Inorganica Chimica Acta, 111 (1986) 25–30

The Stability of the Palladium(II) Complexes with Ethylenediamine, Diethylenetriamine and Tris(β-aminoethyl)-amine

GIORGIO ANDEREGG

Laboratorium für Anorganische Chemie, ETHZ, Universitätstrasse 6, CH-8092 Zurich, Switzerland

Received April 13, 1985

Abstract

Complex formation of Pd^{2+} with ethylenediamine, diethylenetriamine, and tris(β-aminoethyl)amine was investigated at 25 °C and ionic strength 1 using pH and UV-measurements. Bromide and hydroxyl ions were used as auxiliary ligands. Pd^{2+} forms the strongest complexes of the divalent cations hitherto investigated. In the case of the latter amine, because of its structure a coordination number of four is obtained forming a dimeric complex. The coordination number of the metal ion never exceeds four. The following values of $\log(K_n/M^{-1})$ were obtained: 23.6 ± 0.1 (n = 1) and 18.6 ± 0.1 (n = 2) for the first, and 32.6 ± 0.2 (n = 1) and 7.8 b 0.1 (n = 2) for the second ligand. For the last ligand: $\log(([Pd_2L_2]/([Pd]^2[L]^2))/M^{-3}) = 77.4 \pm 0.3$.

Introduction

If each of the hydrogen atoms in ammonia NH_3 is successively substituted by the β-aminoethyl group $NH_2{-}CH_2{-}CH_2{-}$, the three amines $NH_2CH_2CH_2NH_2$ ethylenediamine (en), $(NH_2CH_2CH_2NH$ diethylenetriamine (dien) and $(NH_2CH_2CH_2)_3N$ tris(N-aminoethyl)-amine (tren) are obtained, which contain two, three, and four nitrogen atoms in a favourable position for the formation of 5-membered chelate rings. For this reason the above amines have aroused intense interest as complexing agents. The stability constants of their complexes [1–4] with 3d and some other B divalent cations have been determined, and preparative work [5] has also been done. We report here the quantitative investigations of the equilibria of the complexes formed by palladium(II).

With all three ligands the 1:1 complexes of that cation are already completely formed in 1 M $HClO_4$, but the use of competing ligands allows the investigation of exchange equilibria. The combination of the constants for such equilibria finally gives the desired stability constants. In this work the bromide ion is used as competing ligand, because in 1 M HBr the tetrabromo complex $[PdBr_4]^{2-}$ is stable in the presence of an equimolar amount of each of the three amines. On the other hand, the same mixture in neutral solution contains the 1:1 complex of the amine with eventually coordinated bromide ions, giving a coordination number of four for the central ion. Therefore, on decreasing the pH a ligand exchange should occur.

In the case of ethylenediamine the species present in neutral solution is $[PdenBr_2]$ and equilibrium (I) takes place. This is accompanied by a strong increase of the absorbancy at 332 nm.

$$2H^+ + [PdenBr_2] + 2Br^- \rightleftharpoons [PdBr_4]^{2+} + H_2en^{2+} \qquad (I)$$

Using spectrophotometric and pH measurements it is possible to obtain the constant of equilibrium (I), *i.e.* K_I. In order to calculate the stability constant $K_1 = [Pden]/([Pd][en])$ of $[Pden]^{2+}$, the constant K_I should be combined with that of equilibrium (II) as well as the overall constants of $[PdBr_4]^{2-}$ and of H_2en^{2+}. However, for the constant $K_2 = [Pd(en)_2]/([Pden][en])$ the spectrophotometric measurements at different pH values near to 1 for solution in presence of an excess of ligand can be used. This method was already used by Rasmussen and Jϕrgensen [6], who obtained $\log K_2 = 18.4$ from the measurements of two solutions with different amounts of H_2en^{2+}. For the other two amines no value of the stability constants have yet been published. Mann and Pope [7] prepared the complex $[Pdtren]I_2$, and a coordination number 4 for the metal ion was postulated. As described here, the use of the equilibria mentioned above allowed the determination of all desired stability constants for the three amines with palladium(II). The values of constants are given omitting their dimensions, *e.g.* for K_1 and K_2: M^{-1} and for K_I: M^{-3}.

$$[Pden]^{2+} + 2Br^- \rightleftharpoons [PdenBr_2] \qquad (II)$$

Experimental

The three amines (Fluka) were purified by distillation and by separation of the pure ammonium salts with Cl^-, ClO_4^-, and NO_3^-. Palladium perchlorate

TABLE I. Spectral Data (wavelength λ_{max} and Molar Absorptivity ϵ_{mol} of the Maxima) of Palladium(II) Complexes with the Three Amines

Species	λ_{max} (nm)	ϵ_{mol} (cm^{-1} M^{-1})	Number of coordinated N-atoms
$[Pden]^{2+}$	342	271	2
$[Pd(en)_2]^{2+}$	287	320	4
$[Pddien]^{2+}$	314	590	3
$[Pd(dien)_2]^{2+}$	307	540	4
$[Pd(Htren)]^{3+}$	320	490	3
$[Pd_2(tren)_2]^{4+}$	299	1010	4

TABLE II. Protonation Constants of the Three Amines at 25 °C at Ionic Strength 1

Amines	Inert salt	log K_1	log K_2	log K_3
Ethylenediamine	$NaClO_4$	10.22	7.50	
Diethylenetriamine	NaBr	10.30	9.53	4.85
	$NaClO_4$	10.11	9.43	4.76
Tris(β-aminoethyl)amine	NaBr	10.51	10.02	9.03
	KNO_3	10.39	9.81	8.89
	$NaClO_4$	10.44	9.89	8.94

The standard deviation of log K_1 and log K_2 is 0.005.

solutions were prepared starting from the pure metal or from palladium nitrate (Fluka). $NaClO_4 \cdot H_2O$, NaBr, $HClO_4$ p.a. (Merck) were used.

The spectra (Table I) were measured with a Beckman ACTA III UV-visible spectrophotometer. The assignment of the number of coordinated N atoms was made as described by Jφrgensen *et al.* [6]. Note that only four of the six N atoms in $[Pd(dien)_2]^{2+}$ are coordinated and that for $[Pd_2(tren)_2]^{4+}$ the chromophore is PdN_4.

For the pH measurements 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 ion [H]: pH = –log[H], in the standard state given by the inert electrolyte in pure water. For solutions with [H] = 0.02 ÷ 1 M this quantity cannot be measured exactly, but it is calculated accurately from the compositions, taking into consideration the equilibria involved. The protonation constants of the amines were controlled (Table II). The values of ethylenediamine are in good agreement with those of Näsänen *et al.* [7–9] (log K_1 = 10.238 and log K_2 = 7.478) for the same conditions.

Some caution is necessary concerning the attainment of the equilibria, and repeated measurements within large time intervals (hours or days) are sometimes necessary. In the case of the formation of $[Pddien(Hdien)]^{3+}$ from $[PddienH_2O]^{2+}$ and H_3dien^{3+} between pH 5 and 7 no stable pH value was obtained.

Equilibrium Studies

The Stability Constants of the Palladium(II) Complexes with Ethylenediamine

These correspond to the constants of equilibria (III) and (IV) with $K_1 = [Pden]/([Pd][en])$ and $K_2 = [Pden_2]/([Pden])$. A simple way to obtain K_1 is by

$$Pd^{2+} + en \rightleftharpoons [Pden]^{2+} \qquad (III)$$

$$[Pden]^{2+} + en \rightleftharpoons [Pd(en)_2]^{2+} \qquad (IV)$$

determining the constants of equilibria (I) and II), whereas K_2 is obtained from that of equilibrium(V).

$$[Pden]^{2+} + H_2en^{2+} \rightleftharpoons [Pd(en)_2]^{2+} + 2H^+ \qquad (V)$$

Thus the relationships (1) and (2) are obtained, where κ_2 and β_4 are the overall constants of H_2en^{2+}

$$K_1 = (([PdenBr_2][H]^2[Br]^2)/([PdBr_4][H_2en])) \\ (Pden][Br]^2)/[PdenBr_2][PdBr_4]/([Pd][Br]^4) \\ [H_2en]/([H]^2[en]) = (\beta_4\kappa_2)/(K_{\rm I}K_{\rm II}) \qquad (1)$$

$$K_2 = (([Pd(en)_2][H])/([Pden][H_2en])) \\ [H_2en]/([H]^2[en]) = K_{\rm V}\kappa_2 \qquad (2)$$

(= $[H_2en]/([H]^2[en])$) and $[PdBr_4]^{2-}$ (= $[PdBr_4]/([Pd][Br]^4) = 10^{14.95}$) [11–12].

(a) Determination of the Constant K_I for the Equilibrium (I): The neutral complex $[PdenBr_2]$ shows a very low solubility in 0.1 M NaBr (2.97×10^{-4} M) which increases on addition of strong acid. At pH values lower than 2.5 the color of the solution changes, due to the very large absorptivity of $[PdBr_4]^{2-}$ which is formed following reaction (I). This allows the determination of the concentration of the latter species by use of a stoichiometric relation (3), and that for the absorbance A (4) expressed in

$$[Pd]_t = [PdBr_4]' + [PdenBr_2]' \quad (3)$$

$$A = (\epsilon'_{PdBr_4}[PdBr_4]' + \epsilon'_{PdenBr_2}[PdenBr_2]') \quad (4)$$

terms of the two absorbing species and their molar absorptivities. $[PdBr_4]'$ represents the sum of the concentration of all $[PdBr_n]^{(2-n)+}$ (n = 1,2,3, and 4) in 0.1 M NaBr at I = I. From the Elding's data [11] the complexes $[PdBr_4]^{2-}$ (94.29%) and $[PdBr_3]^{-}$ (5.68%) have to be considered. Similarly, because of its low stability $[PdenBr_2]$ is partially (5.69%) dissociated to $[PdenBr]^+$. Both effects give rise to a small correction, which has to be taken into account in order to obtain K_I (= $[PdBr_4][H_2en]/([PdenBr][H]^2[Br]^2)$). Some of the obtained spectra at different pH values are given in Fig. 1. From them one obtains $K_I = 10^{3.10}$ at ionic strength 1 with 0.1 M NaBr and $NaClO_4$. For $I = 1$ (NaBr) the same constant is $10^{2.80}$.

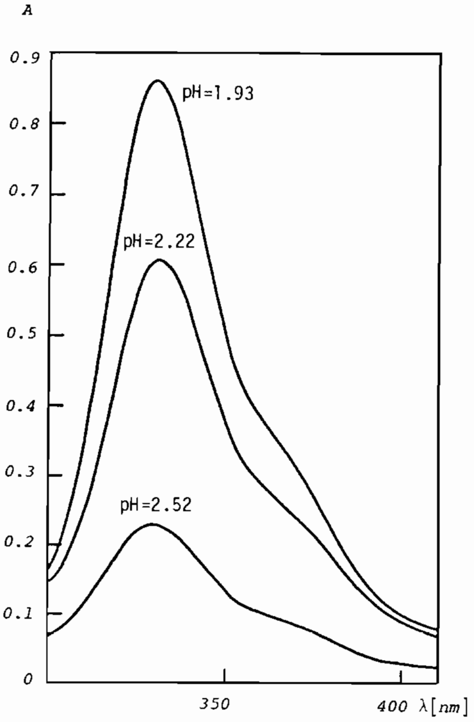

Fig. 1. The pH-dependence of the electronic spectra of $[Pden]^{2+}$ in presence of 0.1 M NaBr at $I = 1$ ($NaClO_4$). $[Pd] = 5 \times 10^{-4}$ M, 0.2 cm cells.

(b) Determination of the Constant K_{II} of the Equilibrium (II): An acidic solution of the 1:1 complex $[Pden]^{2+}$ gives, by addition of strong base, a titration curve due to the formation in a first step (III') of a dimeric $[Pd_2(en)_2(OH)_2]^{2+}$, which consumes a further mole of base on depolymerisation (IV'). As expected in similar cases, the graphical representation of the experimental data shows that an increase of the concentration of the acid $[Pden]^{2+}$ is accompanied by a displacement of the curve toward lower pH values for neutralization degrees lower than 1 and toward larger pH values for neutralization degrees higher than 1. As expected, the pH displacement on changing the acid concentration by a factor of 2 corresponds to $\frac{1}{2}$ log2, *i.e.* 0.150. The resulting equilibrium constant for the two steps are: $K_{III'} = 10^{-8.25}$ and $K_{IV'} = 10^{-22.6}$. In the presence of bromide ions the pH range for the formation of the dimeric species is displaced to higher pH values, because of the presence of the bromo species $[PdenBr]^+$ and $[PdenBr_2]$. Elaboration of the data gives the constants K_1 and K_2 for the mixed complexes: $K_1 = [PdenBr]/([Pden][Br]) = 10^{3.72}$ and $K_2 = [PdenBr_2]/([PdenBr][Br]) = 10^{2.22}$ and shows that no mixed species of type [Pden(OH)Br] is present.

$$2[Pden]^{2+} \rightleftharpoons [Pd_2(en)_2(OH)_2]^{2+} + 2H^+ \quad (III')$$

$$[Pd_2(en)_2(OH)_2]^{2+} \rightleftharpoons 2[Pden(OH)_2] + 2H^+ \quad (IV')$$

(c) Determination of the Constant K_V for Equilibrium (V): If one adds different amounts of protonated ethylenediamine to a solution of $[Pden]^{2+}$ at pH = 1 and the spectrum of the resulting mixture is measured, one can follow the formation of $[Pd(en)_2]^{2+}$ from $[Pden]^{2+}$. Indeed, as can be seen in Fig. 2, such additions cause a displacement toward short wavelengths of the d–d band of $[Pden]^{2+}$ (curve 1), in agreement with the expectation [6]. This displacement is characterized by the presence of an isosbestic point. These data allow the calculation of log K_V for equilibrium (V), which is 0.89.

$$[Pden]^{2+} + H_2en^{2+} \rightleftharpoons [Pd(en)_2]^{2+} + 2H^+ \quad (V)$$

Stability Constants of the Palladium(II) Complexes with Diethylenetriamine

By analogy with the case of ethylenediamine, the 1:1, $[Pddien]^{2+}$, and 1:2, $[Pddien_2]^{2+}$, complexes are formed. The stability constant K_1 was determined similarly taking into consideration equilibria (VI) and (VII). In the case of the former equilibrium, the spectrophotometric method given for equilibrium (I)

$$[PdBrdien]^+ + 3Br^- + 3H^+ \rightleftharpoons [PdBr_4]^{2-} + H_3dien^{3+} \quad (VI)$$

$$[Pddien]^{2+} + Br^- \rightleftharpoons [PdBrdien]^+ \quad (VII)$$

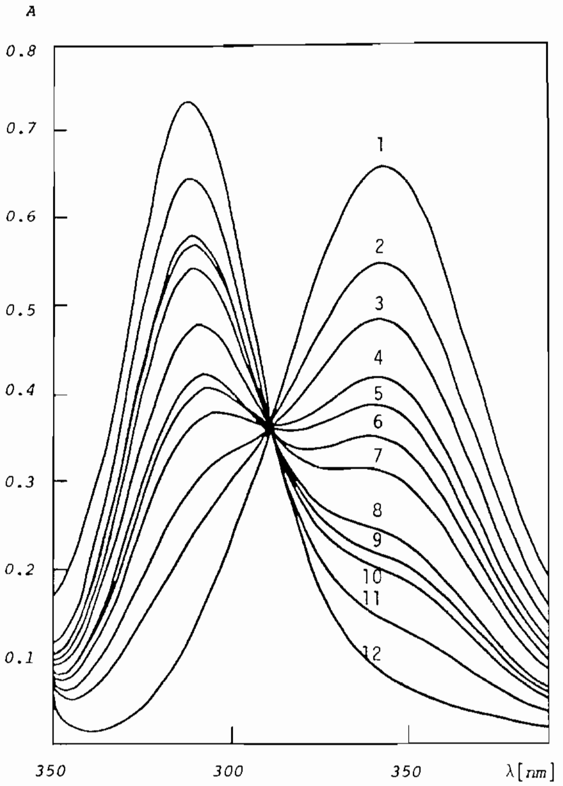

Fig. 2. The electronic spectra of $[Pden]^{2+}$ in presence of different amounts of protonated ethylenediamine $[H_2en]_e$ in 0.1 M $HClO_4$ and $I = 1$ ($NaClO_4$) $[Pden]_t = 5 \times 10^{-3}$ M. $[H_2en]_e = 0$ for curve 1, 1.25×10^{-3} M for curve 2, 2×10^{-3} M for curve 3, 3×10^{-3} M for curve 4, 3.5×10^{-3} M for curve 5, 4×10^{-3} M for curve 6, 5×10^{-3} M for curve 7, 7×10^{-3} M for curve 8, 8×10^{-3} M for curve 9, 9×10^{-3} M for curve 10, and 15×10^{-3} M for curve 11. Curve 12 gives the spectrum of $[Pden_2]^{2+}$ at the concentration of 5×10^{-3} M. 1 cm cells, scale 2.

was used. For the latter, solutions of the 1:1 complex $[PddienH_2O]^{2+}$ with and without added bromide ions were titrated with strong base, resulting in the formation of $[Pddien(OH)]^+$. Because of the presence of $[PdBrdien]^+$, the titration curves of the solutions with bromide ions are displaced to higher pH values. From the difference Δ of the pK values of $[PddienH_2O]$ in the presence and in the absence of bromide ions (= 7.8) and the known free bromide ions concentrations, the constant K_{VII} is obtained ($K_{VII} = 10^{\Delta}/[Br]$). Relationship (5) is then used to obtain K_1.

$$K_1 = (([PdBr(dien)][Br]^3[H]^3)/([PdBr_4][H_3dien])) \\ ([Pd(dien)][Br])/[PdBr(dien)] \\ [PdBr_4]/([Pd][Br]^4)[H_3dien]/([H]^3[dien]) \\ = (\beta_4 \kappa_3)/(K_{VI}K_{VII}) \qquad (5)$$

Some caution is necessary in these investigations because the formation of $[Pddien(OH)]^+$ occurs over the intermediate $[Pd_2(dien)_2OH]^{3+}$. For this reason, the titration curves of $[Pddien(H_2O)]^{2+}$ have different shapes, depending on the concentration involved, and give $[Pd_2(dien)_2(OH)]/([PddienH_2O][Pddien(OH)]) = 10^{2.5}$. The constant K_2 of $[Pd(dien)_2]^{2+}$ was obtained with eqn. (6) from the measurements on solutions of the mixed complex $[PdBrdien]^+$ and $[H_3dien]^{3+}$ in 1 M NaBr by titration with strong base. Equilibria (VIII) and (IX) take place in two separate pH ranges and the brown solution becomes colorless on neutralization.

$$[PdBrdien]^+ + H_3dien^{3+} \rightleftharpoons [Pddien(Hdien)]^{3+} \\ + 2H^+ + Br^- \qquad (VIII)$$

$$[Pddien(Hdien)]^{3+} \rightleftharpoons [Pd(dien)_2]^{2+} + H^+ \qquad (IX)$$

$$K_2 = (([Pddien(Hdien)][H]^2[Br])/ \\ ([PdBrdien][H_3dien]))([Pd(dien)_2][H])/ \\ [Pddien(Hdien)][PdBrdien]/([Pddien][Br]) \\ [H_3dien]([H]^3[dien]) = K_{VIII}K_{IX}K_{VII}\kappa_3 \qquad (6)$$

The Stability of the Palladium(II) Complexes with Tris-(β-aminoethyl-)amine

Only complexes with equimolar amounts of Pd^{2+} and tren are found. In acidic solutions a protonated species is formed $[Pd(Htren)]^{3+}$. This species is deprotonated in the pH range 3–5 with formation of a complex containing a PdN_4 chromophore. This can only be reached if the dimeric species, expressed by

$$2[Pd(Htren)]^{3+} \rightleftharpoons [Pd_2(tren)_2]^{4+} + 2H^+ \qquad (X)$$

equilibrium (X), is formed. Also in this case bromide is used as auxiliary ligand. The stability constant of $[Pd_2(tren)_2]^{4+}$ is obtained by investigating equilibria

$$[PdBr(Htren)]^{2+} + 2H^+ + 3Br^- \rightleftharpoons [PdBr_4]^{2-} \\ + H_3tren^{3+} \qquad (XI)$$

$$[Pd(Htren)]^{3+} + Br^- \rightleftharpoons [PdBr(Htren)]^{2+} \qquad (XII)$$

(X), (XI) and (XII) which give $[Pd_2(tren)_2]/([Pd]^2 \cdot [tren]^2)$. The dimeric complex is not soluble in the presence of $NaClO_4$, thus KNO_3 was used as supporting electrolyte at $I = 1$.

Discussion

The stability constants of the palladium(II) complexes with the three amines are given in Table III. Also in this case the constants are much larger than those for the 3d divalent metal ions (Cu^{2+}: log K_1(en) = 10.15; log K_2(en) = 9.28; log K_1(dien) = 16.0; log K_2(dien) = 5.3; log K_1(tren) = 18.8) and B cations (Hg^{2+}: log K_1(en) = 14.34; log β_2(dien) = 25.06) [14–

TABLE III. Stability Constants of the Palladium(II) Complexes with the Three Amines at 25 °C and $I = 1$

Amines	Medium	$\log K_1$	$\log K_2$	$\log \beta_2$
Ethylenediamine	$1(NaClO_4)$	23.6(1)	18.6(1)	42.2(2)
Diethylenetriamine	$1(NaClO_4)$	32.6(1)	$7.8^a(1)$	40.4(2)
Tris(β-aminoethyl)amine	$1(KNO_3)$	$\log[Pd_2L_2]/[Pd]^2[L]^2\ ^b = 77.4(3)$		

In parentheses three times the standard deviation of the last figures. ^{a}pK of $[Pd(HL_2)]^{3+}$: 9.92 ($1(NaClO_4)$ or 1(NaBr)). ${}^b\log[Pd(HL)]/[Pd][HL] = 30.1$ (1(KBr)).

15]. In the case of ethylenediamine, Mellor and Maley [13] have also determined these constants, but obtained incorrect results as they used solutions containing chloride ions without taking into account their effect on the equilibria. Rasmussen and Jϕrgensen [6] obtained a value $K_2 = 10^{18.4}$, which is similar to ours, but were not able to obtain K_1.

The comparison of the stability constants of the complexes with ethylenediamine with those of ammonia shows a larger chelate effect [16] for palladium(II) than for the 3d divalent cations [14]. Because the entropic gain by chelation for all cations should be similar in magnitude, this could be due to a larger ligand field stabilization [6].

The stability constants of NH_3, ethylenediamine and diethylenetriamine with palladium(II) and copper(II), give values of $\log K_1(\text{en}) - \log \beta_2(NH_3) = 4.1(\text{Pd})$ and 2.8(Cu) and of $\log K_1(\text{dien}) - \log \beta_3(NH_3) = 5.6(\text{Pd})$ and 5(Cu), *i.e.* the difference between each pair of values decreases strongly from 1.3 to 0.6. This could be explained with increasing steric strain on going from ethylenediamine to diethylenetriamine, which is more marked for the bigger Pd^{2+} ($r = 0.9$ Å) with respect to Cu^{2+} (0.72 Å).

The value of $\log K_2(\text{dien})$ is 1 unit larger than $\log K_4(NH_3)$. This can be explained in terms of the larger statistical contribution of the polyamine for the presence of three instead of one N atom in the ligand to be coordinated, forming a PdN_4 chromophore as supported by the spectral data of Table I [6].

A very rough estimate of the stability constant of the dimeric complex $[Pd_2L_2]^{4+}$, with a tetraamine L without steric strains, can be obtained from the value of K_1 of $[Pd(2,3,2\text{-tet})]^{2+}$ [17] taking into account the difference in basicity using the overall protonation constants of tren ($10^{29.5}$) and of 2,3,2-tet ($10^{33.2}$). One obtains $\log K_1 = 46.3 - 3.7 = 42.6$ and for the dimer species without further gain in stability $\log K = 2 \log K_1 = 85.2$, to be compared with the experimental value 77.4. The difference represents the stability loss due to the arrangement imposed by the central ion in order to reach an almost square planar coordination of four N atoms for each palladium(II) with the tripod ligand: each Pd of the dimeric unit is bound with three N atoms of the same ligand molecule and a further N atom of another ligand molecule. A similar arrangement was already found in the case of the tripod ligand NTA, although the presence of the weaker O^- donors allows the simultaneous foramtion of a 1:1 complex [12].

The stability constants of the mixed complexes with the unidentate ligands X^- formed by the 1:1 complexes of the three amines here investigated are given in Table IV. They show the expected magnitudes and trends within the series of the ligands investigated.

Thus, in the presence of all the above ligands, palladium(II) seems to be unable to achieve a coordination number larger than four.

TABLE IV. Stability Constant of the Mixed Complexes $[PdLX_n]^{\lambda+}$ Relative to $[PdL]^{\mu+}$ and X^- at 25 °C and $I = 1$

X^-	Complex	Medium	$\log K_1$	$\log K_2$
Cl^-	$[Pddien]^{2+}$	$1(NaClO_4)$	2.65(5)	
Cl^-	$[Pd(Htren)]^{3+}$	$1(KNO_3)$	3.17(5)	
Br^-	$[Pden]^{2+}$	$1(NaClO_4)$	3.72(5)	2.22(10)
Br^-	$[Pddien]^{2+}$	$1(NaClO_4)$	3.30(5)	
Br^-	$[Pd(Htren)]^{3+}$	$1(KNO_3)$	3.79(5)	
I^-	$[Pd(Htren)]^{3+}$	$1(KNO_3)$	5.64(8)	
SCN^-	$[Pd(Htren)]^{3+}$	$1(KNO_3)$	6.33(8)	

In parentheses three times the standard deviation of the last figures.

Acknowledgements

The author wishes to express his thanks to Messrs. B. Rüttimann, A. Baumann, K. Zollinger, P. Hanselmann and F. Ercegovich for their help with the experimental work.

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