Contribution from the Department of Inorganic Chemistry, University of Aarhus, 8000, Denmark, and Cyanamid European Research Institute, Cologny (Geneva) 1223, Switzerland.

Palladium(II) Complexes. III. Experiments with Pyridine and Phenanthroline

Lene Rasmussen and C. K. Jørgensen

Received March 22, 1969

The pyridine complexes have log K_2 above 7.4 but log K_3 about 6.5. At sufficiently high [py], $Pd(py)_4^{2+}$ can be prepared. The mixed diethylenetriamine complex $Pd(den)py^{2+}$ is discussed. Absorption spectra of the mixed 1,10-phenanthroline complexes $Pd(phen)X_2$ with many different ligands, such as water, hydroxide, ammonia, ethylenediamine, glycinate and pyridine are measured and compared with high-spin $Ni(tren)phen^{2+}$. The bidentate group $Pd(phen)^{2+}$ is so stable toward dissociation that it can be considered as a new heterocyclic system. Doubts are expressed regarding the ready preparation of $Pd(phen)_2^{2+}$.

J. Bjerrum[1] proposed the general rule that the change of free energy by exchange of coordinated water with pyridine, represented by log $K_n + 1.76$ where 1.76 is the logarithm of the water concentration, is 0.6 times as large as for the corresponding exchange of water by ammonia. Since we have determined[2] the four consecutive formation constants log K_n = 9.6, 8.9, 7.5 and 6.8 for the palladium(II) ammonia complexes, J. Bjerrum's rule suggests log K_n decreasing from 5 to 3.4 for the pyridine complexes.

In most cases, the pyridine complexes are so relatively weak that one has to apply a large free concentration [py], and several formation constants have been determined in high concentrations of pyridinium pyH^+ salts as well. J. Bjerrum[3] pointed out that pyridine shows strong salting in effects in such solutions and highly decreased activity coefficients. He carefully determined log K_n = 2.408, 1.880, 1.137 and 0.605 for copper(II) complexes in 0.5 *M* pyridinium nitrate. We have the opposite problem of very strong complexes coinciding with the relatively low value of pK = 5.7 which we determined in 1 *M* $NaClO_4$. However, pK is even lower in strong pyridinium salt solutions[3] and is 5.215 in 0.5 *M* $pyH^+NO_3^-$.

The left-hand part of Figure 1 shows the absorption spectra as a function of time in minutes at approximately 25°C of a solution having the initial composition 1 m*M* $Pd(H_2O)_4^{2+}$, 0.02 *M* pyH^+, 0.98 *M* H^+, 1 *M* ClO_4^-. The right-hand part shows the evolution of another solution originally containing 1 m*M* $Pd(H_2O)_4^{2+}$ (for the preparation of the aqua ion, see ref. 2), 0.1 *M* pyH^+, 0.9 *M* H^+, 1 *M* ClO_4^-. By comparison with the spectrum[2] of $Pd(NH_3)_2(H_2O)_2^{2+}$ having the maximum at 341 mμ, it is nearly certain that the main component of the final state of the left-hand case is $Pd(py)_2(H_2O)_2^{2+}$ with a possible minor contribution of $Pd(py)(H_2O)_3^{2+}$. Since [py] is $10^{-7.4}$ *M* according the pK value in 1 molar perchlorate, log K_2 seems to be above 7.4 and hence at most 1.5 unit below that of the corresponding ammonia complex.

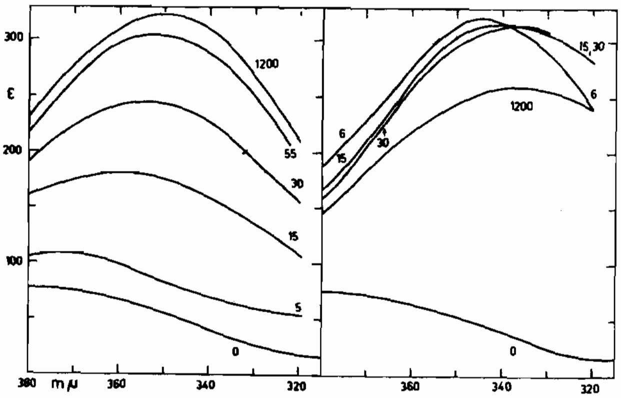

Figure 1. Left-hand manifold of curves: the near ultraviolet spectra of a solution 0.001 *M* $Pd(H_2O)_4^{2+}$, 0.02 *M* pyridinium perchlorate and 1 *M* perchloric acid after 5, 15, 30, 55 and 1200 minutes at approximately 25°C. Right-hand curves: the evolution after 6, 15, 30 and 1200 minutes of a solution 0.001 *M* $Pd(H_2O)_4^{2+}$, 0.1 *M* pyH^+ ClO_4^- and 0.9 *M* $HClO_4$.

Already after six minutes, the solution described in the right-hand side of Figure 1 had the spectral evolution more progressed than the final state of the former solution. We do not insist on the apparent fact that the kinetics is of higher than first order in [pyH^+], repeated experiments are needed to confirm this situation. The final state was somewhat perturbed by the fact that after two days, $Pd(py)_4(ClO_4)_2$ started crystallizing. These white cry-

---

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

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

[3] J. Bjerrum, *Acta Chem. Scand.*, *18*, 843 (1964).

[4] H. H. Schmidtke and D. Garthoff.

stals are far less soluble than $Pd(NH_3)_4(ClO_4)_2$, and their formation interferes with direct determination of log K_n via pH measurements in 1 *M* $NaClO_4$. Anyhow, the maximum at 337 mμ of the 1200 minutes curve suggests a mixture of the bis-and tris-complexes having $n = 2.4 \pm 0.2$, and the corresponding value for log K_3 on the solution having $p(py) = 6.7$ is 6.5. Obviously, this is a very crude estimate, and it is necessary to perform further work to determine the log K_n for the pyridine complexes.

It is interesting to compare with the mixed diethylenetriamine complex $[Pd(den)py](ClO_4)_2$ prepared by Schmidtke and Garthoff.[4] The following spectral measurements were made in 1 *M* $NaClO_4$ in order to allow comparison with pH measurements. This solvent has $\varepsilon = 0.02$ at 220 mμ, 0.04 at 210, 0.08 at 205, 0.13 at 200 and 0.30 at 195 mμ, relative to water, and has no disturbing effect on the bands measured here. The solution of 0.125 m*M* Pd(den)-py^{2+} has a broad band at 298 mμ with $\varepsilon \sim 560$ (the half-width $\delta(-) = 2.6$ kK caused by an internal $4d^8$-transition like in other Pd(den)X complexes[5]) and three narrow bands at 264.5 mμ ($\varepsilon = 2320$); 258 mμ ($\varepsilon = 3280$); and 252 mμ ($\varepsilon = 2680$). This vibrational structure is caused by an internal transition in the pyridine ligand and is shifted 1.5 mμ to higher wavelengths relative to the dilute aqueous solution of pyridine.[6] The similar shift for *trans*–$Irpy_4Cl_2^+$ is 8 mμ.[6] Fortunately, the spectrum of pyH^+ has higher ε and the vibrational structure is blurred out to some extent so the reaction:

$$Pd(den)py^{2+} + H_{aq}^{+} \longrightarrow Pd(den)H_2O^{2+} + pyH^{+} \qquad (1)$$

is relatively easy to follow spectrophotometrically. Thus, 0.125 m*M* $[Pd(den)py](ClO_4)_2$ and 5 m*M* $HClO_4$ (*i.e.* pH = 2.30) in 1 *M* $NaClO_4$ was found to react according to (1) almost (95%) to completion, with a half-life of about 8 minutes. Since free py reacts almost instantaneously with H^+, this very fact poses a lower limit for log $K_{py} = 4.4$, the formation constant of the mono-pyridine complex of $Pd(den)^{2+}$. The solution after 40 minutes has a broad band at 313 mμ ($\varepsilon \sim 500$) which may be compared with the previously measured aqua complex.[5] The solution, 1 m*M* $HClO_4$ in 1 *M* $NaClO_4$ reacts in the beginning with the same half-life, 8 minutes, so the kinetics of (1) is zero-order in $[H^+]$ in analogy to several other dissociations of palladium(II) ammines.[2] The final solution has reacted 65%. Finally, a solution, 0.125 m*M* $Pd(den)py^{2+}$, 0.1 m*M* $HClO_4$ (initial pH = 4.00) and 1 *M* $NaClO_4$ has found its stable spectrum after 20 minutes corresponding to 25% reaction according to (1). The two latter facts both correspond to log $K_{py} = 6.5$. Though this value may be uncertain ±0.2 unit, it is just slightly smaller than log $K_a = 6.9$ determined[5] for $Pd(den)NH_3^{2+}$.

This deviation from J. Bjerrum's rule[1] has a certain connection with Pearson's concept of soft and hard anti-bases and bases.[7-10] It is quite conceivable that the relative affinity for pyridine compared with ammonia increases for the softer anti-bases and is larger for Pd^{II} than for Cu^{I}, Ag^{I} and Hg^{II}. This might be illustrated if the comparatively hard anti-base Cr^{III} binds pyridine much less well than ammonia, or if the soft central atom Cr^0 forms stronger $Cr(CO)_5$ py than $Cr(CO)_5NH_3$.

Livingstone[11] prepared several 1,10-phenanthroline complexes (necessarily *cis*-) $Pd(phen)X_2$ with X = Cl, Br, I, SCN, NO_2, ... We prepared the dull orange $Pd(phen)Cl_2$ and found that it is extraordinarily insoluble in water (according to the absorption spectrum of the saturated solution in 0.05 *M* HCl, it is about 10^{-5} *M*) but nevertheless soluble in aqueous ammonia, ethylenediamine, sodium glycinate Na^+gly^-, and a variety of other ligands. We confirmed (independently) Livingstone's preparation of slightly soluble, cream-coloured crystalline $[Pd(phen)(NH_3)_2]$-$(ClO_4)_2$ and $[Pd(phen)en](ClO_4)_2$. In the case of the glycinate solution, we did not isolate any solid, but the spectrum turned out to be identical in the interval from the Hgly/gly^- buffer region to pH = 12.7 with 0.05 *M* excess NaOH, and is almost certainly caused by a definite species $Pd(phen)gly^+$.

The ultra-violet spectrum of phenanthroline is rich in details, and the minor changes by complex formation, *e.g.* in $Fe(phen)_3^{2+}$ and $Ni(phen)_3^{2+}$ has previously been discussed[12] partly on the basis on the observations by Roberts and Field[13] of fine-structure in the 350-300 mμ region. Figures 2 and 3 and Table I give a series of spectra. The solution of phen in 0.1 *M* $HClO_4$ is normally assumed to contain the species phen H^+ formed with pK close to 5.0. It is highly improbable, of steric reasons, that $phenH_2^{2+}$ would be formed. In crystalline materials,

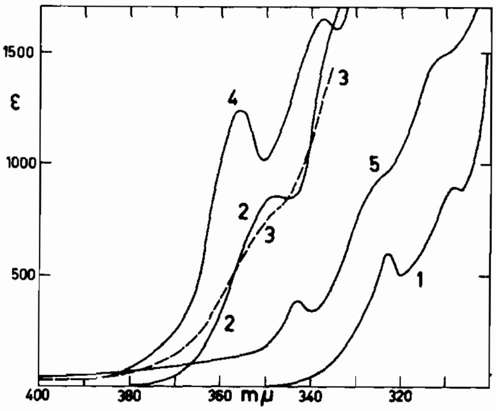

Figure 2. Near ultra-violet absorption spectra. Curve 1: phenanthroline in 2% ethanol, 98% water. Curve 2: $phenH^+$ in 0.1 *M* $HClO_4$. Curve 3 (dashed): $Pd(phen)(H_2O)_2^{2+}$ in 1 *M* $HClO_4$ from the aqua ion and $phenH^+$. Curve 4: $Pd(phen)(OH)_2$ in 0.005 *M* NaOH from $Pd(phen)Cl_2$ heated with 0.1 *M* NaOH, and subsequently diluted. Curve 5: $Ni(tren)phen^{2+}$ in 50% ethanol, 50% water.

---

(5) L. Rasmussen and C. K. Jørgensen, *Inorg. Chim. Acta.* (1969).
(6) C. K. Jørgensen, *Acta Chem. Scand.*, *11*, 151 (1957).
(7) R. G. Pearson, *J. Am. Chem. Soc.*, *85*, 3533 (1963).
(8) R. G. Pearson, *J. Chem. Educ.*, *45*, 581 and 643 (1968).
(9) S. Ahrland, *Helv. Chim. Acta*, *50*, 306 (1967).
(10) S. Ahrland, Structure and Bonding, *5*, 118 (1968).
(11) S. E. Livingstone, *J. Proc. Roy. Soc. N. S. Wales*, *85*, 151 (1952).
(12) C. K. Jørgensen, *Acta Chem. Scand.*, *11*, 166 (1957).
(13) G. L. Roberts and F. H. Field, *J. Am. Chem. Soc.*, *72*, 4232 (1950).

Table I. Near-ultraviolet absorption bands of phenanthroline complexes, Wavelength in mμ, wavenumbers in kK (=1000 cm^{-1}) and molar extinction coefficients ε. Shoulders in parentheses.

	λ(mμ)	ν(kK)	ε	λ(mμ)	ν(kK)	ε	λ(mμ)	ν(kK)	ε
phen(pH = 7 to 12,7)	323.5	30.9	620	308.5	32.4	1000	—	—	—
phen H$^+$ (pH=1)	348.5	28.7	860	(332)	(30.1)	1800	315.6	31.6	4400
$Pd(phen)(H_2O)_2^{2+}$	(350)	(28.6)	750	(336)	(29.8)	1300	(318)	(31.4)	2800
$Pd(phen)(OH)_2$(pH=11.7 to 13)	356	28.1	1240	337.5	29.6	1650	—	—	—
$Pd(phen)(NH_3)_2^{2+}$	350	28.6	570	(333.5)	(30.0)	1230	—	—	—
$Pd(phen)en^{2+}$	350	28.6	600	(333.5)	(30.0)	1250	(317.5)	(31.5)	3500
$Pd(phen)gly^+$	350.5	28.5	830	333	30.0	1400	(317.5)	(31.5)	2000
$Pd(phen)py_2^{2+}$	350	28.6	960	(332)	(30.1)	1700	(317.5)	(31.5)	3500
$Ni(tren)phen^{2+}$	342.5	29.2	390	326.5	30.6	900	(313)	(31.9)	1500
$Ni(phen)_3^{2+}$	343.5	29.1	1500	327	30.6	2400	(312.5)	(32.0)	3300

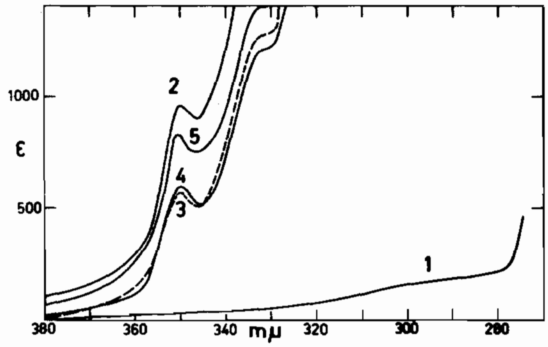

Figure 3. Near ultra-violet absorption spectra: Curve 1: $Pd(py)_4^{2+}$ from 0.002 *M* $PdCl_4^{2-}$ in 0.1 *M* aqueous pyridine treated with the stoichiometric amount of $AgClO_4$ and filtered from AgCl formed. Curve 2: $Pd(phen)py_2^{2+}$ from $[Pd(phen)py_2](ClO_4)_2$ in 0.1 *M* pyridine. Curve 3: (dashed): $Pd(phen)(NH_3)_2^{2+}$ from $[Pd(phen)(NH_3)_2](ClO_4)_2$ in 1 molar ammonia. Curve 4: $Pd(phen)en^{2+}$ from the perchlorate in water. Curve 5: $Pd(phen)gly^+$ from $Pd(phen)Cl_2$ in 0.05 *M* $Na^+NH_2CH_2CO_2^-$.

the hydrogen-bonded $phen_2H^+$ has recently been detected[14] but is of no importance in the concentration ranges we consider. Of reasons to become clear below, it is important to note that the spectrum of phen is not modified by OH^-.

If 5 m*M* $Pd(H_2O)_4^{2+}$ in 1 *M* $HClO_4$ is treated with 5 m*M* phenH$^+$, there is little doubt that the equilibrium corresponds to almost exclusive formation of $Pd(phen)(H_2O)_2^{2+}$ the perchlorate of which can be precipitated as a pale yellow material. In solution, there is only a small difference between the spectrum of this complex and of phenH$^+$. The reaction seems completed in a few minutes, whereas the reaction between 2.5 m*M* $Fe(H_2O)_6^{2+}$ and 0.5 m*M* phenH$^+$ in 0.1 *M* $HClO_4$ to form $Fe(phen)_3^{2+}$ (to the extent of 1% only in the final solution) had a half-time of some 30 minutes. However, there is a major difference in spectral behaviour by addition of base, where the formation of neutral phen is accompanied by a shift toward lower wavelengths and of $Pd(phen)(OH)_2$ by a shift in the opposite direction (see Figure 2). When $Pd(phen)Cl_2$ is heated with 1 *M* NaOH, a yellow compound is formed which seems to be the hydroxide. By further heating, it dissolves at least to the extent of forming a 10 m*M* solution.

It might be argued that the solubility in strong base suggests a five-coordinated anion $Pd(phen)(OH)_3^-$. However, the spectrum is identical at pH = 11.7 to 13.0, and the di-hydroxo complex may rather be comparable with many alkyl organo-metallic derivatives having a quite definite number of residual coordination positions which can be occupied by halides, hydroxide, etc..

For the comparison with our phenanthroline complexes in Table I, we measured the spectrum of $Ni(tren)phen^{2+}$ and isolated also the pink perchlorate of this cation. The violet crystals $Ni(tren)(NCS)_2$ with tren=tris(2-aminoethyl)amine were shown by S. E. Rasmussen[15] to be octahedral high-spin $Ni^{II}N_6$ as previously suggested from the visible spectra.[16] Certain mixed complexes such as $Ni(tren)gly^+$ have an unusually large sub-shell energy difference Δ, and it has also been noted[17] that the strawberry-red solutions of nitrite added to $Ni(tren)(H_2O)_2^{2+}$ have even larger Δ, which is not entirely surprising in view of the enormous Δ = 13.7 kK reported[18] for $Ni(NO_2)_6^{4-}$. In Table II are tabulated the $3d^8$-transitions of $Ni(tren)phen^{2+}$ indicating Δ = 11.25 kK comparable to the value[16] for $Ni(tren)en^{2+}$ and well below 12.3 kK for $Ni(phen)_3^{2+}$. It is seen that the symmetry is not strictly regular octahedral, but it does not deviate much. The broad back-ground at 400-360 mμ of $Ni(tren)phen^{2+}$ with ε increasing from 50 to 130 is most probably an inverted electron transfer band[19] from the upper sub-shell (e_g) to the low-lying, empty M. O. of the ligand.

A similar band is known[12,13] for $Ni(phen)_3^{2+}$ and is much weaker, by two orders of magnitude, than the inverted electron transfer band from the lower sub-shell (t_{2g}) in the low-spin $Fe(phen)_3^{2+}$ with shorter internuclear distances. Day, Sanders[20] and Mason[21] have recently given a theoretical description of the latter type of complex.

The first internal phen-band of $Ni(tren)phen^{2+}$ at 342.5 mμ still has lower wavelength than phenH$^+$ whereas all our palladium(II) complexes have higher wavelengths. Among those, the extreme is represented by the hydroxo complex, most probably Pd-

---

(14) M. P. Marzocchi and P. Paoletti, *Chem. Comm.* (London), 1063 (1968).

(15) S. E. Rasmussen, *Acta Chem. Scand.*, *13*, 2009 (1959).

(16) C. K. Jørgensen, *Acta Chem. Scand.*, *10*, 887 (1956).

(17) C. K. Jørgensen, ASTIA document no. 157158, September 1958.

(18) B. J. Hathaway and R. C. Slade, *J. Chem. Soc.* (A), 85 (1968).

(19) C. K. Jørgensen, *Acta Chem. Scand.*, *16*, 2406 (1962).

(20) P. Day and N. Sanders, *J. Chem. Soc.* (A), 1530 and 1536 (1967).

(21) S. F. Mason, *Inorg. Chim. Acta, Reviews*, *2*, 89 (1968).

Table II. Visible absorption bands of Ni(tren)phen^{2+}. Notation as in Table I; Mulliken Symmetry types for excited levels.

	λ(mμ)	ν(kK)	ε	Band shape
$^3T_{2g}$	888	11.25	14.8	asymmetric, δ(−) 1.0, δ(+) 1.8 kK
^1E_g	(800)	12.5	12	shoulder
$a\,^3T_{1g}$	533	18.75	11.0	δ(−) 1.65, δ(+) 1.55 kK

(phen)(OH)$_2$ There is one case known of comparable perturbation of the phenanthroline transitions by the central atom, *viz.* the blue Fe(phen)$_3^{3+}$. We measured this species in 0.01 *M* $HClO_4$ (in weaker acid, it decomposes rapidly, and in stronger acid, the perchlorate tends to precipitate) and found the two first transitions of Table I as a narrow peak at 353 mμ (28.3 kK) and a shoulder at 337 mμ (29.7 kK) besides the broad electron transfer band at 595 mμ (16.8 kK).

The spin-allowed internal 4d^8-transitions in quadratic Pd^{II}N$_4$ chromophores normally occur[2] in the region 300 to 280 mμ. Figure 3 shows the spectrum of Pd(py)$_4^{2+}$ in 0.1 *M* aqueous pyridine, where the narrow py-transitions cut off the spectrum close to the extrapolated maximum at 280 mμ of a rather broad band with moderate intensity, ε ~200.

Livingstone[11] reported that Pd(phen)Cl$_2$ is soluble in an aqueous solution of excess phenanthroline forming Pd(phen)$_2^{2+}$ which can be precipitated as the perchlorate. We did not observe any reaction between solid Pd(phen)Cl$_2$ standing for six months with excess phen in ethanolic solution. However, we repeated Livingstone's preparation by dissolving 0.9 g Pd(phen)Cl$_2$ (2.5 millimole) and 1.6 g phen, H_2O (8 millimoles) in 20 ml boiling water which turned weakly red-brown. By addition of 30 ml 1 *M* NaClO$_4$ kept at room temperature, a copious pale yellow precipitate was formed. Free phen can be washed away with acetone, and the residue is quite insoluble in water. C. E. Schäffer was so kind as to micro-analyze the residue, finding a composition close to that of Pd(phen)$_3$(ClO$_4$)$_2$. Erik Pedersen (also in Cophenhagen) measured the substance to be diamagnetic ($-0{,}51\times10^{-6}$ c.g.s.). Rather than six-coordinate, it may be a mixture of [Pd(phen)(H$_2$O)$_2$](ClO$_4$)$_2$ and free phen, but we do not argue that Pd(phen)$_2^{2+}$ does not exist. However, it must be so apt to dissociation that the steric hindrance between the two ligands must be considerable. Actually, Rund[22] indicates that a crystal structure of Pd(phen)$_2$(ClO$_4$)$_2$ is under elaboration, and that the two ligands are not strictly coplanar. Livingstone and Wheelahan[23] present evidence that the 2,2′-dipyridyl complex Pd(dip)$_2^{2+}$ and Pd(phen)$_2^{2+}$ add halide anions in nitromethane solution. Their figure shows increasing absorption from 500 to 400 mμ of Pd(dip)$_2$(ClO$_4$)$_2$ which must be strongly yellow. In this connection, it is interesting that Andersen *et al.*[24] demonstrated that all known M(dip)$_2$X$_2^+$ and M(phen)$_2$X$_2^+$ for M = Cr, Co, Rh and Ir are *cis* indicating a considerable steric repulsion preventing the coplanar *trans* isomers from being isolated. Similar conclusions were recently drawn by Gillard and Heaton[25] and Kulasingam, McWhinnie and Miller[26] whereas the larger scandium(III) may occur in *trans*–[Sc(phen)$_2$(NCS)$_2$]NCS according to Crawford and Melson.[27] According to Delépine, both *trans*- and *cis*–Ir py$_4$Cl$_2^+$ exist, and one of the reasons why *trans*-tetrakispyridine complexes are the better known may be kinetic like in the case of Delépine's alcohol catalysis of Rh^{III} reactions explained by the formation of traces of rhodium(I).[22]

We only conclude that one phenanthroline molecule is so strongly bound to palladium that one may consider Pd(phen)$^{2+}$ as a new 15-atomic heterocyclic ring system. The two residual coordination positions are moderately labile and accept all conventional ligands. By acidification of solutions containing chloride, Pd(phen)Cl$_2$ is rapidly precipitated, even from Pd(phen)en.$^{2+}$ The moiety Pd(phen)$^{2+}$ is a constrained example of the *cis*-stabilization[2] of Pd^{II}X$_2$Y$_2$ which was first discussed on the basis of preparative evidence by Drew, Pinkard, Preston and Wardlaw.[28] Pd(dip)Cl$_2$ was first prepared by Mann and Purdie[29] and recently, Cattalini and Martelli[30] prepared the unstable *cis*–Pd(py)$_2$Cl$_2$ (it transforms to the *trans*-isomer) by replacement of a bidentate thio-ether by pyridine. Of course, one should be careful not to exaggerate a weakly pronounced effect of the characteristic coordination number 2 in the formation constants.[2] Thus, Powell and Curtis[31] found that the changes of the enthalpy by adding the first and the second bidentate amine to copper(II) are roughly identical, whereas the changes of free energy differ, the ratio (K_1/K_2) between 15 and 35 for various diamines being larger than the statistical value 4. On the other hand, Pd(phen)$^{2+}$ is closely similar to the σ-bonded (and not δ-bonded as said in the title of the paper) pale yellow 2-phenylpyridine complex LPdCl$_2$PdL studied by Kasahara[32] where L$^-$ can be considered as dipyridyl in which one nitrogen atom has been replaced by C$^-$ L. Madeja *et. al.*[33] reported orange CrL$_3$. We hope in the future to determine the formation constants of amines A bound in Pd(phen)A$_2^{2+}$.

Experimental Section

Absorption spectra were measured in 2 cm cells on a Cary MS 14 recording spectrophotometer.

---

[22] J. V. Rund, *Inorg. Chem.*, *7*, 24 (1968).

[23] S. E. Livingstone and B. Wheelahan, *Austral. J. Chem.*, *17*, 219 (1964).

[24] P. Andersen, J. Josephsen, G. Waind-Nord, C. E. Schäffer and R. L. Tranter, *Chem. Comm.* (London), 408 (1969).

[25] R. D. Gillard and B. T. Heaton, *J. Chem. Soc.* (A), 451 (1969).

[26] G. C. Kulasingam, W. R. McWhinnie and J. D. Miller, *J. Chem. Soc.* (A), 521 (1969).

[27] N. P. Crawford and G. A. Melson, *J. Chem. Soc.* (A), 427 (1969).

[28] H. D. K. Drew, F. W. Pinkard, G. H. Preston and W. Wardlaw, *J. Chem. Soc.*, 1895 (1932).

[29] F. G. Mann and D. Purdie, *J. Chem. Soc.*, 873 (1934).

[30] L. Cattalini and M. Martelli, *Gazz. Chim. Ital.*, *98*, 831 (1968).

[31] H. K. J. Powell and N. F. Curtis, *J. Chem. Soc.* (A), 1441 (1967).

[32] A. Kasahara, *Bull. Chem. Soc. Japan*, *41*, 1272 (1968).

[33] K. Madeja, E. Hüsing and N. Ahrens, *Z. Chem.*, *7*, 22 (1967).

The preparation of solutions in 1 *M* $HClO_4$ of palladium(II) aqua ions via $PdSO_4$ was described previously.[2] The white crystals of $[Pd(den)py](ClO_4)_2$ were prepared by Schmidtke and Garthoff.[4] The starting material for $Pd(phen)X_2$ was the chloride, obtained by dissolving 3.27 g (10 millimoles) K_2PdCl_4 (H. Drijfhout & Zoon, Amsterdam) in 50 ml water and adding 1.98 g phenanthroline monohydrate (p.a., Fluka) dissolved in 20 ml ethanol. The dull orange precipitate is washed with water and ethanol. Addition of 1 *M* aqueous $NaClO_4$ to the solution of $Pd(phen)Cl_2$ in 1 *M* NH_3, or in a slight excess of dilute ethylenediamine, produced cream-coloured crystalline $[Pd(phen)(NH_3)_2](ClO_4)_2$ and $[Pd(phen)en](ClO_4)_2$.

Violet crystals of $Ni(tren)(NCS)_2$ obtained by working-up[17] of Union Carbide technical triethylenetetramine(trien) in Copenhagen 1958 were measured as an 0.05 *M* aqueous solution. Exactly 0.05 *M* phen in ethanol was added in equal amount, and the spectrum of $Ni(tren)phen^{2+}$ given in Table II measured. From this solution, 1 *M* $NaClO_4$ precipitates pink $[Ni(tren)phen](ClO_4)_2$ which is rather insoluble in water. Quite generally, mixed phen-complexes have a tendency to precipitate from aqueous solution, in contrast to corresponding mixed complexes of aliphatic amines.

Acknowledgments. We would like to thank Mr. Bernard Dusonchet for experimental assistance and Dr. Claus Schäffer for valuable information about the apparent impossibility of preparing *trans*-$M(phen)_2X_2^+$.