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Palladium(II) Complexes. II. Diethylenetriamine and Additional Ligands, Protons and Silver(I) Ions

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Though the reaction between $Pd(H_2O)_4^{2+}$ and the fully protonated diethylenetriamine $denH_3^{3+}$ is practically irreversible in acidic solution, it goes slowly through a bidentate intermediate. The residual position in the tridentate species shows unexpected chemical behaviour; thus, the addition of half an equivalent of OH^- suggests the presence of binuclear complexes. $Pd(den)_2^{2+}$ has two uncoordinated nitrogen atoms which can be protonated with pK values 6.1 and ~2.5 suggesting a hydrogen bond H_2NHNH_2 between the two loose ends. This is supported by the observation that one equivalent of Ag^+ added to the bis-complex retards the protonation by several units of pK. Ammonia is bound in $Pd(den)NH_3^{2+}$ with $\log K = 6.9$, and provisional kinetic studies have been performed.

Recently,[1] we determined formation constants for palladium(II) ammonia and ethylenediamine (=«en») complexes at 25°C in a 1 molar salt medium either consisting essentially of $NaClO_4$ or of a mixture of sodium perchlorate and perchloric acid. The results were:

$$NH_3:\ \log K_1=9.6;\quad \log K_2=8.9;\quad \log K_3=7.5 \text{ and } \log K_4=6.8$$

$$\text{en:}\ \log K_1>20 \text{ (probably 24)},\ \log K_2 = 18.4 \qquad (1)$$

According to Prue and Schwarzenbach[2] the protonation constants for the tridentate diethylenetriamine (= «den»; the abbreviation «dien» is slightly too olefinic for our taste) $NH_2CH_2CH_2NHCH_2CH_2NH_2$ are $\log K_n = 3.65$, 8.7 and 9.8 at great dilution and 4.9, 9.4 and 10.1 in 1 *M* $NaNO_3$ at 25°C. It is seen that the protonation of the central, secondary amine is strongly influenced by the salt solution. We find from titration curves in 1 *M* $NaClO_4$ at 25°C $\log K_1 = 4.7$, $\log K_2 = 9.2$ and $\log K_3 \sim 10$. Consequently, 1 m*M* $denH_3^{3+}$ at pH = 0 produces the free diethylenetriamine p(den) = 27.

There is no doubt that $\log K_1$ for the mono-diethylenetriamine complex is considerably larger than 27 and hence cannot be evaluated via conventional pH-measurements. When corrected for the logarithm of the molar water concentration[3] 1.74, the first three ammonia molecules in (1) are bound by a free energy represented by $9.6+8.9+7.5+5.2=31.2$; and in addition, a chelate effect about 4 units per ring containing two nitrogen atoms can be seen for the ethylenediamine complexes. Hence, $\log K_1$ for the $Pd(den)^{2+}$ is expected to be $26.0+8 \sim 34$, and steric stress would have to be very serious to decrease this value so much that $\log K_1$ can be measured.

Actually when the lemon-yellow solution of $Pd(H_2O)_4^{2+}$ in 1 *M* $HClO_4$ (prepared from $PdSO_4$ as previously described[1]) is added to 0.2 *M* $denH_3^{3+}$ in 0.4 *M* $HClO_4$, the maximum at 379 mμ (ε = 78) is gradually replaced by another maximum at 323 mμ (ε ~240) with a first-order kinetics with a half-time of 35 minutes. However, this species is transformed during a few days to another species having the maximum at 315.5 mμ (ε = 490) as seen on Figure 1. When compared with the maxima[1] of $Pd(H_2O)_2en^{2+}$ at 340 mμ (ε = 200) and of $Pd\ en_2^{2+}$ at 286 mμ (ε = 285) and in view of the moderate shift toward higher wavenumbers induced by formation of chelate rings,[4] the simplest interpretation of the two species involves the approximately quadratic chromophores $Pd^{II}N_2O_2$ and $Pd^{II}N_3O$. In acidic solution the former would be expected to occur in protonated $Pd(denH)(H_2O)_2^{3+}$ with one primary and one secondary amine bound in *cis*-position to the central atom, since a bridging *trans*-structure bound by the two terminal nitrogen atoms is highly improbable of reasons to become clear below.

However, the truth may be somewhat more complicated. Firstly, we have the general kinetic problem that the attack of $denH_3^{3+}$ on the Pd^{II} tetra aqua ion may produce a mixture of bidentate and tridentate species in a fixed proportion, which then rearranges to the tridentate form. It can be argued that the spectrum of the bidentate form would look rather unusual if it was a minor constituent of the mixture; but it may very well be the major component with a weaker band at 330 mμ, the isosbestic point being at 348 mμ. The reaction rate of formation of the bidentate species cannot involve a mechanism invoking the fixed concentration of $10^{-24.4}$ *M* den, and even $10^{-14.6}$ *M* $denH^+$ as effective reactant

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[1] L. Rasmussen and C. K. Jørgensen, *Acta Chem. Scand.*, *22*, 2313 (1968).

[2] J. E. Prue and G. Schwarzenbach, *Helv. Chim. Acta*, *33*, 985 (1950).

[3] J. Bjerrum, *Chem. Rev.*, *46*, 381 (1950).

[4] C. K. Jørgensen, *Acta Chem. Scand.*, *10*, 887 (1956).

involves a natural velocity of above 10^{11} sec^{-1} and is not likely. The slow rearrangement of the protonated bidentate form can be compared with recent studies by Mønsted and Bjerrum[5] of the deprotonation of unidentate enH^+ immediately followed by chelation in Pt^{II} complexes. In this connection, it may be mentioned that solid salts of $Cr(enH)enCl_3^+$ prepared by Werner have kept for 50 years.[6,7]

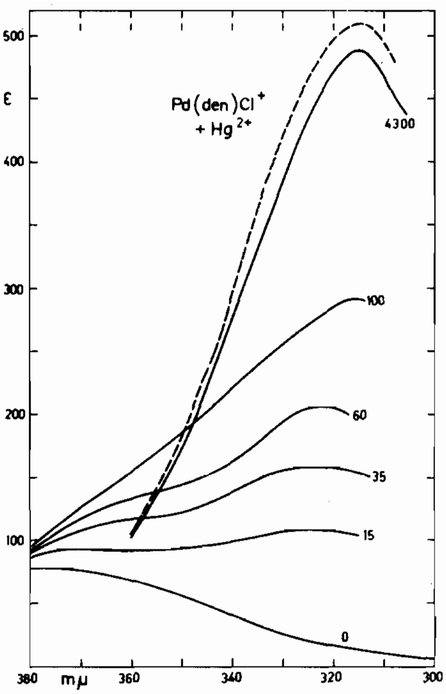

Figure 1. Absorption spectra of the palladium(II) aqua ion (marked O) and of mixtures, originally 2.5 m*M* $PdSO_4$, 0.1 *M* $denH_3^{3+}$, 0.7 *M* H^+, 1 *M* ClO_4^- after 15, 35, 60, 100 and 4300 minutes. The dashed curve refers to 2 m*M* [Pd(den)Cl]Cl in 1 *M* $HClO_4$ from which the chloride was removed with 5m*M* $Hg(ClO_4)_2$.

A much more unexpected problem arises in the case of the tridentate, final complex which is not necessarily planar $Pd(den)H_2O^{2+}$. The high extinction coefficient ε ~500 is already rather surprising. It was found previously[8] that the corresponding species in alkaline solution, presumably $Pd(den)OH^+$, has a maximum at a lower wavelength, 311 mμ (which is not entirely surprising because the solution of Pd(II) in strong base has the band at 368 mμ) and also a lower ε, which is entirely unheard of. Basolo *et al.*[9-11] isolated salts of many anion complexes $Pd(den)X^+$. The band of $Pd(den)Cl^+$ has been reported at 335,[8] 338[10] or 330 mμ[11,12] with ε values between 460 and 510. Schmidtke and Garthoff[13] recently improved the method of preparing [Pd(den)Cl]Cl and we treated their sample as a 2 m*M* solution in 1 *M* $HClO_4$ (the maximum at 327 mμ, ε = 440 indicates incipient aquation[11]) with 5 m*M* $Hg(ClO_4)_2$ and obtained a band at 316 mμ (ε = 510). The spectrum was unchanged after three days at room-temperature. We never succeeded in crystallizing any salt of the expected $Pd(den)H_2O^{2+}$ in analogy with the experience of Goddard and Basolo[14] who studied the N,N,N″,N″-tetraethylsubstituted ligand. These authors prepared $Pd(et_4den)H_2O^{2+}$ *in situ* having ε = 1140 at 329 mμ and ε = 11100 at 231 mμ (this intense band is due to electron transfer from the odd linear combination of σ-orbitals of the rather reducing tertiary amine lone-pairs) and, with pK = 7.5, forming $Pd(et_4den)OH^+$ with ε = 728 at 322 mμ and ε = 17900 at 212 mμ.

On several occasions we reacted [Pd(den)Cl]Cl, dissolved in water or dilute perchloric acid, with two equivalents of $AgClO_4$ in solution. The AgCl was filtered off, and the filtrate was titrated with OH^- and the pH was measured. The unexpected result was that half an equivalent of OH^- was taken up by the complex with pK = 6.8 and a second half equivalent of OH^- with pK ~8.9, though the latter value is slightly less reproducible. This observation cannot be a mistake for one equivalent of OH^- because the slopes of the titration curves are entirely different, and it would normally be taken as evidence for the formation of M_2OH^{3+} where M is $Pd(den)^{2+}$ and the presence of coordinated water molecules is neglected. However, it is diagnostic for such hydrolysis reactions that the apparent pK value of the aqua ion is a linear function of log[*M*] until Sillén's « mononuclear wall » is reached. When we repeated the experiment with 12 m*M* rather than 50 m*M* of freshly prepared de-chloridated MCl^+, the pK values were 6.9 and 8.5 in the former and 6.7 and 9.0 in the latter case. If M_2OH^+ were formed from two equivalents of M^{2+} and one of OH^-, the more dilute solution was expected to have both pK 0.6 units higher. A possible explanation is that the so-called aqua ion is dimeric M_2^{4+}. The high intensities might suggest a rather distorted structure, and it is indeed conceivable that two diethylenetriamine connect two palladium atoms but it is not easy to understand how M^{2+} can dimerize so rapidly.

It would perhaps be more satisfactory to remove Cl^- from MCl^+ without a heterogenous catalysis being possible on the surface of the precipitated silver chloride. We already mentioned the spectroscopic studies involving Hg^{II} forming limpid solutions; but they are not appropriate for pH studies. Addition of Tl_2CO_3 is only sufficient for precipitating the ionic chloride of [Pd(den)Cl]Cl and only removes a minor proportion of the innersphere chloride. We reacted $PdSO_4$ (1.08 g ≡ 5 mmoles) with 0.2 M $denH_3(ClO_4)_3$ (26 ml), in $HClO_4$ (0.4 *M*) and allowed the mixture to stand three days when it was filtered from minor by-products. The reversible titration curve of the filtrate (first with NaOH and back with $HClO_4$)

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[5] O. Mønsted and J. Bjerrum, Proceed. 11. ICCC (Haifa and Jerusalem, September 1968) p. 103. Editor: M. Cais, Elsevier, Amsterdam, 1968.

[6] G. B. Kauffman, *Naturwiss.*, *54*, 573 (1967).

[7] C. K. Jørgensen, Advances in Chemistry Series, 62, 161 (1967).

[8] C. K. Jørgensen, ASTIA document no. 157158. Copenhagen, 1958.

[9] F. Basolo, H. B. Gray and R. G. Pearson, *J. Amer. Chem. Soc.*, *82*, 4200 (1960).

[10] W. H. Baddley, F. Basolo, H. B. Gray, C. Nölting and A. J. Poë, *Inorg. Chem.*, *2*, 921 (1963).

[11] W. H. Baddley and F. Basolo, *J. Amer. Chem. Soc.*, *88*, 2944 (1966).

[12] D. J. Hewkin and A. J. Poë, *J. Chem. Soc.* (A), 1884 (1967).

[13] H. H. Schmidtke, private communication.

[14] J. B. Goddard and F. Basolo, *Inorg. Chem.*, 7, 936 (1968).

indicated half an equivalent of hydroxide was taken up with pK = 6.8.

After these confusing results, we tried to titrate 67 m*M* [Pd(den)Cl]Cl in 1 *M* $NaClO_4$ directly with 1 *M* NaOH. Interestingly enough, this gave a nice titration curve for one equivalent of OH^- with pK = 9.2. Actually the experiment was interrupted when half an equivalent of OH^- was added per palladium, and the slope was just slightly too weak. This is also expected theoretically. If $Pd(den)OH^+$ was in equilibrium with monomeric aqua and chloro complexes, the apparent pK is the real pK for the aqua ion to which is added ($\log K_{Cl} + \log[Cl^-]$) where K_{Cl} is the formation constant of $Pd(den)Cl^+$ from Cl^- and the monomeric $Pd(den)H_2O^{2+}$. It is quite reasonable that the apparent pK is increased 1.5 to 2.5 units, corresponding to $\log K_{Cl}$ between 2.5 and 3.5. When two equivalents of Ag^+ were added to the half-titrated solution, the pH dropped suddenly from 9.2 to 7.75. Further addition of 0.5 equivalent of OH^- produced a low-slope curve reaching 10.25. However, back-titration with 1 *M* $HClO_4$ was not reversible and clearly showed the two half-proton additions with pK around 9 and at 6.7. In other words, the mononuclear behaviour had ceased when the palladium no longer was present nearly exclusively as $Pd(den)OH^+$ and $Pd(den)Cl^+$. It appears that the hydroxo complex has a greater tendency to be monomeric than the aqua ion.

Schmidtke and Garthoff[13] prepared white $[Pd(den)NH_3](ClO_4)_2$. We titrated this material with perchloric acid in 1 *M* $NaClO_4$ waiting for equilibrium to be established as in the case[1] of $Pd(NH_3)_n(H_2O)_{4-n}^{2+}$. The experimental points of the formation curve (n of ammonia between 0.4 and 0.92) agree quite well with log K = 6.9 (using[1] pK of NH_4^+ 9.36) assuming the mononuclear reaction

$$Pd(den)H_2O^{2+} + NH_3 = Pd(den)NH_3^{2+} + H_2O \qquad (2)$$

in good agreement with $\log K_4 = 6.8$ for $Pd(NH_3)_4^{2+}$. However, in view of the complications mentioned above, one might expect sidereactions:

$$Pd_2(den)_2(NH_3)(H_2O)^{4+} + NH_3 = Pd_2(den)_2(NH_3)_2^{4+} + H_2O \qquad (3)$$

accompanying the monomers. At this point, kinetic evidence may be of some interest. Thus, 10 m*M* $Pd(den)NH_3^{2+}$ maintained (original pH = 2.52 increasing to 4.40) a production of ammonia by S_N1 dissociation amounting to 0.19 m*M*/minute (*i.e.* the reaction was 80% complete after 13 minutes, $[H^+]$ decreasing as a linear function of time until this point). The corresponding rate constant $k_{-1} = 3.2 \cdot 10^{-4}$ sec^{-1} is slightly lower than $k_{-4} = 7.8 \cdot 10^{-4}$ sec^{-1} in the ammonia system.[1] However, mixtures with lower n have lower production rates of ammonia than proportional with n. Thus, the partly reacted solution nominally containing 4 m*M* $Pd(den)H_2O^{2+}$ and 6 m*M* $Pd(den)NH_3^{2+}$ maintains the ammonia production 0.1 m*M*/minute (final pH = 3.71) and a solution with n = 0.4 only has an initial ammonia production of 0.043 m*M*/minute. This might suggest $Pd(den)_2(NH_3)(H_2O)^{4+}$ losing ammonia less rapidly than $Pd(den)NH_3^{2+}$, although further studies are necessary: $\varepsilon = 530$ at 296 mμ of the latter species is a rather high intensity, although the band position is quite normal for $Pd^{II}N_4$. We return in part III to the problem of $Pd(den)py^{2+}$.

In many ways, the absorption spectra of copper(II) complexes are very similar, also in regard to intensity, to palladium(II) complexes having roughly half as large band wavelengths and twice as high excitation energies. It is instructive to compare[4] with $Cu(den)NH_3^{2+}$ having $\varepsilon = 84$ at 576 mμ and with $Cu\ en_2^{2+}$ having $\varepsilon = 63$ at 549 mμ. The mono-complex $Cu(den)H_2O^{2+}$ ($\varepsilon = 74$ at 611 mμ) is comparable with $Cu(NH_3)_3(H_2O)^{2+}$ ($\varepsilon = 41$ at 630 mμ)[15] but $Cu(den)_2^{2+}$ has a much stronger band ($\varepsilon = 106$ at 630 mμ) having a shoulder[4] at 850 mμ with $\varepsilon \sim 70$. This complex is quite similar to $Cu(NH_3)_5^{2+}$ first identified by Bjerrum.[15] At this particular point, Pd^{II} does not behave like Cu^{II}. The species $Pd(den)_2^{2+}$ formed in excess diethylenetriamine has $\varepsilon \sim 300$ at 295 mμ, less intense than the monomeric or dimeric mono-complex, and suggesting $Pd^{II}N_4$, most probably with two symmetrically bound bidentate ligands. Mann[16] argued that the tridentate 1,2,3-triaminopropane (forming pink, high-spin octahedral[4] nickel(II) complexes $Ni(ptn)_2^{2+}$) also forms six-coordinated $Pd(ptn)_2^{2+}$, although $Pt(ptn)_2^{2+}$ should be square-planar with two loose nitrogen ends, which can be protonated and form characteristic picrates. We would like to return later to the question of palladium(II) and platinum(II) complexes of multidentate ligands, but we would like to emphasize that all available spectroscopic evidence suggests that $Pd(den)_2^{2+}$ is only four-coordinate.

We do not here touch the difficult problem of protonation of $Pd(den)^{2+}$; the interference with hydroxo complexes of the type $Pd(denH)OH^{2+}$ or their oligomers might be disturbing. On the other hand, we found rather unexpected results for the protonation of $Pd(den)_2^{2+}$. With sufficient stirring, K_2PdCl_4 (from which $KClO_4$ can be removed beforehand with $NaClO_4$) is soluble in water containing 2 den/Pd. The colourless solution can then be treated with exactly 4 equivalents of $AgClO_4$ or of $AgNO_3$ and the AgCl can be removed by filtration. When such a solution is titrated in 1 *M* $NaClO_4$ with $HClO_4$, the first protonation step (see Figure 2) is found to have $pK_1 = 6.1$. This is obviously a compromise between the normal pK 9 to 10 of the uncoordinated primary amine and the repulsion of the proton by the positive charge of the central atom, as may be discussed in connection with local dielectric constants.[17] However, the second proton is taken up much more reluctantly, and pK_2 for the formation of $Pd(denH)_2^{4+}$ can be shown to be approximately 2.5. The deviation of the difference ($pK_1 - pK_2$) from the statistical value 0.6 is so large that it cannot be explained away by N. Bjerrum's theory for dissociation of two adjacent protons from an acid. It is much more probable that one proton forms a

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(15) J. Bjerrum, *Mat. fys. Medd. Dan. Vid. Selskab, 11,* no. 10 (1932).

(16) F. G. Mann, *J. Chem. Soc.*, 890 (1928) and 651 (1929).

(17) G. Schwarzenbach and W. Schneider, *Helv. Chim. Acta, 38,* 1931 (1955).

hydrogen bond between the two loose ends in the same way as the inter-molecular hydrogen bond stabilizing nickel(II) dimethylglyoximate $Ni(dmgH)_2$. Incidentally, the dissolution of $Pd(dmgH)_2$ in base with the formation of five-coordinated $Pd(dmgH)_2OH^-$ according to Burger and Dyrssen[18] might also be due to the formation of $Pd(dmgH)dmg^-$, which only differs in composition by a water molecule.

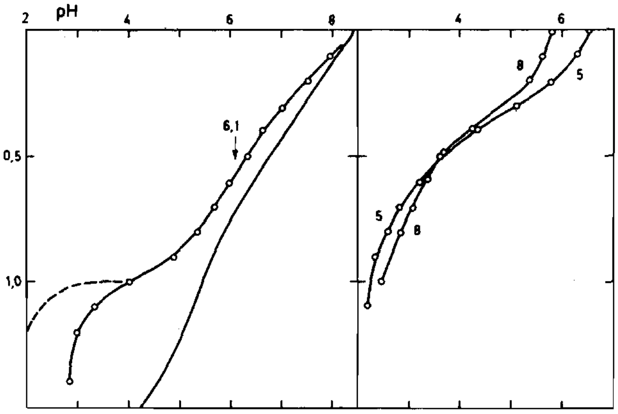

Figure 2. The left-hand curve with circles indicates the titration of 50m*M* $Pd(den)_2^{2+}$ from which the 200 m*M* Cl^- (originating in $PdCl_4^{2-}$) has been removed by 200m*M* $AgClO_4$, the whole in 1 *M* $NaClO_4$. The vertical scale indicates the amount of $HClO_4$ added per palladium (in the form of 1 *M* acid). The dashed curve indicates the theoretical behaviour of a dilute strong acid, if $Pd(den)_2^{2+}$ did not take up a second proton. The full curve without circles indicates the titration curve of 0.1 *M* $Pd(den)_2^{2+}$ in 1 *M* $NaClO_4$ from which the 0.4 *M* Cl^- has not been removed. The competition between amine groups and chloride for the four coordination positions shift the curve to higher pH. The right-hand curve marked 5 is a similar experiment with 50 m*M* $Pd(den)_2^{2+}$ to which 250 m*M* $AgClO_4$ was added and the AgCl was removed by filtration. As discussed in the text, $Pd(den)_2Ag^{3+}$ with much weaker proton affinity is a major constituent of such a solution. The curve marked 8 corresponds to 50 m*M* Pd and 400 m*M* Ag.

When the experiment is repeated with 5 equivalents of Ag^+ per $PdCl_4^{2-}$, a very pale lemon-yellow solution of $Pd(den)_2^{2+}$ is formed which has nearly lost its affinity to protons. The apparent pK_1 is now well below 3. The only acceptable explanation of this loss of proton affinity is the formation of $Pd(den)_2Ag^{3+}$, most probably having silver(I) bridging the two loose ends in the same way as the proton mentioned above. It is important to note that the excess of more than one equivalent of Ag^+ per $Pd(den)_2^{2+}$ is not needed. The concentration ranges used are such that the formation constant of this silver complex must be above 10000. This value may be compared with the formation constant of 25 found by Prue and Schwarzenbach[2] for the reaction between $Ag(den)^+$ and Ag^+ to form Ag_2den^{2+}. We had hoped to determine such constants for fixation of additional silver ions using a silver electrode, but it became poisoned, probably by the presence of palladium.

Many palladium(II) complexes in aqueous solution have a tendency to undergo photochemical decomposition, slowly precipitating black palladium. This tendency is far more pronounced for $Pd(den)_2Ag^{3+}$ solutions and we intend to study the photochemical behaviour of the simultaneous presence of these two elements.

Experimental Section

The absorption spectra of solutions were measured on a Cary MS 14 recording spectrophotometer. The pH measurements were made on a glass-electrode Philips PR 9400 apparatus. The arrangement of a calomel reference electrode with careful exclusion of chloride in the palladium solutions was previously described.[1] A thermostat with flowing water at 25°C was used. The compounds have been described previously.[1,13] Contrary to the case of triethylenetetramine, the best commercial quality of diethylenetriamine (Fluka, Buchs SG.) was shown to be very good and, did not change perceptibly on further fractional distillation.

Acknowledgments. We would like to thank Mr. Bernard Dusonchet for assistance with the measurements.

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[18] K. Burger and D. Dyrssen, *Acta Chem. Scand.*, *17*, 1489 (1963).