Palladium (II) Complexes

I. Spectra and Formation Constants of Ammonia and Ethylenediamine Complexes

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At 25°C in a medium of 1 M ionic strength (mainly $NaClO_4$) the formation constants for palladium(II) ammonia complexes have been determined:

$\log K_1 = 9.6$, $\log K_2 = 8.9$, $\log K_3 = 7.5$ and $\log K_4 = 6.8$. The absorption spectra show small deviations from the rule of "average environment". The relatively high intensity may be correlated with the weakly pronounced characteristic coordination number 2, and the $Pd(NH_3)_2(H_2O)_2^{2+}$ seems to be mainly the *cis*-isomer. The formation constants for ethylenediamine complexes are $\log K_1 > 20$ and $\log K_2 = 18.4$. The determination of the very large constants has only been possible because the solid compounds $Pd(NH_3)_4ts_2$ and $Pd\ en_2ts_2$ ($ts^- = p$-toluenesulphonate) can be prepared, and because the aqua ion is shown to be readily accessible by dissolving $PdSO_4$ in at least 0.1 M $HClO_4$. Attempts to make $Pd(H_2O)_4^{2+}$ described in the literature have most frequently produced brown solutions with far too strong light absorption.

The reactions of $PdCl_4^{2-}$ with Br^-, I^-, and OH^- are very rapid. In the latter case, a brown hydroxide is precipitated somewhat similar to Fe(III) and Tl(III). It is amphoteric, redissolving in 1 M OH^- to a nearly colourless species, possibly $Pd(OH)_4^{2-}$, and having a band at 368 mμ with $\varepsilon = 165$. One may remove Cl^- from this solution with freshly prepared Ag_2O and adding the filtrate to excess perchloric acid. However, as we shall see below, much easier methods exist for preparing satisfactory Pd(II) perchlorate solutions. On the other hand, the (partly colloidal) solutions of the brown hydroxide in perchloric acid have much higher extinction and precipitate slowly dark decomposition products. Boiling of K_2PdCl_4 produces insoluble K_2PdCl_6,

and surprisingly enough, Na_2PdCl_4 produces brick-red Na_2PdCl_6. Sundaram and Sandell[1] heated Pd with fuming HNO_3 and 60 % $HClO_4$ and obtained a reasonable spectrum (380 mμ, $\varepsilon \sim 80$) but their method is slightly dangerous. Livingstone[2] obtained crystalline, and highly hygroscopic, $[Pd(H_2O)_4]$ $(ClO_4)_2$ which has a band at 382 mμ (when dissolved in 1 M $HClO_4$) but having $\varepsilon = 200$ which is either an error or indicates strongly absorbing impurities. Izatt, Eatough and Christensen[3] give $\varepsilon = 84.1$ for the solution in 5.8 M $HClO_4$. Many people have reported spectra of the coffee-like brown solutions; thus, 400 mμ and $\varepsilon = 170$ has been suggested.[4] There is no doubt that nitrate solutions have higher bands at lower wave-numbers than the aqua ion; this is comparable to the behaviour of the analogous silver(II) aqua ion.[5]

Kane[6] reported in 1842 that palladium(II) sulphate can be prepared by boiling powdered Pd with a mixture of HNO_3 and H_2SO_4. The material exists as a brick-red, anhydrous and as a brown, partly hydrated, form. The former produced by prolonged boiling with H_2SO_4 is rather unreactive and dissolves only by agitation for several hours in 1 M $HClO_4$. The hydrated form containing until $PdSO_4,2H_2O$ is highly hygroscopic. The yellow solution in 1 M $HClO_4$ (0.01 M Pd(II) and below) has the same spectrum before and after addition of $Ba(ClO_4)_2$ and filtering off the precipitated $BaSO_4$. No inner-sphere sulphate complexes are formed at this concentration with a significant change of the spectrum. The shoulder ($\varepsilon = 62$) at 410 mμ is a genuine characteristic of the tetra-aqua ion; it is comparable to shoulders at 950 mμ for the copper(II) and at 575 mμ (maximum 475 mμ) for the silver(II) aqua ions.[5] When $PdSO_4$ is dissolved in 0.1 M $HClO_4$, a slightly higher ε (84) is observed at 380 mμ, but the solution is no longer stable, and after a week starts precipitating the brown material. Izatt et al.[3] indicate that the hydrolysis of Pd(II) involves mononuclear complexes like those of Hg(II) and of Tl(III), and with log $K_1 = 13.0$ and log $K_2 = 12.8$ for the hydroxo complexes. However, we tend to believe that the almost instantaneous formation of mononuclear hydroxo complexes proceeds to a somewhat smaller extent, and that, on the other hand, the polynuclear or even colloidal hydroxo complexes are formed slowly with much higher formation constants, much in the same way as is the case for Rh(III) and for Cr(III) close to the boiling point of water.

FORMATION CONSTANTS OF AMMONIA COMPLEXES

We prepared a solution of 0.5 M K_2PdCl_4 in 10 M NH_3 (the intermediate pink solid formed being Vauquelin's salt $[Pd(NH_3)_4][PdCl_4]$) and found that neither univalent anions such as ClO_4^- or BF_4^- nor bivalent anions such as sulphate, chromate, oxalate, phthalate, naphthalate, . . . produced any crystallization after one day. However, $ts^- = p$-toluenesulphonate (frequently called "tosylate") turned out to form a rather insoluble, nicely crystalline, white $[Pd(NH_3)_4]ts_2$. Fig. 1 gives the formation curve,[7] i.e. the average number $\bar{n}$ of ligands per palladium central ion as a function of $pNH_3 = -\log_{10} [NH_3]$. The points having $\bar{n}$ larger than 1 have been determined by adding a quantity of a solution, 0.1 M $HClO_4$, 0.9 M $NaClO_4$ to a solution between 2.5 and 12 mM $Pd(NH_3)_4ts_2$ and 1 M $NaClO_4$. Actually, the salt is not soluble to a higher
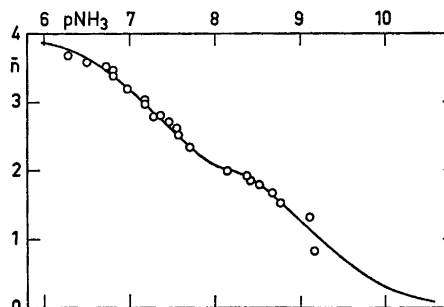
Fig. 1. Formation curve for palladium(II) ammonia complexes at 25°C in 1 M NaClO$_4$. The curve for $\bar{n}$ below 1 has been calculated from log $K_1 = 9.6$ determined in 1 M HClO$_4$.

extent than some 6 mM if no further acid is added. In principle, the points are directly given by [H$^+$] being measured *via* the pH value, $\bar{n}$ being 4—([NH$_4^+$]/C_{Pd}), and (the very small) [NH$_3$] related to the other quantities

$$pNH_3 = 9.36 - \log_{10}[NH_4^+] - pH \tag{1}$$

since the acidity constant of NH$_4^+$ was determined to 9.36 in 1 M NaClO$_4$ at 25°C. However, two main difficulties prevent the ready evaluation of the points of the formation curve. For values of $\bar{n}$ above 2, the equilibrium for dissociation of Pd(NH$_3$)$_4^{2+}$ by H$^+$ is established after some 20 to 40 min (the development during the first 12 min is shown on Fig. 2) and for $\bar{n}$ values below 2, the reaction takes many hours. The kinetic aspects of this question are discussed below. The points of Fig. 1 are obtained in most cases from solu-
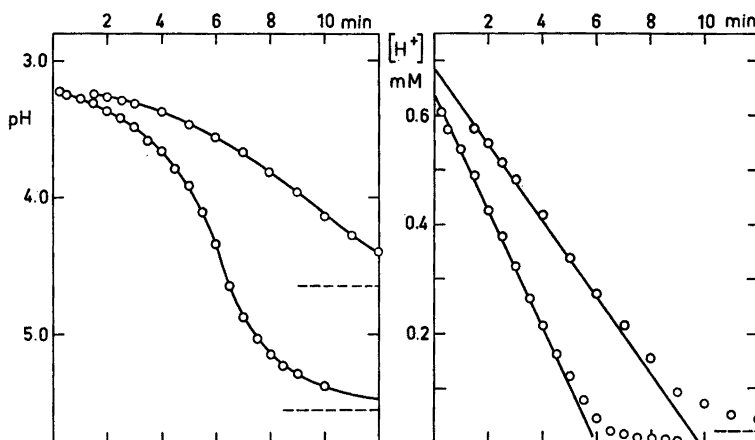

Fig. 2. Left-hand: evolution of pH with time of a solution originally 2.47 mM Pd(NH$_3$)$_4$ts$_2$ and 1.17 mM HClO$_4$ in 1 M NaClO$_4$ at 25°C (final $\bar{n}=3.52$ and pH$=5.56$) and of another solution having $C_{Pd}=2.43$ mM and originally having $\bar{n}=3.08$, 0.75 mM HClO$_4$ (final values $\bar{n}=2.77$, pH$=4.65$). No attempts were made to fix an absolute zero-point of time for the mixing of the initial solutions. Right-hand: the actual [H$^+$] as a function of the time. The slope of the lines corresponds to a production of 0.108 mM NH$_3$/minute in the former solution and 0.070 mM NH$_3$/minute in the latter solution.

tions which have been equilibrated at 25°C for two days after the acidifica-
tion, whereas some have been obtained by titration with successive amounts
of acid and waiting for the thermostated solution establishing its equilibrium.
It is important to note that there are no systematic deviations between points
obtained for different total concentrations of palladium C_{Pd} such as 2.5 and
10 mM. If hydroxo complexes influence the measurements, there is a depend-
ence of $\bar{n}$ on $[NH_4^+]$ for a given value of $[NH_3]$. Only the tetra-aqua ion seems
to be much more acidic than the mixed aqua-ammonia complexes. When
values of $\bar{n}$ of 1 are approached, the measurements become too uncertain as
seen from the scattering on Fig. 1. This is not so much caused by $[H^+]$ and
$[NH_4^+]$ becoming of comparable magnitude as because the pH scale is not
ideally represented below 2. This difficulty could be remedied by various
comparative measurements, but one would probably in any case have to use
radically different means to determine K_1.

As seen from Fig. 3, we choose to add 0.05, 0.1, and 0.2 M ammonium
perchlorate to 0.95, 0.9, and 0.8 M solutions of perchloric acid containing
5 mM $Pd(H_2O)_4^{2+}$. The value of $\bar{n}$ was estimated by various approximations.
The maxima of the observed spectra are a smooth, though not exactly linear
function of $\bar{n}$. The position 340 mμ of the very intense band of $Pd(NH_3)_2(H_2O)_2^{2+}$
is sufficiently well-known to allow Tsuchida's rule of average environment to
fix $Pd(NH_3)(H_2O)_3^{2+}$ at 360 mμ. Whereas the former argument indicates $\bar{n}$
between 0.3 and 0.4 for the solution 0.2 M NH_4ClO_4 (corresponding to log K_1
between 9.52 and 9.78 according to eqn. (1), if higher complexes are neglected),
the second argument allows $\bar{n}$ to be evaluated more accurately as 0.33 for
this solution. Fig. 3 gives the extrapolated spectrum for $Pd(NH_3)(H_2O)_3^{2+}$
thus obtained. The wavelength λ has been plotted, rather than the wave-
numbers on Figs. 4 and 5, in order to increase the accuracy of the small spectral
differences obtained from the recorder-paper. The equilibrium of the NH_4ClO_4
containing solutions was not perfect after one day, but stabilized after three
days. We found the necessity of avoiding the "coffee" products in solutions
containing substantial amounts of the tetra-aqua ion more imperative than
the disadvantage of replacing essentially 1 M $NaClO_4$ by 1 M $HClO_4$. It may
be noted that the same equilibrium solutions were obtained by decomposition
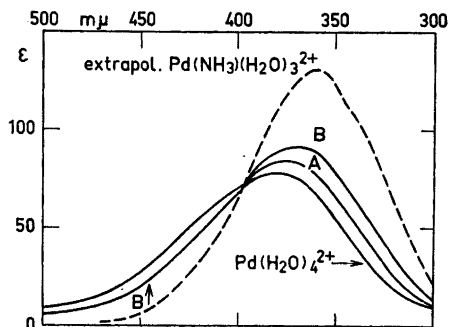of $Pd(NH_3)_4ts_2$ by mixtures of NH_4ClO_4 and $HClO_4$.

Fig. 3. Absorption spectra of $Pd(H_2O)_4^{2+}$
(in 1 M $HClO_4$) and of equilibrium solutions
at 25°C. A: 0.1 M NH_4ClO_4 and 0.9 M
$HClO_4$; B: 0.2 M NH_4ClO_4 and 0.8 M $HClO_4$.
The spectrum of $Pd(NH_3)(H_2O)_3^{2+}$ is ob-
tained assuming the solution B to contain
one part of this complex and two parts of
the tetra-aqua ion. The wavelength is
given in mμ.

The formation curve Fig. 1 shows some tendency toward the characteristic coordination number $N_C = 2$. Actually, the two parts above and below $\bar{n} = 2$ are each essentially statistical curves each for the uptake of two ammonia molecules. The provisional constants obtained from log $K_n' = pNH_3$ for $\bar{n} = n - \frac{1}{2}$ are for $n =$

$$1:\ 9.7 \qquad 2:\ 8.8 \qquad 3:\ 7.6 \qquad 4:\ 6.7 \qquad\qquad (2)$$

and have to be corrected via eqn. (5) on p. 38 of Ref. 7, which fortunately converges rapidly in our case. The final constants are

$$\log K_1 = 9.6 \qquad \log K_2 = 8.9 \qquad \log K_3 = 7.5 \qquad \log K_4 = 6.8 \qquad (3)$$

and are undoubtedly uncertain ± 0.1 unit of many different reasons. The most remarkable feature is the break at $\bar{n} = 2$, the ratio (K_2/K_3) being 25 and not the statistical value for quadratic complexes 2.25. On the other hand, (K_1/K_2) and (K_3/K_4) are both 5, just slightly higher than the value 4 appropriate for two statistical curves each involving two ligands.

The spectra of various ammonia complexes are given in Fig. 4. They are discussed below in a separate section.

FORMATION CONSTANTS OF ETHYLENEDIAMINE COMPLEXES

Only two complexes are expected of en$=NH_2CH_2CH_2NH_2$, viz. Pd en$_2{}^{2+}$ and (necessarily cis-) Pd en$(H_2O)_2{}^{2+}$. We prepared [Pd en$_2$]ts$_2$ which is somewhat more soluble than the tetrammine tosylate. This salt decomposed slowly in 1 M HClO$_4$ (thus, the band moved to 288 mμ with $\varepsilon = 222$ after 20 min and showed the next day a band at 347 mμ having $\varepsilon \sim 190$). On the other hand, adding 0.05 M enH$_2{}^{2+}$ to 0.004 M Pd$(H_2O)_4{}^{2+}$ produced after some days (see Fig. 5) $\varepsilon = 164$ at 341 mμ with a shoulder obviously due to Pd en$_2{}^{2+}$. Actually, we had no means to detect Pd$(H_2O)_4{}^{2+}$ produced by acid decomposition of
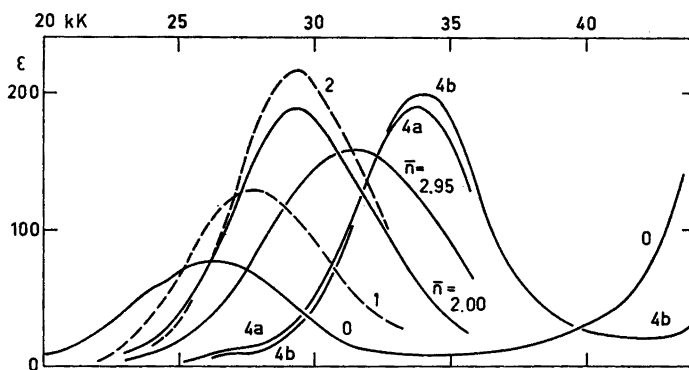

Fig. 4. Absorption spectra of 0: Pd$(H_2O)_4{}^{2+}$ and 1: Pd$(NH_3)(H_2O)_3{}^{2+}$ (see Fig. 3); and of equilibrium solutions in 1 M NaClO$_4$ at 25°C having $\bar{n} = 2.00$ and $n = 2.95$; 2: Pd$(NH_3)_2(H_2O)_2{}^{2+}$ calculated from eqn. (6); 4a: 5 mM Pd$(NH_3)_4$ts$_2$ in 1 M NaClO$_4$; 4b: Pd$(NH_3)_4{}^{2+}$ measured in 2 M NH$_3$. The wavenumber is given in kK ($= 1000$ cm^{-1}).
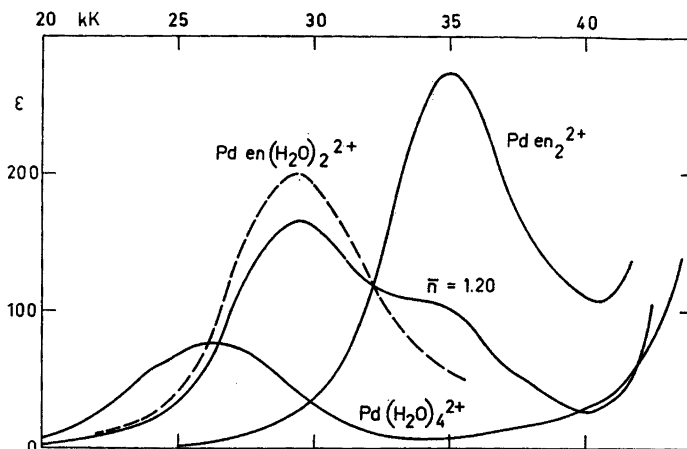
Fig. 5. Absorption spectra of Pd en$_2^{2+}$ and of an equilibrium solution at 25°C (0.05 M enH$_2^{2+}$, 0.95 M H$^+$, 1.05 M ClO$_4^-$). The spectrum of Pd en(H$_2$O)$_2^{2+}$ is calculated from the assumption that the latter solution contains four parts of the mono-complex and one part of the bis-complex.

Pd en(H$_2$O)$_2^{2+}$ in any solution, not even in 9 M HClO$_4$. We only conclude that log K_1 >20. Obviously, the activity corrections in extremely strong acids would not make it particularly interesting to make a great effort to determine K_1. On the other hand, we were lucky with the solutions equilibrated containing 0.05 M enH$_2^{2+}$ showing 20 % bis- and 80 % mono-complex, and 0.2 M enH$_2^{2+}$ (0.8 M H$^+$) showing 60 % Pd en$_2^{2+}$ and 40 % Pd en(H$_2$O)$_2^{2+}$. In both cases, log K_1 turns out to be *18.4*, since pK_1 and pK_2 of enH$_2^{2+}$ and enH$^+$ are known [7] to be 7.5 and 10.2 in media such as ours, giving p(en)=18.2 and 19.0 in the two solutions. This is the largest known formation constant of any ethylenediamine complex.

A comparison with eqn. (2) shows the chelate effect

$$Chel = 18.4 - 7.5 - 6.8 = 4.1 \qquad (4)$$

when the second ethylenediamine ligand is compared with the third and fourth ammonia ligands. 3d group complexes containing a partly filled shell generally [8] has *Chel* between 2 and 3 logarithmic units, whereas Zn(II) and Cd(II) run around 1 unit. The latter contribution is mainly due to entropy terms, whereas the former cases involve contributions from "ligand field" stabilization as well.[9] As discussed below, there is every reason [10] to expect the latter type of quantity to be 1.5 times as large in the 4d as in the corresponding 3d group complex. If *Chel* is between 4 and 5 units for the two first ligating nitrogen atoms, log K_1 for Pd en(H$_2$O)$_2^{2+}$ should be between 23.5 and 24.5.

PRELIMINARY KINETIC REMARKS

As seen from Fig. 2, we frequently found the pH value of an acidified solution of $Pd(NH_3)_4^{2+}$ increasing slowly, and then, after 5 or 10 min, suddenly increasing rapidly, and finally adapting the equilibrium value after many more minutes. Actually, there is nothing auto-catalytic about this behaviour; as seen from Fig. 2, the hydrated proton concentration $[H^+]$ simply decreased as a linear function of time until the reverse reaction of the minute concentration $[NH_3]$ finally competes successfully close to the equilibrium. Said in other words, the palladium complex maintains a constant production of ammonia independent of pH in the range studied, corresponding to the S_N1 dissociation which is frequent for Cr(III) ammine complexes. However, whereas some of the intermediate Cr(III) aqua-ammonia complexes dissociate more rapidly [11] than $Cr(NH_3)_6^{3+}$, we find that the dissociation rate k_{-4} of $Pd(NH_3)_4^{2+}$ is somewhat higher than k_{-3} of $Pd(NH_3)_3H_2O^{2+}$. Analysis of several independent experiments indicate the approximate rate constants:

$$
\begin{array}{ccc}
 & 25°C & 20°C \\
k_{-4} & 7.8 \times 10^{-4} \text{ sec}^{-1} & 4.0 \times 10^{-4} \text{ sec}^{-1} \\
k_{-3} & 4.0 \times 10^{-4} \text{ sec}^{-1} & 1.7 \times 10^{-4} \text{ sec}^{-1}
\end{array}
\tag{5}
$$

the dissociation of $Pd(NH_3)_2(H_2O)_2^{2+}$ is so much slower that k_{-2} could not be determined from our titrations. The values in eqn. (5) are slightly smaller than the limiting values $k_{-4}=11 \times 10^{-4}$ and $k_{-3}=9 \times 10^{-4}$ sec^{-1} measured at 25°C and ionic strength 1 M by Reinhardt and Sparkes [12] who varied $[Cl^-]$ as well and found a linear dependence, the tetrammine dissociating twice as rapidly at 0.15 M Cl$^-$ and the triammine at 0.03 M Cl$^-$. Most other kinetic studies of palladium(II) complexes have also involved chloride and amines simultaneously [13,14] and have allowed [14] the detection of unidentate, protonated ethylenediamine as an intermediate step. Reinhardt and Sparkes [12] give the complexity constant of replacement of ammonia by chloride $Pd(NH_3)_4^{2+}-$ $\rightarrow Pd(NH_3)_3Cl^+$ as 1.6×10^{-5}. When combined with the previously [15] reported aquation constant 10^{-3} for $Pd(NH_3)_3Cl^+$ (which is rather on the low side in our opinion) log K_4 would be 7.8 and not 6.8 as in eqn. (3).

ABSORPTION SPECTRA

Table 1 combines data on definite palladium(II) complexes. The spectra of $PdCl_4^{2-}$ and $PdCl_2(H_2O)_2$ have only been published in a technical report,[16] where Pd(II) chemistry was discussed as well. The extrapolation to $Pd(NH_3)(H_2O)_3^{2+}$ shown on Fig. 3 was discussed above. On Fig. 4, the spectrum of $Pd(NH_3)_2(H_2O)_2^{2+}$ is obtained from the formation constants and the observed spectrum of a solution having $\bar{n}=2.00$ ($C_{Pd}=4.54$ mM; pH$=3.26$; $[NH_4]=9.1$ mM; pNH$_3=8.14$) which must contain a seventh of its total palladium concentration C_{Pd} as the mono-ammine, $\frac{5}{7}C_{Pd}$ as the diammine and $\frac{1}{7}C_{Pd}$ as the tri-ammine.

The linear relations

$$
\varepsilon_{obs} = \tfrac{1}{7}\ \varepsilon_1 + \tfrac{5}{7}\ \varepsilon_2 + \tfrac{1}{7}\ \varepsilon_3
$$
$$
i.e.\ \ \varepsilon_2 = \varepsilon_{obs} + \tfrac{1}{5}[2\varepsilon_{obs} - \varepsilon_1 - \varepsilon_3]
\tag{6}
$$

Table 1. Wavelengths λ in mμ, wavenumbers σ in kK ($=1000$ cm^{-1}) and molar extinction coefficients ε of the first maximum of palladium(II) complexes. The half-widths towards smaller, $\delta(-)$, and larger, $\delta(+)$, wavenumbers are also given in kK. The shoulder at 24.4 kK of the tetra-aqua ion has been disregarded.

	λ	σ	ε	$\delta(-)$	$\delta(+)$
$PdCl_4{}^{2-}$	474	21.1	166	1.6	2.5
$PdCl_2(H_2O)_2$	418	23.9	210	2.3	2.3
$Pd(H_2O)_4{}^{2+}$	379	26.4	78	(3.5)	3.1
$Pd(NH_3)(H_2O)_3{}^{2+}$	360	27.8	130	2.8	2.4
$Pd(NH_3)_2(H_2O)_2{}^{2+}$	341	29.3	215	2.6	3.2
$Pd(NH_3)_3(H_2O)^{2+}$	~317	~31.6	—	—	—
$Pd(NH_3)_4{}^{2+}$	295	33.9	200	2.5	2.6
Pd en$(H_2O)_2{}^{2+}$	340	29.4	200	2.9	3.3
Pd en$_2{}^{2+}$	286	35.0	285	2.5	3.6

are used under the second form on Fig. 3. It is not possible to derive the spectrum of $Pd(NH_3)_3(H_2O)^{2+}$ as readily, because an equilibrium solution having $\bar{n}=3$ would contain about half of the palladium as tri-ammine and about a quarter of each of the two adjacent complexes. Fortunately, $(\varepsilon_2+\varepsilon_4)$ tends to be a roughly constant function close to the maximum of ε_3 and the spectrum is seen to have a maximum close to 31.6 kK. The spectra of $Pd(NH_3)_4ts_2$ in 1 M $NaClO_4$ (or in H_2O) are slightly different from that of the solution of $PdSO_4$ in 2 M NH_3. As seen from Fig. 4, the small difference can hardly be ascribed to dissociation to $Pd(NH_3)_3(H_2O)^{2+}$ which anyhow should proceed to the extent of less than 1 % according to the formation constants determined, but it may be due to some kind of a solvent effect. As seen from Fig. 5, there is hardly any practical difficulty in obtaining reasonably accurate spectra of Pd en$(H_2O)_2{}^{2+}$ and Pd en$_2{}^{2+}$.

The most striking result of Table 1 is the small deviations from Tsuchida's rule of average environment. The shifts of the maximum by introduction of each new ligand are in kK:

$$NH_3: \quad 1.4 \quad 1.5 \quad \sim\!2.3 \quad \sim\!2.3$$
$$en: \quad\quad 3.0 \quad 5.6 \tag{7}$$

These deviations can be compared with the spectra [17,18] of $RhCl_n(H_2O)_{6-n}{}^{+3-n}$ having their first maximum (in kK):

$$n = \quad\; 0 \quad\;\; 1 \quad\;\; 2 \quad\;\; 3 \quad\;\; 4 \quad\;\; 5 \quad\;\; 6$$
$$\quad\quad 25.5 \quad 23.5 \quad 22.4 \quad 21.3 \quad 20.4 \quad 19.8 \quad 19.3 \tag{8}$$

modifying slightly previous conclusions [10] based on Tsuchida's rule. It can be seen from Table 1 that the half-coordinated chloro complex $PdCl_2(H_2O)_2$ has a higher wavenumber than the mean value of $PdCl_4{}^{2-}$ and $Pd(H_2O)_4{}^{2+}$ whereas $RhCl_3(H_2O)_3$ shows the opposite deviation according to eqn. (8).

Though eqn. (7) suggests an influence of $N_C=2$ for Pd(II), it actually has the opposite sign of what one would expect from a "ligand field" stabilization model. Somewhat arbitrarily, one may assume that the coefficient to the first spin-allowed transition is -1.6 like it is -2.4 for low-spin octahedral

Table 2. "Ligand field" stabilizations calculated from the wavenumbers given in Table 1. Actually, $1.6(\sigma - \sigma_{\mathrm{aqua}})$ is translated to logarithmic units of formation constants at 25°C.

	$\sigma - \sigma_{\mathrm{aqua}}$	"ligand field" stabilization	log β_n		
			observed	corrected statistics	corrected l.f.s.
$PdCl_4{}^{2-}$	-5.3 kK	-17.8 units	12	12	~29.8
$PdCl_2(H_2O)_2$	-2.5	-8.4	8	7.2	~15.6
$Pd(NH_3)(H_2O)_3{}^{2+}$	$+1.4$	$+4.7$	9.6	9.0	4.3
$Pd(NH_3)_2(H_2O)_2{}^{2+}$	$+2.9$	$+9.8$	18.5	17.7	7.9
$Pd(NH_3)_3(H_2O)^{2+}$	~5.2	~17.5	26.0	25.4	7.9
$Pd(NH_3)_4{}^{2+}$	$+7.5$	$+25.2$	32.8	32.8	7.6
$Pd\ en(H_2O)_2{}^{2+}$	$+3.0$	$+10.1$	~23.8	~24.1	~14.0
$Pd\ en_2{}^{2+}$	$+8.6$	$+28.8$	~42.2	~42.2	~13.4

d^6 systems. Table 2 shows "ligand field" stabilizations translated to logarithmic units of formation constants at 25°C, and the observed values of log β_n without and with corrections for the purely statistical effects.[7] It is obvious that this treatment only has qualitative validity; however, it is striking that without the "ligand field" effects, the two first ammonia ligands would have had log $\beta_2 = 8$ and the first ethylenediamine ligand log $K_1 = 14$, quite similar to the values found [7,19] for Hg(II), whereas the third and fourth nitrogen ligating atoms would have log $K_n \sim 0$. However, in our opinion, it cannot be concluded that $N_C = 2$ corresponds to an intrinsic tendency toward linear or *trans*-quadratic coordination of palladium(II). The main argument is the very high intensity (*cf.* Figs. 4 and 5) of $Pd(NH_3)_2(H_2O)_2{}^{2+}$ and $Pd\ en(H_2O)_2{}^{2+}$ compatible with predominant *cis*-configuration of the former complex. It has frequently been argued that $Pd(II)X_2Y_2$ are most stable in *trans*-configuration, as is true for crystalline $Pd(NH_3)_2Cl_2$. However, the kinetic evidence presented here suggests that the two ammonia molecules *trans* to other ammonia ligands leave at first, making it plausible that $Pd(NH_3)_2(H_2O)_2{}^{2+}$ is *cis*. Further on, Cu(II) and Pd(II) complexes have far higher intensities of their inter-sub-shell transitions than can be explained from the low wavenumber of electron transfer bands alone.[20] One simple explanation would be an antistatistical tendency of the central atom being out of the plane of the four strongly bound ligands, forming a quadratic pyramid of symmetry C_{4V}. This might conceivably also explain the observation [21] of $Cu(NH_3)_5{}^{2+}$. However, the absence of a centre of inversion might have another origin. Mr. Gerhard Degischer, ETH, Zürich, suggested to one of us the possibility D_{2d} (like in many compounds containing $CuCl_4{}^{2-}$) of two ligands in *trans*-position being above and two below the average plane. In our opinion, the ammine complexes studied here might suggest a third possibility, *viz.* C_{2v} with two short and two long ligand distances. It may be mentioned that the nitrate-dimethylsulphoxide complex [22] $Pd(ONO_2)_2((CH_3)_2SO)_2$ contains *cis*-$Pd(II)O_2S_2$.

The absorption growing up above 45 kK of $Pd(H_2O)_4{}^{2+}$ (Fig. 4) is not due entirely to hydrolysis products. Actually, the solution in 0.1 M $HClO_4$ has only moderately higher ε (120 at 250 mμ; 200 at 240 mμ) though the concentra-

tion of hydroxo complexes must be at least ten times higher. Since the first strong electron transfer band [10,16,23] of $PdCl_4^{2-}$ occurs at 35.8 kK, $i.e.$ 14.7 kK above the first spin-allowed $4d^8$-transition, and since aqua ions are known [24] to have electron transfer bands 16 kK higher than the corresponding chloro complexes, $Pd(H_2O)_4^{2+}$ is expected to have an electron transfer band at $26.4+14.7+16 \sim 57$ kK, quite compatible with the absorption edge observed, when the very large half-width $\delta(-)$ of the electron transfer bands of aqua ions is taken into account. The more reducing character of ammonia and ethylenediamine is rather accurately compensated by the increasing energy of the (x^2-y^2) orbital, and the electron transfer transitions are expected at roughly the same wavenumbers as for the aqua ion.

EXPERIMENTAL

The pH measurements were made on a Philips PR 9400 pH-meter with a glass electrode and a calomel electrode. Actually, the presence of Cl^- in the palladium-containing solution would be disastrous, and it was thought at first to use mercury sulphate or thallium-amalgam reference electrodes. However, in both cases, the effects of contact with the solution are nearly as bad as for the calomel electrode, and it turned out that a U-tube (internal diameter 0.6 cm) filled with 1 M $NaClO_4$ and stoppered with two plugs of kleenex tissue connecting two 50 ml beakers, one containing the Pd-solution and glass electrode at a tiny bit of a higher level than the other containing 1 M $NaClO_4$ and the calomel electrode, was a more satisfactory arrangement. The pH values were standardized by a solution 5 mM $HClO_4$ in 1 M $NaClO_4$ giving 2.30 per definition, but were also controlled by a titration of 0.1 M $HClO_4$, 0.9 M $NaClO_4$ with varying amounts of 1 M NaOH, 1 M $NaClO_4$. The $pK=9.36$ for NH_4^+ was determined from the titration curve of 0.1 M NH_4ClO_4, 0.9 $NaClO_4$ with 1 M NaOH. The solutions were thermostated with flowing water at 25°C.

Great care was taken to avoid the presence of Cl^- in $NaClO_4$ (monohydrate, $p.a.$ Fluka) and the other materials used. A combined photochemical nephelometric detection of Cl^- with $AgClO_4$ in daylight was developed. 0.1 mM Cl^- rapidly produces a violet suspension, and smaller amounts can readily be estimated.

Palladium metal was supplied by Métaux Précieux, S.A. in Neuchâtel and by H. Drijfhout & Zoon, Amsterdam. 5.4 g Pd (0.05 g.atom) was dissolved in a mixture of 20 ml conc. HNO_3 and 10 ml conc. H_2SO_4. After boiling to copious fumes of SO_3, cooling produces brick-red powder (in strongly concentrated reaction mixtures) to brown crystallites (in the case of slightly water-containing acid). A typical analysis of the latter product (gravimetry as Pd dimethylglyoximate and as $BaSO_4$) is Pd 48.1 %, SO_4 43.5 %, very closely corresponding to $PdSO_4,H_2O$. The brick-red products are closer to anhydrous $PdSO_4$ and keep better. However, they are only slowly soluble in aqueous perchloric acid. Chapman and Sherwood [25] prepared a solution of Pd(II) in 0.8 M sulphuric acid for the purpose of spectrophotometric determination of Cl^- and Br^-.

$Palladium(II)$ $tetra$-$ammonia$ p-$toluenesulphonate.$ 3.3 g K_2PdCl_4 (10 mmoles) from H. Drijfhout & Zoon are heated 1 hour at 50°C with 100 ml 6 M NH_3 until the pink precipitate has completely redissolved. The lemon-yellow solution (containing some $Pd(NH_3)_3Cl^+$) is cooled to room temperature and turns colourless, at latest after addition of some 12 M NH_3. A solution of 5.7 g p-toluenesulphonic acid monohydrate (30 mmoles), $p.a.$ Fluka, in excess concentrated ammonia is added, and an almost quantitative yield of white crystals (not very wettable by water) of $Pd(NH_3)_4ts_2$ are obtained. (Found: Pd 20.7; C 32.83; H 5.12; N 10.65; S 12.37: $PdC_{14}H_{26}N_4O_6S_2$ requires: Pd 20.6; C 32.55; H 5.07; N 10.83; S 12.42). (Micro-analysis by Mr. Kurt Eder, Geneva).

$Palladium(II)$ bis-$ethylenediamine$ p-$toluenesulphonate.$ 3.3 g K_2PdCl_4 and 4 ml ethylenediamine monohydrate, Merck No. 946, in 50 ml H_2O are heated with stirring to complete dissolution. After cooling to room temperature, 5.7 g p-toluenesulphonic acid monohydrate in 10 ml H_2O is added. After some hours, the white crystals of $[Pd(NH_2CH_2CH_2NH_2)_2](CH_3C_6H_4SO_3)_2$ are filtered off and washed with water.

The anion ts⁻ has a benzene-like spectrum with a progression of narrow bands at 271, 266, 260.5, and 255 mμ having ε between 200 and 400. These bands prevent the palladium transitions from being readily measured below 275 mμ.

The absorption spectra were measured at least twice (one in each direction) on a Cary MS 14 recording spectrophotometer at the dispersion of 5 mμ per division of paper and the speed of ten divisions of paper per minute. 1 cm and 2 cm cells were used; the solvent in the reference beam was also measured once each day in the sample beam for control.

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