159. Komplexone XLVII. The Stability of Palladium(II) Complexes with Aminopolycarboxylate Anions

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Summary. The formation of Pd(II) complexes with aminopolycarboxylate anions has been investigated using pH and UV.-spectrophotometric measurements at ionic strength 1 M and 20°. In some cases bromide or thiocyanate ions have been used as auxiliary ligands. Pd^{2+} forms the strongest complexes of the hitherto investigated divalent metal ions. The stability constants are discussed in relation to the particular stereochemistry of Pd(II) complexes.

1. Introduction. – Stability constants data for complexes of Pd(II) are still rather scarce despite its extensive preparative chemistry. This arises because such stability constants are more difficult to obtain than those of the corresponding complexes of divalent cations such as Ni^{2+}, Cu^{2+} and Zn^{2+}. One of the major problems follows from the fact that the aquo ion Pd^{2+} is stable only in very acid solutions and slow hydrolysis sets in at pH ~1 [1]. As a consequence equilibria involving the aquo ion have to be investigated at pH values below 1. There are also several limitations to the technique that can be used: (1) the simple pH method is not accurate enough for such acid solutions, because the concentration of the free hydrogen ions can only be determined with an error of 3–5 mM which normally corresponds to the total concentration of the metal ion[2]); (2) although potential measurements with palladium metal electrode have been used [11], these do not give reliable results (see 4.). It follows that the only general applicable method is spectrophotometry. This method has been successfully used by *Elding* [2] in his accurate investigation of the complexes of Pd^{2+} with Cl^- and Br^-. It should be added here that, in the case of uncharged complexes, one can also use distribution measurements of these species between water and an organic solvent [3]. The present paper reports equilibrium studies between Pd^{2+} and the following ligands: 1) glycinate (GLY), 2) iminodiacetate (IDA), 3) nitrilotriacetate (NTA), 4) ethylenediaminetetraacetate and its higher homologues: $(^-OOCCH_2)_2N\text{–}(CH_2)_n\text{–}N(CH_2COO^-)_2$: n = 2 EDTA, n = 3 TMTA, n = 4 TETA, n = 5 PETA and n = 6 HDTA, 5) 1,2-diaminocyclohexanetetraacetate (DCTA) and 6) diethylenetriaminepentaacetate (DTPA).

In addition to the direct investigation of the equilibria between Pd^{2+} and the ligands $H_\mu L$, exchange equilibria in the presence of a second ligand X^- have been

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[1]) Some results are taken from the thesis of *S.C.M.*, ETH, Zurich, 1970.

[2]) The system Pd^{2+}/ammonia, however, is an exception as one does obtain reliable results using the pH method as long as the ligand number $\bar{n}$ values remain above 1 [1].

studied. These are equilibria between $PdCl_4^{2-}$, $PdBr_4^{2-}$ or $Pd(SCN)_4^{2-}$ and the protonated ligands $H_iL^{(\mu-i)-}$:

$$PdX_4^{2-} + H_iL^{(\mu-i)-} \rightleftarrows PdLX_m^{(2-\mu-m)+} + (4-m)\ X^- + i\ H^+$$

2. Methods of investigation. – 2.1. *The spectrophotometric method.* This method is used to determine p*K* values of acidic complex species (see 3.1.a. for $H_3PdEDTA^+$) or stability constants of complexes (see 3.3. for $PdGLY^+$) [24].

2.2. *pH Method.* 2.2.1. *Protonation and deprotonation equilibria.* These can be quantitatively investigated as done for simple acids and bases [4] [5]. Evidence for the formation of $HPdEDTA^-$ and $H_2PdEDTA$ has been obtained by this method.

2.2.2. *Ligand-exchange reactions.* It is known that complexes PdX_4^{2-} ($X = Cl^-$, Br^- and SCN^-) are stable in acidic medium but undergo hydrolysis in neutral or alkaline solutions. The exchange reactions (1) in which Cl^-, Br^- or SCN^- of the highly colored PdX_4^{2-} are replaced by organic ligands containing N- and O-donors, are accompanied by color-fading and by production of hydrogen ions which can be titrated with strong base. For this purpose solutions of complexes $Na_2[PdX_4]$ are mixed with solutions of the corresponding organic ligand and the mixtures are titrated with a strong base in presence of an excess of NaX to avoid hydrolysis of PdX_4^{2-}. It is found that only the 1:1 complexes can still have halide ions coordinated to Pd^{2+}.

$$PdX_4^{2-} + H_iL^{(\mu-i)-} \rightleftarrows PdLX_m^{(2-\mu-m)+} + (4-m)\ X^- + i\ H^+ \qquad (1.a)$$

$$PdLX_m^{(2-\mu-m)+} + H_iL^{(\mu-i)-} \rightleftarrows PdL_2^{(2-2\mu)+} + m\ X^- + i\ H^+ \qquad (1.b)$$

When the organic ligand is EDTA, for $X^- = Cl^-$ reaction (1.a) takes place at pH < 3 even when $[Cl]_t = 1$ M. If, however, an excess of thiocyanate is present (0.01–0.1 M, $[Pd]_t = 1 \cdot 10^{-3}$ M) the exchange reaction takes place between pH 5 and 8 (see Fig. 2). The determination of the number m in the complex $PdLX_m^{(2-\mu-m)+}$ required more extensive investigations using solutions containing different total concentration of halide ion. In the case of L = EDTA it was found m = 1 for $[SCN]_t \leq 0.02$ M, and m = 2 for higher thiocyanate concentrations (0.1 M). The pH range for the ligand-ligand exchange as well as the complexes formed are given in Table 1. An exact evaluation of the respective equilibrium constants by the pH method is only possible for solutions with pH values between 3 and 9, otherwise protonation equilibria of the ligands become important. In systems with high and constant concentration[3]) of X^- the complex formation between a protonated ligand $H_\mu L$ and PdX_4^{2-} can be studied by the pH method [6] in the same way as the complex formation between $H_\mu L$ and $M^{\nu+}$. But from measurements at the same $[X^-]_t$, it is not possible to decide about an eventual participation of X^- in the formation of mixed complexes. The apparent stability constants obtained, β_n^*, are then equal to $(\sum_{m=0} [PdL_nX_m])/([PdX_4][L]^n)$ and depend on the value of $[X^-]_t$. For each complex

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[3]) This treatment has some analogy to that used by *Schwarzenbach* [25] for the interpretation of measurements with metal polyamine systems in presence of a large concentration of metal ion.

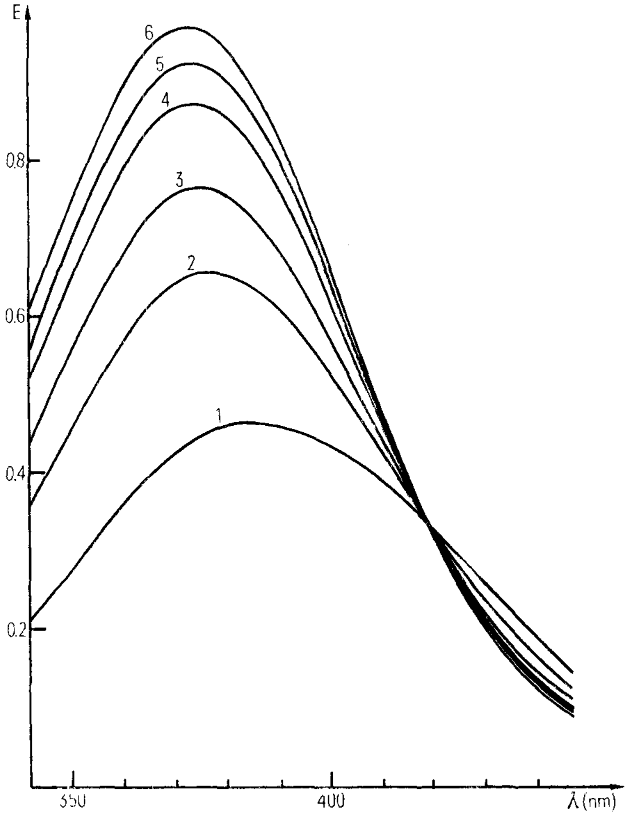

Fig. 1. *Spectra of $PdEDTA^{2-}$ solutions at different pH between 0 and 2 at I = 1* (H, Na)ClO_4. $[PdEDTA]_t = 10^{-3}$ M, 1 cm cell. 1: pH = 0; 2: pH = 0.3; 3: pH = 0.7; 4: pH = 1; 5: pH = 1.3; 6: pH = 1.6

Table 1. *The pH range for the ligand exchange* (eqs. 1) *with different ligands for mM solutions of Pd^{2+}.* I = 1 ($NaClO_4$), 20° The complexes formed are given in parenthesis

L	ligand X^-		
	Cl^- 0.1 M	Br^- 0.1–0.3 M	SCN^- 0.01–0.1 M
$EDTA^{4-}$	<3	<3	5–7($PdL(SCN)^{3-}$, $PdL(SCN)_2^{4-}$)
$CDTA^{4-}$	<3	<3	5–7 ?
$DTPA^{5-}$	<3	<3	5–7($PdL(SCN)^{4-}$, PdL^{3-})
NTA^{3-}	<3	4–5($PdLBr^{2-}$) 6–7(PdL_2^{4-})	>9
IDA^{2-}	<3	4–7($PdLBr_2^{2-}$, PdL_2^{2-})	>9
GLY^-	<3	4–6($PdLBr_2^-$, PdL_2)	7–8

$PdL_n^{(n\mu-2)-}$ the pH method allows only the determination of the sum: $[PdL_n] + [PdL_nX] + [PdL_nX_2] + \cdots = [PdL_n](1 + \alpha_1(n)[X] + \alpha_1(n)\alpha_2(n)[X]^2 + \cdots)$, where $\alpha_m(n) = [PdL_nX_m]/([PdL_nX_{m-1}][X])$ is the stability constant of the mixed comlexes PdL_nX_m. This relation allows the rearrangement of β_n^* as given by equation (I).

$$\beta_n^* = ([PdL_n]/([PdX_4][L]^n))(1 + \alpha_1(n)[X] + \alpha_1(n)\alpha_2(n)[X]^2 + \cdots) = \\ = \frac{[PdL_n][X]^4}{[PdX_4][L]^n}\left(\frac{1 + \alpha_1(n)[X] + \alpha_1(n)\alpha_2(n)[X]^2 + \cdots}{[X]^4}\right) \qquad \text{(I)}$$

β_n^* must be constant at constant $[X^-]_t$. In principle, it could be possible to have more species with the same n value and different m values, but in the cases examined only one mixed complex is formed (Table 1). For a given n, the different β_n^* obtained at different $[X^-]_t$ are then used to determine the number m of X^- bound to $PdL_n^{(n\mu-2)-}$

$$\beta_n^*[X]^{4-m} = \frac{[PdL_nX_m]}{[PdX_4][L]^n}[X]^{4-m} = K_{n,m} \qquad \text{(II)}$$

Indeed, the product $\beta_n^*[X]^{4-m}$ must be constant for a given n, because the equilibrium in question can be given by equation (2).

$$PdX_4^{2-} + n\,L^{\mu-} \rightleftarrows PdL_nX_m^{(n\mu+m-2)-} + (4-m)\,X^- \qquad (2)$$

3. Description of the systems investigated. – 3.1. *$Pd^{2+}/EDTA$.* Solutions of $PdEDTA^{2-}$ were obtained by dissolving the solid complex $H_2[PdEDTA]$ or by dissolving equimolar amounts of H_4EDTA and $PdCl_2$ and precipitating Cl^- as AgCl by addition of the stoichiometric quantity of $AgNO_3$ or $AgClO_4$. The final concentration of the solution must be lower than 10^{-2}M to avoid precipitation of $H_2PdEDTA$.

3.1.1. *Protonation of $PdEDTA^{2-}$.* The protonation constants $K_p = [H_pPdEDTA^{(p-2)+}]/([H_{p-1}PdEDTA^{(p-3)+}][H^+])$ are calculated from alkalimetric titrations of acidic solutions of $PdEDTA^{2-}$. Comparison of the values obtained (see Table 2) with those for $PtEDTA^{2-}$ [7] shows that also for the species $PdEDTA^{2-}$, in which the EDTA is acting as a quadridentate ligand, the two free carboxylate groups are first protonated and only at very low pH values $H_3PdEDTA^+$ can be formed, probably by opening of a $-COO^-$ chelate ring. A similar value of K_3 was obtained spectrophotometrically where it was observed that the deprotonation of $H_3PdEDTA(H_2O)^+$ is slow, which could be due to a slow ring closure reaction. Thelow energy absorption band of $PdEDTA^{2-}$ at 337 nm (molar absorbivity $\varepsilon = 1350$) occurs at the same wavelength for $H_2PdEDTA$ but with decreased intensity ($\varepsilon = 930$) while the corresponding band of $H_3PdEDTA(H_2O)^+$ occurs at 355 nm with $\varepsilon = 700$. The large intensity for the first two species could be due to chelate ring strain and/or deviation from planarity of the chromophore PdN_2O_2.

Table 2. *Protonation constants of $M(EDTA)^{2-}$ for M = Pd and Pt [7] at I = 1*

	T	inert salt	log K_1	log K_2	log K_3	log K_4
$PdEDTA^{2-}$	20°	$NaClO_4$	3.01 ± 0.05	2.31 ± 0.05	0.9 ± 0.1 [a]	<0
$PtEDTA^{2-}$	25°	KNO_3	2.88	2.18	0.5	<0

[a] From spectrophotometric measurements (Fig. 1). Log $K_3 = 0.8 \pm 0.5$ was obtained from pH measurements. The larger error of the latter value is due to the presence of only small amounts of $H_3PdEDTA^+$ under the particular experimental conditions.

3.1.2. *Reaction of* $PdEDTA^{2-}$ *with* OH^-. This reaction does not correspond to the formation of a simple species such as $PdEDTA(OH)^{3-}$ as a change from 0.4 to 0.5 of the neutralisation degree requires a change of pH from 10.64 to 11.27 when $[PdL^{2-}]_t = 5 \cdot 10^{-3}$ M, *i.e.* $\Delta pH = 0.63$ instead of 0.176 as found with monoprotonic acids. This reaction is likely to be due to a partial decomposition process and this hypothesis is supported by the observation that the amount of base used up decreases when an excess of EDTA is present. Therefore, no detailed investigation of this reaction was undertaken.

3.1.3. *Formation of chloro- and bromocomplexes* $Pd(EDTA)X^{3-}$ *and of their protonated species.* Spectrophotometric studies show that $PdEDTA^{2-}$ binds one chloride or one bromide ion. Solution at $I = 1$ with $[X^-] + [ClO_4^-] = 1$ M give isobestic points in both cases, *i.e.*, only complexes $Pd(EDTA)X^{3-}$ are formed. The low energy absorption of $Pd(EDTA)X^{3-}$ is $\varepsilon = 782$ at 376 nm for X = Cl and $\varepsilon = 790$ at 387 nm for X = Br. By alkalimetric titrations of acidic solutions of $PdEDTA^{2-}$ in the presence of Cl^- or Br^- it can be shown that $Pd(EDTA)X^{3-}$ can be protonated. The following species have been detected and characterized by their stability constants: $HPd(EDTA)X^-$, $H_2Pd(EDTA)X$ and $H_3Pd(EDTA)X^+$ (see Table 3). These constants are generally 0.4–0.6 log-units lower than those for the corresponding Pt^{2+} complexes. With X = Br partial decomposition of the EDTA complexes occurs in the course of the alkalimetric titration and $PdBr_4^{2-}$ is formed. The results of alkalimetric titrations of $PdEDTA^{2-}$ in 1 M KBr or in 1 M NaBr can be accounted for in terms of the equilibrium:

$$H_2EDTA^{2-} + PdBr_4^{2-} \rightleftarrows H_pPd(EDTA)Br^{(p-3)+} + 3Br^- + (2-p)\,H^+ \qquad (3)$$

Table 3. *Logarithm of the stability constants*a) *of the complexes formed by* $H_pPdEDTA^{(p-2)+}$ *and* $H_pPtEDTA^{(p-2)+}$ *with the monodentate ligands* X^- *at* $I = 1$

	$H_pPdEDTAX^{(p-3)+}$ (20°)				$H_pPtEDTAX^{(p-3)+}$ (25° [7])			
X	p = 0	p = 1	p = 2	p = 3	p = 0	p = 1	p = 2	p = 3
Cl^-	0.6	1.0	1.5	*ca.* 2.5	1.02	1.57	2.14	*ca.* 4
Br^-	1.1	1.45	1.9	*ca.* 3	1.47	2.02	2.62	*ca.* 4.5

a) $K_{p,1} = [H_pPd(EDTA)X^{(p-3)+}]/([H_p(Pd\ EDTA)^{(p-2)+}][X^-])$

From titration experiments at $[Br^-] = 1$ M only the sum $[H_pPdEDTA^{(p-2)+}] + [H_pPdEDTABr^{(p-3)+}]$ can be determined and therefore only apparent stability constants will be obtained: $K^*_{0,1} = ([PdEDTA^{2-}] + [Pd(EDTA)Br^{3-}])/([PdBr_4^{2-}][EDTA^{4-}])$ and $K^*_{1,1} = ([HPdEDTA^-] + [HPd(EDTA)Br^{2-}])/([PdBr_4^{2-}][EDTA^{4-}][H^+])$. Results are given in Table 4. K_1 is calculated by combining $K^*_{0,1}$, $K_{0,1}$ from Table 3 and β_4 of $PdBr_4^{2-}$ ($\log \beta_4 = 14.9$, see footnote on Table 7).

3.1.4. *Ligand-ligand exchange with* SCN^-. The protonated ligand H_2EDTA^{2-} reacts with the complex $Pd(SCN)_4^{2-}$ on addition of strong base with formation of Pd^{2+} ethylenediaminetetraacetate complexes. In these cases one obtains a plateau in the alkalimetric titration curves (Fig. 2), *e.g.* between pH 5 and 8 for $[SCN^-]_t =$

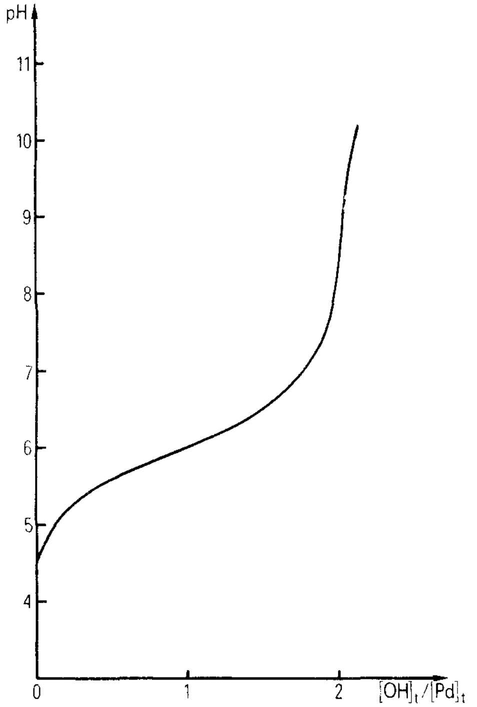

Fig. 2. *Titration curve of $Pd(SCN)_4^{2-}$ in presence of an equimolar amount of Na_2H_2EDTA with strong base.* $[Pd]_t = [EDTA]_t = 10^{-3}$ M; $[SCN]_t = 0.1$ M; I = 1 ($NaClO_4$)

0.01–0.1 M. A mathematical analyses of these curves shows that reaction (4) takes

$$Pd(SCN)_4^{2-} + H_2EDTA^{2-} \rightarrow Pd(EDTA)SCN^{3-} + 3\,SCN^- + 2\,H^+ \qquad (4)$$

place when the total concentration of SCN^- is 0.01 or 0.02 M. Similarly, one can obtain values for $K_{(IV)} = [Pd(EDTA)SCN^{3-}][SCN^-]^3/([Pd(SCN)_4^{2-}][EDTA^{4-}])$ which are $\log K_{(IV)} = -0.1 \pm 0.04$ and -0.12 ± 0.05. However, when the total concentration of SCN^- is 0.1 M significant amounts of $Pd(EDTA)(SCN)_2^{4-}$ are also formed: $([Pd(EDTA)(SCN)_2^{4-}][SCN^-]^2/([Pd(SCN)_4^{2-}][EDTA^{4-}]) = K_{(V)} = 10^{-1.1}$. The formation constants of $Pd(EDTA)SCN^{3-}$ and $Pd(EDTA)(SCN)_2^{4-}$ (Table 9) were calculated from the above exchange constants and the value of β_4 for $Pd(SCN)_4^{2-}$ (see 3.2.).

3.1.5. *Stability constants of complexes of EDTA and its homologues.* The procedure used for the calculation of K_1 of $PdEDTA^{2-}$ can be applied for the higher homologues of EDTA (Table 4), whereby the formation of mixed bromo complexes can be neglected as found by spectrophotometry.

The K_1 value for $PdEDTA^{2-}$ was corroborated by some preliminary investigation of equilibrium (5) which is easy,

$$PdBr_4^{2-} + LuEDTA^- + H^+ \rightleftarrows HPd(EDTA)Br^{2-} + 3\,Br^- \qquad (5)$$

due to the color of $PdBr_4^{2-}$. Equal amounts of $LuEDTA^-$ and $H_pPd(EDTA)Br^{(p-2)+}$ were present in solutions containing 10^{-2} M Br at pH 2.8. Using the value of stability constant of $LuEDTA^-$ for I = 0.1 and all other values for I = 1 one obtains $\log K_1 = 26.4$ for the stability constants of $PdEDTA^{2-}$. Although this value must be considered as approximate because different standard states of the constants were used, it allowed to find, without difficulty, the more appropriate interpretation of the measurements done in 1 M NaBr and KBr solutions.

Table 4. *Stability constants of Pd^{2+} complexes*[1]) *of EDTA homologues at* $I = 1$ *and 20°*

Ligand and medium	pK of HL, H_2L, H_3L and H_4L	log $K^*_{0,1}$	log $K^*_{1,1}$	log K_1
EDTA (KBr)	9.95; 6.26; 2.3; 2.2	11.7	14.8	25.5
EDTA (NaBr)	8.85; 6.21; 2.36; 2.04	10.7	13.8	24.5
TMTA (NaBr)	9.80; 7.82; 2.5; 1.9	13.75	16.5	28.7
TETA (NaBr)	10.09; 8.89; 2.65; 2.29	10.85	–	25.8
PETA (NaBr)	10.27; 9.36; 2.62; 1.99	11.5	–	26.4
HDTA (NaBr)	10.39; 9.61; 2.65; 2.2	11.4	–	26.3

[1]) See 3.1.3.

3.2. *Pd^{2+}-DTPA Complexes.* (pK of HL: 9.48; of H_2L: 8.22; of H_3L: 4.20; of H_4L: 2.7; of H_5L: 2.2 (1 M NaBr)). Alkalimetric titrations of acidic solutions of $PdDTPA^{3-}$ were carried out in the presence of different concentrations of Br^- (Table 5). In $PdDTPA^{3-}$ the three nitrogen atoms and one carboxylate oxygen atom are coordinated and, thus, the remaining four carboxylate groups are easily protonated. Mixed complexes are normally formed to an insignificant extent (log $K_{p,Br}$[4]) < -1 (p = 0); ~0.3 (p = 1); ~0.7 (p = 2); ~1.3 (p = 3)). For $PdDTPA^{3-}$ no detectable spectral changes (wavelength of the absorption maximum $\lambda = 325$ nm, $\varepsilon = 1460$) are observed for solutions containing $[Br^-]_t < 0.2$ M and it is concluded that its association constant with this anion is < 0.1. Even in 1 M NaBr the protonated ligand $H_pDTPA^{(5-p)-}$ and $PdBr_4^{2-}$ form only $PdDTPA^{3-}$ on addition of strong base. Calculations similar to those done for Pd^{2+}-EDTA system give log $K_1 = 29.7$. Ligand-ligand exchange with $[SCN^-]_t = 0.01$–0.02 M gives $[PdDTPA^{3-}][SCN^-]^4/([Pd(SCN)_4^{2-}][DTPA^{5-}]) = 10^{2.1}$, which combined with K_1 leads to $\beta_4 = [Pd(SCN)_4^{2-}]/([Pd^{2+}][SCN^-]^4) = 10^{27.6}$. At high enough $[SCN^-]_t$ (> 0,02 M) the species $Pd(DTPA)SCN^{4-}$ is formed ($[Pd(DTPA)SCN^{4-}]/([PdDTPA^{3-}][SCN^-]) = 10^{1.45}$.

Table 5. pK *values of* $H_pPdDTPA^{(3-p)-}$ *in presence of NaBr at* $I = 1$ ($[ClO_4^-] + [Br^-]$) *and 20°*

Medium	$HPdDTPA^{2-}$	$H_2PdDTPA^-$	$H_3PdDTPA$	$H_4PdDTPA^+$
1 M $NaClO_4$	3.49	2.93	2.56	1.93
0.05 M NaBr 0.95 M $NaClO_4$	3.50	2.95	2.56	1.9
0.1 M NaBr 0.9 M $NaClO_4$	3.48	3.04	2.66	2.2
0.2 M NaBr 0.8 M $NaClO_4$	3.50	3.06	2.73	2.3

3.3. *Pd^{2+}-NTA Complexes* (pK of HL: 8.96; of H_2L: 2.14; of H_3L: 1.97; of H_4L: 1.10 (1 M $NaClO_4$)). Alkalimetric titrations of a solution containing $PdBr_4^{2-}$ and $HNTA^{2-}$ in a 1:2 ratio ($[Pd]_t = 1$ mM), in the presence of 0.1 M NaBr, show two

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[4]) $K_{p,Br} = [H_pPd(DTPA)Br^{p-4}]/([H_pPdDTPA^{p-3}][Br^-]$.

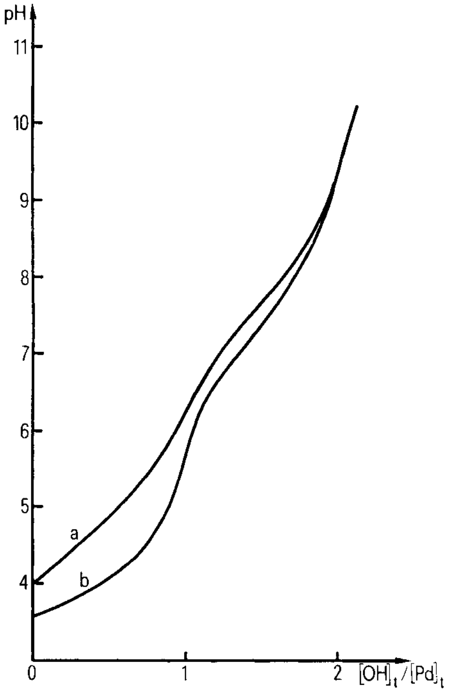

Fig. 3. *Titration curve of $PdBr_4^{2-}$ in presence of a double amount of $Na_2H(NTA)$ with strong base.*
$[Pd]_t = 10^{-3}$M; $[NTA]_t = 2 \cdot 10^{-3}$M;
I = 1 ($NaClO_4$). a) $[Br^-]_t = 0.3$M;
b) $[Br^-]_t = 0.1$M

distinct buffer zones (Fig. 3), the first between pH 3 and 5 and the second between pH 6 and 8. Each zone correspnds to the take up of 1 mol of strong base per mol of palladium. In the presence of 0.3M NaBr, however, the two buffer zones overlap to a certain extent. From the values of β_1^* and β_2^* (see 2.2.2.) obtained for the two different total bromide concentrations, it would be concluded that the first step corresponds to the formation of $Pd(NTA)Br^{2-}$ which, subsequently, goes over to $Pd(NTA)_2^{4-}$ according to reaction (1.b). The results of the spectrophotometric measurements are summarized in Table 6.

Table 6. *Summary of the results from spectrophotometric measurements of Pd^{2+} complexes with NTA, IDA and GLY at I = 1* ($NaClO_4 + HClO_4$)

Ligand	Characterized species, involved equilibria, spectral data[a]) and experimental conditions
NTA	H_2PdNTA^{2+}(log([H_2PdL]/([Pd][H_2L])) = 8.9; $[Pd]_t = [L]_t \simeq 10^{-4}$M, pH = 0) H_2PdNTA^{2+}(pK = 0.5; λ = 363 nm, ε = 482; $[PdL]_t = 10^{-3}$M) $PdNTA^-$ (λ = 363 nm, ε = 650) $Pd(NTA)_2^{4-}$ (λ = 329 nm, ε = 390)
IDA	$HPdIDA^+$ (log([HPdL]/([Pd][HL])) = 9.0; $[Pd]_t = [L]_t = 10^{-3}$M, pH = 0) $HPdIDA^+$ (pK = 0.75; λ = 370 nm, ε = 823) PdIDA (λ = 360 nm, ε = 600) $Pd(IDA)_2^{2-}$ (λ = 322 nm, ε = 342)
GLY	$PdGLY^+$ (log K_1 = 15.25; λ = 372 nm, ε = 208; $[Pd]_t = [L]_t = 10^{-3}$M, pH = 0) $Pd(GLY)_2$ (log K_2 = 12.25; λ = 322 nm, ε = 270; $[Pd]_t \leqslant [L]_t \simeq 10^{-3}$M, pH = 1–4

a) λ = wavelength of the absorption maximum.

A metal-metal exchange equilibrium (6) could be observed spectrophotometrically

$$Zr^{4+} + H_2PdNTA^+ \rightleftarrows ZrNTA^+ + Pd^{2+} + 2H^+ \qquad (6)$$

on mixing solutions of zirconium(IV) and of $PdNTA^-$ at pH = 0. Combining the constant for reaction (6), with the previously determined stability and protonation constant for $PdNTA^-$, the stability constant for $ZrNTA^+$ could be calculated. The value obtained, log $K_1 = 20.15$, in 1 M $HClO_4$. Martell reports a value of 20.8 [8] at lower ionic strength (0.1 M).

Alkalimetric titrations of Pd(II)-NTA solutions in 1 M $NaClO_4$ gave the pK values of HPdNTA (2.48) and $PdNTA^-$ (7.82). The formation of $Pd(NTA)OH^-$ occurs together with that of the binuclear complex $Pd_2(NTA)_2OH^{3-}$ ($[Pd_2(NTA)_2OH^{3-}]/([PdNTA^-][Pd(NTA)OH^{2-}]) = 10^{3.1\pm0.3}$). This last species is formed as an intermediate between $PdNTA^-$ and $Pd(NTA)OH^{2-}$. Moreover, the formation constant K_2 ($= 10^{6.6}$) for $Pd(NTA)_2^{2-}$ from $PdNTA^-$ could be calculated. The presence of the binuclear complex $Pd_2(NTA)_2^{2-}$ ($[Pd_2(NTA)_2^{2-}]/[PdNTA^-]^2 = 10^2$) could be

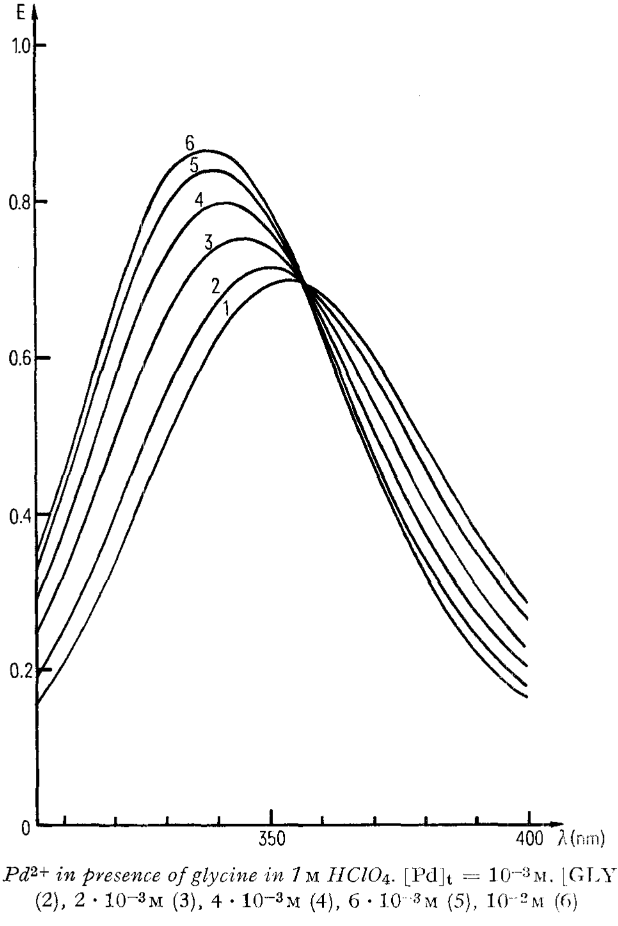

Fig. 4. *Spectra of Pd^{2+} in presence of glycine in 1 M $HClO_4$.* $[Pd]_t = 10^{-3}$ M, $[GLY]_t = 0$ (1), 10^{-3} M (2), $2 \cdot 10^{-3}$ M (3), $4 \cdot 10^{-3}$ M (4), $6 \cdot 10^{-3}$ M (5), 10^{-2} M (6)

deduced from measurements at different total concentrations of the components ($[Pd]_t = 10^{-3}$–10^{-2} M, $[NTA]_t = 2\ 10^{-3}$–$2\ 10^{-2}$ M). Low solubility prevented the investigation of solutions containing $PdNTA^-$ in concentration higher than 10^{-2} M.

3.4. *Pd^{2+}-IDA, -GLY and -DCTA Complexes.* Complex formation with the ligands IDA (pK of HL: 9.32; of H_2L: 2.64; of H_3L: 1.9 (1 M $NaClO_4$)), GLY (pK of HL: 9.83; of H_2L: 2.43 (1 M $NaClO_4$)) and DCTA have been investigated by ligand-ligand exchange and spectrophotometric measurements (Table 1 and 6). For DCTA ligand-ligand exchange needs some days to reach equilibrium. Therefore no measurements with the stable $PdDCTA^{2-}$ have been performed. For GLY spectrophotometry allows the direct determination of the stability constants of $PdGLY^+$ and $Pd(GLY)_2$. Addition of glycine to 10^{-3} M solution of Pd^{2+} at pH = 0 causes a strong increase of the absorbance (Fig. 4) due to the formation of $PdGLY^+$. An isobestic point is obtained for $[L]_t/[Pd]_t \leq 10$ and the stability constant $K_1 = [PdGLY^+]/([Pd^{2+}]$-$[GLY^-])$ can be calculated [24]. The free ligand concentration is obtained taking into consideration the protonation constant of the ligand.

4. Discussion. – The stability constants $K_1 = [PdL]/([Pd][L])$ and $K_2 = [PdL_2]/([PdL][L])$ are summarized in Table 7. As different experimental methods had to be used, it was not possible to use a common ionic medium, although all constants were measured at I = 1. Thus, each value is strictly valid for the given medium (spectrophotometry: at pH = 0: $HClO_4$; at pH > 0: $HClO_4 + NaClO_4$; exchange reactions: of IDA, NTA and GLY: $NaBr + NaClO_4$; of EDTA and its homologues: NaBr or KBr). The accuracy of these individual values is estimated to be ± 0.05 log-units. In spite of this fact the values K_1 and K_2 will be discussed as such without making doubtful corrections to account for the different standard state. Comparison of the data of Table 7 with literature values is not meaningful as the latter were obtained by inadequate methods. Thus, the stability constants with GLY ($\log K_1 = 9.12$ and $\log K_2 = 8.43$ [9]) and IDA ($\log K_1 = 9.62$ and $\log K_2 = 5.25$ [10]) were obtained from alkalimetric titrations of solutions containing the protonated ligands and complexes $PdCl_x^{(2-x)+}$ without taking into account for the latter species. A value of $\log K_1 = 18.5$ [11] for the complex with EDTA was obtained from EMF measurements using a palladium electrode which is not reversible. The value of the stability constant for $H_2PdEDTA$ obtained from spectrophotometric measurements

Table 7. *Logarithm of the stability constants K_1 and K_2 at $I = 1$ and 20°C*

Medium	1 M $NaClO_4$			1 M NaBr					
	GLY a)	IDA	NTA	EDTA	TMTA	TETA	PETA	HDTA	DTPA
$\log K_1$	15.25	17.5	17.1	24.5	28.8	25.8	26.4	26.3	29.7
$\log K_2$	12.25	9.3	6.6						

a) The overall constant, β_4, for $PdBr_4^{2-}$, obtained from the spectrophotometrically determined stability constant for $PdGLY^+$ and $Pd(GLY)_2$ and the Br^--GLY exchange constant is $10^{14.9}$ [13] and compares favourably with that obtained by *Elding* [2] ($10^{14.95}$) at 25° for the same ionic strength (1 M $HClO_4$).

in 1 M chloride solutions at pH between 0.55 and 1.5 [12] cannot be considered reliable because the calculations did not take into account the presence of species such as $H_pPd(EDTA)Cl^{(3-p)-}$, H_5EDTA^+ and H_6EDTA^{2+}.

As can be seen from the data in Table 7, Pd^{2+} forms the strongest complexes among the divalent metal ions investigated hitherto. The increase in K_1 on going from GLY to IDA is caused by the increase in number of coordinated carboxylate groups and is similar in magnitude to that observed for Zn^{2+}, Co^{2+} and Cu^{2+} [14] [15]. Although NTA contains three carboxylate groups, only two of them can coordinate to Pd^{2+} because of its preference for square planar coordination. Thus, one expects, and finds experimentally, that the introduction of the third acetate group, *i.e.* a change from IDA to NTA, cannot alter significantly the magnitude of K_1[5]. *Sawyer* [17], on the basis of IR. and ^{1}H-NMR. studies, has suggested that the 1:1 complex with NTA is dimeric: three coordination sites are occupied by the nitrogen and oxygen atoms of one molecule of NTA acting as a terdentate ligand and the fourth site is occupied by the free carboxylate group of another PdNTA unit. The binuclear complex $Pd_2(NTA)_2^{2-}$, which was identified [17] by ^{1}H-NMR. spectroscopy in solutions containing $[Pd]_t = [NTA]_t = 0.1–0.5$ M, appears to be present also in the system described in the present work. It is worth noting that the coordinated water molecule of $PdNTA^-$, in which NTA is acting as a terdentate, shows a pK very similar to that of the coordinated water of the Pd^{2+} complex with terdentate diethylenetriamine (7.8 [18]). In both cases the intermediate $Pd_2L_2(OH)$ dimer is formed. A marked decrease in K_2 is observed in the series GLY-IDA-NTA because of the decrease in number of the coordinating sites in PdL. This sequence shows some similarities to that of the stability constants of the mixed complexes of the type $PdLBr_n^{(\mu+n-2)-}$ (Table 8). The value of β_2 for $PdGLY^+$ is

Table 8. *Logarithm of the stability constants of mixed complexes* $\beta_n = [PdLBr_n]/([PdL][Br]^n)$ *at 20° and* $I = 1$ ($NaClO_4$)

	$PdGLY^+$	PdIDA	$PdNTA^-$
$\log \beta_1$			2.7
$\log \beta_2$	6.47	3.83	

Table 9. *Stability constants*[a] *for the formation of mixed complexes* $PdLX_n^{(\mu+n-2)-}$ *at 20° and* $I = 1$ ($NaClO_4$)

PdL	Cl^- $\log K_1$	Br^- $\log K_1$	SCN^-	
			$\log K_1$	$\log K_2$
$PdEDTA^{2-}$	0.6	1.1	2.9	1.2
$PdDTPA^{3-}$	–[b]	~1	1.45	

[a] $K_n = [PdLX_n]/([PdLX_{n-1}][X])$.
[b] Not investigated.

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[5] In this context it is worth noting that the difference in configuration between the Pd^{2+} complexes and those of Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} express themselves in the values of $\log K_1(M(NTA)) - \log K_1(M(IDA))$ which are – 0.4; 3.1; 3.4; 3.3; 2.3; 3.4; and 3.1 respectively [15] [16].

somewhat higher than the product of the stepwise constants K_3K_4 ($= 10^{5.5}$ [2]) of Pd^{2+} with bromide. For PdIDA a much lower β_2 value is obtained because the coordination of the second Br^- is opposed by the coordinated $-COO^-$ in $Pd(IDA)Br^-$.

The difference in log K_1 between DTPA [19] and EDTA complexes (5.1) is much higher than that observed for Cu^{2+} (2.6) but similar to that found for Hg^{2+} (4.9) reflecting the effect of increasing the number of coordinated nitrogen atoms. In contrast to coordinated carboxylate groups, coordinated nitrogen atoms are not displaced by halide or thiocyanate anions. The values of the stability constants for the mixed complexes of the PdL species given in Table 9 show a significant decrease if an additional nitrogen atom is coordinated.

A plot of the values of the stability constants for the 1:1 Pd(II) complexes of EDTA homologues $(^-OOCCH_2)_2N-(CH_2)_n-N(CH_2COO^-)_2$ *vs.* the value n (see Fig. 5) shows a trend which is significantly different from that given by other cations investigated [15]. This is likely to be caused by the preferred square planar geometry of the Pd^{2+} complexes. Thus, the increase in K_1 is similar to that observed for the Cu^{2+} complexes with N_4-donors sets, *e.g.*, the log K_1 values for CuL^{2+} complexes with $H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH$ and $H_2N(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$ are 20.2 and 23.9 respectively, and has been attributed to a decrease in the accumulated steric strain in chelate rings by alternation of ring size [20]. The value of K_1 reaches a minimum for the TETA complex and increases again, albeit irregularly, with the observed changes in the protonation constants of the ligand L. Another contributory factor for the increase of K_1 could be the formation

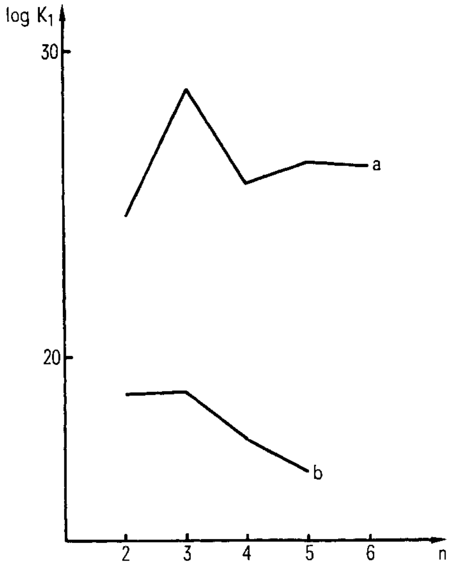

Fig. 5. *Stability constants of the EDTA homologous against number n of $-CH_2-$ of the alkylene chain.* a) Pd^{2+}; b) Cu^{2+}

of species in which the $N(CH_2)_nN$ chelate rings span *trans*-positions with a consequent decrease in carboxylate-carboxylate repulsions in the complexes [21]. The formation of such species could explain the exclusive formation of $PdHDTA^{2-}$ even in 10^{-2}M solutions, in contrast with the polynuclear species obtained for this ligand with other metal ions [22]. In this context it should be noted that the low energy bands in the complexes $PdTETA^{2-}$ and $PdHDTA^{2-}$ show wavelengths of the absorption maxima λ which are similar to those of $Pd(NTA)_2^{4-}$ and $Pd(GLY)_2$ where a *trans*-coordination of the two nitrogen atoms is generally assumed (Fig. 6). The complexes of DTPA and EDTA show very high molar extinctions which are likely to be due to steric strain and deviations from strict planarity of the chromophores. Significant decreases in these effects can be brought about by protonation of the complexes, *e.g.* from $PdEDTA^{2-}$ to $H_2PdEDTA$ and $H_3PdEDTA^{+}$, or by increase in chelate ring size *e.g.* on going from $PdEDTA^{2-}$ to $PdTMTA^{2-}$. Finally, it should be mentioned that the observed values of λ for the mixed complexes are in accordance with those predicted on the basis of the ligand field theory.

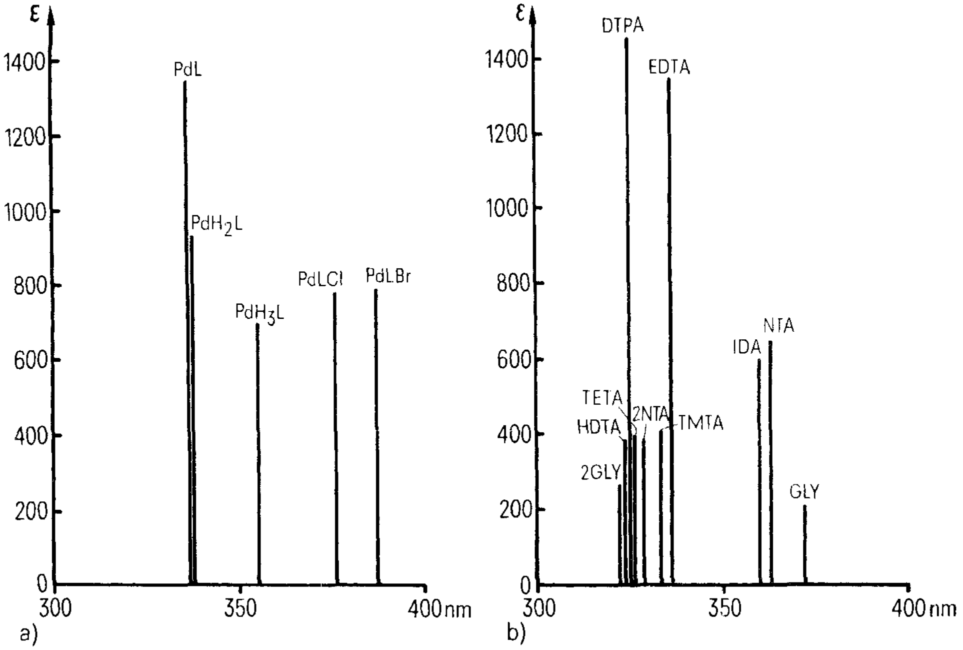

Fig. 6. *Absorption maxima and their molar absorptivities of UV.-spectra of different Pd(II) complexes.*
a) EDTA complexes. b) Aminopolycarboxylate complexes

5. Experimental Part. – All substances used were of the highest purity available and, if necessary, were further recrystallized. Palladium(II)perchlorate solutions have been prepared according to *Elding* [2]. All measurements were done at ionic strength 1 by use of different inert salts ($NaClO_4$, NaBr or KBr) and 20°. To avoid liquid junction potentials the cell for the potentiometric measurements was adapted for the different inert salts and used as described elsewhere [7] [23]. Calibration was done to read hydrogen concentration directly. The absorption spectra have been obtained with a *Cary* 14 or a *Varian* Techtron 635 spectrophotometer. The measurements have been carefully checked to ensure that for each solution equilibrium was reached. This has needed in some cases up to 60 minutes.

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