. $[Pd]_t = [L]_t = 2 \times 10^{-3}$ M. (1) L = 2,n,2-dpa (n = 2,3,4), $[NaBr]_t = 1$ M, (2) L = 2,2,2-tet, $[NaBr]_t = 1$ M, (3) L = 2,4,2-tet, $[NaSCN]_t = 0.1$ M.

TABLE III. The Stability Constant K_1 of 2,n,2-dpa Complexes from Spectrophotometric Measurements at Different Wavelengths.

n	pH range	$[Pd]_t$ [M]	$\log K_1 (\lambda)$				
2	0.09–0.39	2.852×10^{-4}	35.72(325)	35.58(330)	35.53(332)	35.47(335)	35.48(340)
	0.05–0.39	5.704×10^{-5}	35.72(325)	35.65(330)	35.63(332)	35.59(335)	35.54(340)
3	0.09–0.52	4.954×10^{-5}	39.09(325)	39.09(330)	39.08(332)	39.08(335)	39.07(340)
	0.09–0.52	2.477×10^{-4}	39.03(325)	39.05(330)	39.05(332)	39.05(335)	39.05(340)
	0.22–0.70	7.425×10^{-5}		39.03(330)	39.04(332)	39.04(335)	
4	1.04–1.52	2.835×10^{-4}	36.97(325)	37.00(330)	37.00(332)	37.03(335)	37.01(340)
	0.82–1.52	2.835×10^{-5}	37.02(325)	37.02(330)	37.02(332)	37.02(335)	37.02(340)

On the contrary, when 2,2,2-tet is used as ligand, the titration curve of the reaction mixture, in 1 M NaBr or KBr after neutralization of three hydrogen ion equivalents per mole ligand, has a shape which corresponds exactly to the neutralization of a weak acid, $[PdBr(HL)]^{2+}$, with a pK value larger than 4 (see Fig. 4). This result was expected from the data of that system in 1 M $NaClO_4$ which gave the value $10^{4.35}$ for the ratio $[PdBr(HL)]/([PdL][Br][L])$. Therefore, in 1 M NaBr the complex $[PdBr(HL)]^{2+}$ should behave as a weak acid with a pK near to 4.35, depending on the activities of the species present in the two media.

In the case of thiocyanate as auxiliary ligand, its palladium(II) complex, $[Pd(SCN)_4]^{2-}$, in the presence of the tetraamines and a large excess of NaSCN, is stable up to pH = 4. Therefore it is possible to follow the exchange between the inorganic and organic ligands by alkalimetric titration, because following eqn. (V) four protons are set free (see Fig. 4) whereas the initial dark red solution of $[Pd(SCN)_4]^{2-}$ gradually becomes practically colorless. Calculations of the concentrations of the species involved in equilibrium (V) make use of eqns. (10), (11), and (12) for the total concentration of palladium(II) $[Pd]_t$, of the amine $[L]_t$ and of the strong base $[OH]_t$ added to the solution of $[PdX_4]^{2-}$ and to the acid H_4L^{4+}. The number of unknowns in these relationships is reduced by inserting the distribution functions α and γ, which depend on

$$[Pd]_t = [PdX_4] + [PdL] \qquad (10)$$

$$[L]_t = \sum_{i=0}^{4} [H_iL] + [PdL] = \alpha[H_4L] + [PdL] \qquad (11)$$

$$[OH]_t = \sum_{i=0}^{4} (4 - i)[H_iL] + 4[PdL] + [OH] - [H]$$

$$= \gamma[H_4L] + 4[PdL] + [OH] - [H] \qquad (12)$$

the values of the protonation constants $K_i = [H_iL]/([H]^i[L])$ and on the measured hydrogen ions concentration [H]:

$$\alpha = \sum_{i=0}^{4} \frac{K_{4-i}}{K_4[H]^i}, \quad \gamma = \sum_{i=1}^{4} i \times \frac{K_{4-i}}{[H]^i K_4} \quad \text{and } K_0 = 1.$$

As the pH value is lower than 7, the concentration of the hydroxyl ions can be neglected. The exchange with 2,4,2-tet (Table IV) takes place between pH 4.5 and 5.5 and, using the overall formation constant β_4 $(=10^{27.6})$ of $[Pd(SCN)_4]^{2-}$, the stability constant for $[Pd(2,4,2\text{-tet})]^{2+}$ is obtained.

If the absorbancy A of the solution is also known, the concentrations of $[PdX_4]^{2-}$ and $[PdL]^{2+}$ can be calculated by solving the set of eqns. (7) and (8). Finally, for $[Pd]_t = [L]_t$, it follows $[H_4L] = [PdX_4]/\alpha$ and therefore the constant K_V can be calculated. This allows the calculation of the stability constant of $[PdL]^{2+}$.

TABLE IV. The Stability Constant K_1 of $Pd(2,4,2\text{-tet})^{2+}$ from the Titration of $[Pd(SCN)_4]^{2-}$ in Presence of Tetraprotonated 2,4,2-tet with 0.1 M NaOH. $[Pd]_t = [2,4,2\text{-tet}]_t = 2.099 \times 10^{-3}$ M; $[NaSCN]_t = 0.1$ M; $[NaClO_4]_t = 0.894$ M.

NaOH (ml)	$\frac{[NaOH]}{[Pd]_t}$	pH	$\frac{[PdL]}{[Pd]_t}$	$\log K_1$
0.040	0.381	4.477	0.0983	42.07
0.080	0.762	4.586	0.1926	42.04
0.120	1.143	4.635	0.2876	42.14
0.160	1.524	4.716	0.3823	42.08
0.200	1.906	4.810	0.4769	41.96
0.240	2.287	4.858	0.5722	42.04
0.280	2.668	4.959	0.6675	41.93
0.320	3.049	5.054	0.7623	41.92

The Use of 2,2′-bipyridyl as Auxiliary Ligand

The 1:2 bipyridyl complex, $[Pd(bip)_2]^{2+}$, can be used for the formation of the tetraamine complexes $[PdL]^{2+}$, in the presence of the tetraprotonic acid H_4L^{4+}, by addition of strong base in order to neutralize the liberated hydrogen ions according to the exchange reaction (VI). Ligand replacement occurs normally through an intermediate mixed

$$[Pd(bip)_2]^{2+} + H_4L^{4+} \rightleftharpoons [PdL]^{2+} + 4H^+ + 2bip \qquad (VI)$$

complex $[Pd(bip)(H_2L)]^{4+}$. With 2,2,2-tet, the time required for equilibration is of the order of hours whilst with 2,6,2-tet it is of the order of weeks. As the equilibria with 2,2′-bipyridyl have been studied in an ionic medium of 0.1 (KNO_3) or 0.1 (KCH_3SO_3), the former was used for the exchange reactions. The difference in $\log K_1$ between the ionic strengths 1 and 0.1 M used for palladium(II) complexes was assumed to be identical to that observed for the copper(II) complexes with 2,2,2-tet, *i.e.* 0.74, from $\log K_1 = 20.90$ for I = 1 (KNO_3) and $\log K_1 = 20.16$ for I = 0.1 (KNO_3) [1]. As K_1 for $[Pd(2,2,2\text{-tet})]^{2+}$ can be obtained by other methods (see Table VI), this exchange was originally used by us for the determination of the overall constant β_2 of $[Pd(bip)_2]^{2+}$ [8]. From six different batch titrations with 71 experimental points, all values for $\log \beta_2$ were found to fall between 28.5 and 28.8.

Results and Discussion

The Spectra

The values of the wavelengths of the first maximum of the palladium(II) tetraamine complexes

TABLE V. Wavelength Maxima and Corresponding Molar Absorptivities for the Spectra of the 1:1 Palladium(II) Tetraamine Complexes.

n	2,n,2-tet		2,n,2-dpa	
	λ_{max}	ϵ_{mol}	λ_{max}	ϵ_{mol}
2	296	845	293	1350
3	283	380	298	540
4	290	595	298	530
5	292	467	292	436
6	293	450	292	440

(Table V) lie between 283 and 298 nm and are similar to those observed for other PdN_4 chromophores [5]. The molar extinction coefficients ϵ_{mol} are generally larger than those for $[Pd(NH_3)_4]^{2+}$ and $[Pd(en)_2]^{2+}$. This is explained by their greater strain in complexes with polyamines, because the same ligand molecule has to form more connected chelate rings. This is evident for the complex with 2,2,2-tet, in which one terminal chelate ring can be opened by formation of $[Pd(HL)]^{3+}$. As can be seen in Fig. 1, the latter species gives a maximum at longer wavelengths, as expected for PdN_3 chromophores, as well as showing a decrease of the molar absorptivity and thus of the steric strain. The protonated species contains a coordination site occupied by a solvent molecule: in the presence of bromide ions the coordination of this anion occurs giving $[PdBr(HL)]^{2+}$. Within the series 2,n,2-tet, the lowest strain is expected for the complex with n = 3 [7] and this corresponds to the highest value of K_1

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

Ligand	Measured quantity	Auxiliary ligand X^-	Medium[a]	$[Pd]_t$	pH	$\log K_1$	pK of $[PdHL]^{3+}$ or $[PdX(HL)]^{2+}$	$\log K$[b]
2,2,2-tet	pH	SCN^- (0.1 M)	1 ($NaClO_4$)	2×10^{-3} M	3–5	40.1 ± 0.1		46.7 ± 0.1
	sp, pH	SCN^- (0.1 M)	1 ($NaClO_4$)	2×10^{-3} M	3–5	40.2 ± 0.1		
	sp, pH	Br^- (1 M)	1 (KBr)	8×10^{-5} M	1–2	40.1 ± 0.1		44.68 ± 0.1
	pH	Br^- (1 M)	1 (KBr)	2×10^{-3} M	3–6		4.58 ± 0.02	
	pH	Br^- (1 M)	1 (NaBr)	2×10^{-3} M	3–6		4.37 ± 0.02	
	sp, pH	Br^- (0.01 M)	1 ($NaClO_4$)	1×10^{-3} M	1–3		4.34 ± 0.08	
	sp, pH		1 ($NaClO_4$)	8×10^{-4} M	0–7		0.84 ± 0.04	
2,3,2-tet	pH	SCN^- (0.1 M)	1 ($NaClO_4$)	2×10^{-3} M	3–5	46.3 ± 0.1		
	sp, pH	SCN^- (0.1 M)	1 ($NaClO_4$)	2×10^{-3} M	3–5	46.3 ± 0.1		
	sp, pH	Br^- (0.05–0.2 M)	1($NaClO)_4$	1×10^{-3} M	1–2	46.5 ± 0.2 [9]		
2,4,2-tet	pH	SCN^- (0.1 M)	1 ($NaClO_4$)	2×10^{-3} M	4–7	42.0 ± 0.1		
	sp, pH	SCN^- (0.1 M)	1 ($NaClO_4$)	2×10^{-3} M				
2,5,2-tet	pH	bipy (0.004 M)	0.1 (KNO_3)	2×10^{-3} M	3–8	37.9 ± 0.5[c]		
2,6,2-tet	pH	bipy (0.004 M)	0.1 (KNO_3)	2×10^{-3} M	3–7	38.14 ± 0.3[e]		
	calc[d]		1 (KNO_3)			38.9 ± 0.3		
2,2,2-dpa	sp, pH	Br^- (1 M)	1 (NaBr)	$2.7–5.7 \times 10^{-4}$ M	0–0.4	35.6 ± 0.1		
2,3,2-dpa	sp, pM	Br^- (1 M)	1 (NaBr)	$0.5–2.5 \times 10^{-4}$ M	0–0.7	39.1 ± 0.1		
2,4,2-dpa	sp, pH	Br^- (1 M)	1 (NaBr)	$0.28–2.8 \times 10^{-4}$M	0.8–1.52	37.0 ± 0.1		
2,5,2-dpa	sp, pH	Br^- (1 M)	1 (NaBr)	1×10^{-5} M	0.3–1.4	34.7 ± 0.2[f]		36.3 ± 0.3
	pH	bipy (0.004 M)	0.1 (KNO_3)	2×10^{-3} M	3–7	34.0 ± 0.2		
	calc[d]		1 (KNO_3)			34.7 ± 0.2		
2,6,2-dpa	sp, pH	Br^- (1 M)	1 (KBr)	1×10^{-6} M	0.5–1.8	<34.7[g]		

[a] 1 ($NaClO_4$): the ionic strength 1 is held by addition of the inert salt shown in parentheses, taking into consideration all other components present in the solution, in particular the sometimes high concentrations of the strong acid ($HClO_4$) and of salts of the auxiliary ligand. [b] $K_{PdX(HL)} = [PdX(HL)]/[Pd][X][H][L]$. [c] Estimated from few measurements because of the small ligand sample. [d] Calculated value of K_1 for I = 1 (KNO_3) from the corresponding value for I = 0.1 (KNO_3), assuming that the difference in $\log K_1$ for the two media is identical with that observed for the copper(II) complexes of 2,2,2-tet, *i.e.* 0.74. [e] $\log([Pd(H_2L)bipy]/([Pd][H]^2[L][bipy])) = 54.5$. [f] $[PdBr_2(HL)]/([PdL][Br]^2[H]) = 10^{2.5}$; $[PdBr_2(H_2L)]/([PdL][Br]^2[H]) = 10^{3.5}$. [g] Because of the low solubility of the complex only a limiting value can be given.

(see Table 8). In the case of the aromatic amines, on the basis of ϵ_{mol}, the steric strain is larger for $n \leqslant 3$ than that for the complexes of the aliphatic amines. This is also expected, because of the repulsion in the complex $[PdL]^{2+}$ between the two H atoms of the pyridine systems in α-position. In this context it should be pointed out that in the complexes $[PdL_n]^{2+}$, where L is pyridine and n = 1 and 2, the molar absorptivity at λ_{max} is twice as large as that of corresponding complexes where $L = NH_3$. Lack of data prevents the comparison for the corresponding species for n = 3 and 4.

The Stability Constants

The stability constants of the 1:1 complexes $[PdL]^{2+}$ (Table VI) are all very high and correspond to systems in which, under normal conditions, the solutions contain only the complex $[PdL]^{2+}$ which is completely formed even in 1 M $HClO_4$ solution. For this reason such studies are only possible if instead of the palladium(II) aquation some of its complexes are used as reference. Among these, complexes of ligands which, in the pH range used, are not protonated in aqueous solution are especially efficient. For these reasons we have used the complexes with bromide and thiocyanate ions under conditions in which $[PdBr_4]^{2-}$ and $[Pd(SCN)_4]^{2-}$, respectively, are present. The stability constants β_4 of $[PdBr_4]^{2-}$ and $[Pd(SCN)_4]^{2-}$ have been obtained by us [4]; for the former complex our value is identical with that given by Elding [5] (25 °C, I = 1 ($HClO_4$) $\log\beta_4 = 14.94$). Taking into consideration the protonation equilibria of the ligands with their overall constant K_p it should be possible in 1 M HSCN solutions to obtain stability constants by ligand exchange up to *ca.* $10^{\log\beta_4(SCN)+\log K_p}$, *i.e.* 14 orders of magnitude larger with respect to K_1 for the most stable $[Pd(2,3,2\text{-tet})]^{2+}$. Another ligand used for such studies is α,α′-bipyridyl, for which the overall constant β_2 was obtained by us for I = 0.1 (KNO_3) [8]. Some complications arise from the use of these ligands because mixed complex formation is sometimes observed.

The values of the equilibrium constants determined are given in Table VI, where each line corresponds to a different series of measurements and contains the constants obtained directly. For several systems different methods are used but all the results are in good agreement. The mean values of $\log K_1$ are plotted against n in Fig. 5 and the corresponding values for the copper(II) complexes are also given for comparison. For n = 2, 3 and 4 the trend is the same in all cases. The ligands for n = 3 form the more stable complexes as already found for 2,3,2-tet [1], [7] and 2,3,2-dpa [2]. The change in $\log K_1$ with change of n is proportional to the absolute value of their constant, *i.e.* its change is more significant for the more stable palladium(II) complexes. On the contrary, for $n \geqslant 4$, the change in $\log K_1$ is more drastic for copper(II) than for palladium(II) complexes.

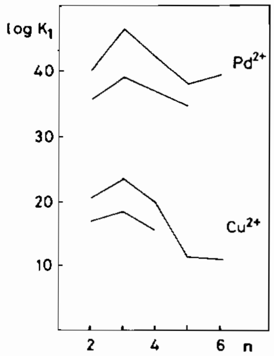

Fig. 5. Stability constants of the 1:1 Pd(II) and Cu(II) complexes of the tetraamines against the number n of $-CH_2-$ of the alkylene chain.

For the latter cation with both ligand series only mononuclear complexes have been observed up to now; the same situation has also been found for the higher EDTA homologues [3]. A *trans* coordination of the two middle N atoms could also explain this particular trend, whereas for copper(II) polynuclear species are also found with all three series of ligands [9].

The 1:1 palladium(II) complexes reported here, in the presence of strong acids, behave analogously to the corresponding complexes of the 3d divalent cations [1]. Only the complexes of the (more basic) aliphatic amines form acids: $[Pd(HL)]^{3+}$ for n = 2 and $[Pd(H_2L)]^{4+}$ for $n \geqslant 4$. The former case was already discussed in relation of the protonation equilibria under 3.1. and under 4.1. The diprotonic acids $[Pd(H_2L)]^{4+}$ seem to form $[PdL]^{2+}$ in one step because of the large chelate effect with ethylenediamine, both N donors of each such groups are coordinated or protonated together [1]. The pH value for half neutralization ($[Pd(H_2L)] = [PdL]$ is ~0 for the complex with 2,4,2-tet and 2.35 for that of 2,6,2-tet.

In order to compare the binding capacity of different ligands forming stable 1:1 complexes with a given cation at different pH values it is usual to plot the negative logarithm of the concentration of the free metal ion $pM = -\log[M]$ for buffered solutions containing equal amounts of the 1:1 complex and the free ligand. Such a representation is given in Fig. 6. As the complex is practically formed completely, pM is independent of the total concentration of the two species. This is the case for the complexes of all ligands under consideration over the whole pH range of the plot. These data show the better sequestering power of the tetraamines with respect to that of the aminopolycarboxylates, and make evident the preference of the palladium(II) cation for N_4 relative to the N_2O_2 donors. Because

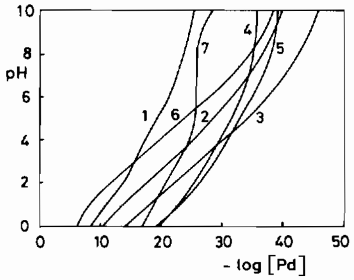

Fig. 6. Sequestering of palladium(II) ion for: (a) (1) EDTA, (2) 2,2,2-tet, (3) 2,3,2-tet, (4) 2,2,2-dpa, and (5) 2,3,2-dpa with $[L]_t = 2[Pd]_t$, and (b) (6) en, and (7) bip with $[L]_t = 3[Pd]_t = 3 \times 10^{-3}$ M; (en = ethylenediamine).

of the impossibility to determine directly the stability constants of complexes which do not dissociate in measurable amount in 1 M $HClO_4$, it has been suggested [6] that it would be easier to measure the enthalpy of complex formation. This is normally not the case, because the formation of palladium(II) complexes needs a long time for equilibration. In fact no results obtained using this approach have appeared. These difficulties can be overcome more simply as in the cases described here, *i.e.*, using an indirect method with inclusion of an auxiliary ligand, as long as its complex is not completely decomposed in presence of the investigated ligand and of 1 M $HClO_4$. This was never found to be the case, for all complexes investigated, when thiocyanate was used.

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