REACTIONS OF PALLADIUM WITH SOME HETEROCYCLIC AZODYES

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The analytical reactions of Pd(II) with heterocyclic dyes were compared and the complexation equilibria of Pd(II) with 2-(2-thiazolylazo)-4-methoxyphenol (TAMP) and 4-(2-thiazolylazo)-resorcinol (TAR) in solution were studied in detail. Methods for the spectrophotometric determination of palladium with TAR, TAMP, 4-(2-pyridylazo)resorcinol (PAR) and 1-(2-thiazolyl-azo)-2-naphthol-3,6-disulphonic acid (2-TAN-3,6-S) were evaluated.

Heterocyclic azodyes with the following analytical group of donor atoms
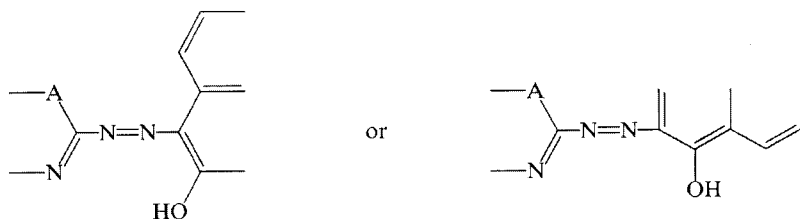
undergo analytically important reactions with Pd(II). Pd(II) complexes are formed even in strongly acidic media with a sharply contrasting colour change compared with the reagent alone. In acid media the Pd(II) chelates can usually be extracted into more polar solvents[1-13]. With resorcinol derivatives, in addition to the green chelate, a markedly different red chelate is formed in weakly acidic media. The stoichiometry of the Pd(II) chelates has been described, but a more detailed reaction mechanism is lacking, except for a recent work[21]. 4-(2-Pyridyl-azo)resorcinol has often been proposed for the spectrophotometric determination of palladium[5,12-15], as have various thiazolyl azodyes[16-19]. The reaction of Pd(II) with heterocyclic azodyes is strongly affected by chlorides, which are commonly present in solutions after decomposition of palladium-containing alloys and materials[14]. Among the platinum metals, only Pd(II) reacts at laboratory temperature; at an elevated temperature, a number of platinum metals in various valence states react. This difference is advantageous for the determination of palladium in the presence of the other platinum metals[13-20].

In the present work, the reactions of Pd(II) with selected heterocyclic azodyes are compared analytically and the reaction mechanisms with 4-(2-thiazolylazo)-

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resorcinol (TAR) and 2-(2-thiazolylazo)-4-methoxyphenol) (TAMP) are studied in detail in a mixed aqueous medium. These reactions are used as a model for study of the reaction mechanism of thiazolyl azodyes with palladium.

EXPERIMENTAL AND RESULTS

Chemicals and Solutions

$4.964 . 10^{-2}$M-Pd(ClO$_4$)$_2$ in 1M-HClO$_4$: 2.7 g of palladium powder (Safina, Vestec near Prague) were gradually dissolved in several portions of concentrated HNO$_3$ at a temperature of $25-35°C$ (palladium is passivated at higher temperatures). The red-brown solution formed was evaporated to a volume of 50 ml, which was repeated $3-4$ times with 25 ml portions of 70% HClO$_4$. The solution was diluted with water, filtered through an S4 frit and diluted with dilute HClO$_4$ to 500 ml to give a final HClO$_4$ concentration of 1M. The absorption spectrum of the solution (λ_{max} 385 nm, $\varepsilon = 85$) excludes the presence of palladium hydroxocomplexes[21,22]. Dilute solutions of Pd(II) perchlorate were prepared for each experiment and the resulting concentration of perchloric acid did not fall below 0.2M.

$2.380 . 10^{-1}$M-palladium(II) chloride in 0.5M-HCl was prepared from the substance manufactured by Safina, Vestec near Prague. The solutions were standardized gravimetrically as Pd (8-hydroxyquinolate)$_2$.

Reagents

The following substances were used as reagents: the disodium salt of 1-(2-thiazolylazo)-2-naphthol-3,6-disulphonic acid tetrahydrate (2-TAN-3,6 S): 10^{-3}M solution in water, chromatographically pure (98·1% of the free acid after standardization with a Cu(II) salt). 2-(2-Pyridylazo)-1-naphthol-4-sulphonic acid (1-PAN-4S): the content of the active substance is 96·6%, found from the sulphur content determined by the flask and titration method. 4-(2-Thiazolylazo) resorcinol (TAR, Lachema, Brno) was recrystallized from methanol and was chromatographically pure. 2-(2-Thiazolylazo)-4-methoxyphenol (TAMP) (Research Institute of Pure Chemicals, Lachema, Brno) was also chromatographically pure. In addition to 4-(2-pyridylazo) resorcinol (PAR), six more heterocyclic azodyes, derived from pyridine, quinoline and benzothiazole (Table I) and prepared for this purpose[23], were qualitatively evaluated. The purity of the reagents was controlled using thin-layer chromatography[23,24]. $5 . 10^{-4}$ or 10^{-3}M stock solutions in 50% or pure dimethylformamide were used. NaClO$_4$ was purified and recrystallized according to the method of Biedermann[25]. Dimethylformamide was redistilled at a pressure of 6 Torr at 52°C. Water was redistilled in a quartz apparatus.

Instruments

The following spectrophotometers were used: an SFD-2 grating instrument with 5, 10, 20 and 30 mm glass cuvettes and Unicam SP-700 and Cary 116-Varian recording instruments. A PHM4 pH-meter (Radiometer) was used with a G202B glass electrode and a K401 saturated calomel electrode with a liquid bridge containing saturated KNO$_3$ solution and closed with an S4 frit. The glass electrode was standardized using an aqueous phosphate buffer at pH 6·52. The pH$_c$ values measured in mixed media with dimethylformamide were not corrected. In HClO$_4$ media with 30% v/v dimethylformamide, acidity function H$_0$ was used, neglecting the effect of the organic solvent[26].

Detection of Palladium(II)

At pH 0—3, an intense green to blue colouration is formed with TAR and PAR in a $HClO_4$ medium; a red-purple colouration is formed with 1-PAN in a weakly acidic medium in the presence of dimethylformamide. No coloured chelates are formed in an acidic medium in the presence of $0.2M$-Cl^-; however, the reaction is not visually disturbed at pH 2—5. Under optimum conditions the negative logarithm of the dilution limit, pD, is not affected if Pd(II) chloride is used instead of the perchlorate: the colouration develops within 2 minutes. The principal data are given in Table I. The absence of an OH-group in the *o*-position with respect to the azo group leads to lower pD values for Pd(II).

Methods of Study

The solutions were always prepared in the same order: the reagent, the solvent, adjustment of the ionic strength (I 0·1 or 1) adjustment of the acidity, a chloride

TABLE I

Reaction of Pd(II) with Some Heterocyclic Azodyes

The components were added in the order: reagent, buffer, Pd(II) solution. The concentrations in the resultant solution are: reagent $2 . 10^{-5}M$, buffer, $0.05M$; the resultant volume, $V = 1$ ml. The resultant colouration was compared with the blank reagent solution.

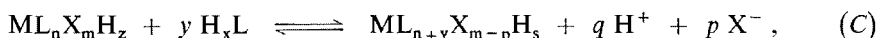| Reagent	pH	Chelate colouration	Optimum pH	Buffer	pD
1-PAN-4S	0—12	blue-green	4·5	acetate	6·4
1-QAN-4S	0—10	green	4·6	acetate	6·4
1-BAN-4S	0—5	green	4·6	acetate	6·1
	5—11	grey-green			
2-(2-pyridylazo)1-naphthol	3—7	green	6·5	urotropine	5·8
	7—12	purple			
4-(2-Pyridyl)azo)- -5-Hydroxy-1-naphthol	3·5—8	green	6·5	urotropine	5·6
4-(2-Pyridylazo)- -1-naphthol-2-sulphonic acid	3·5 9	blue	7·5	tris(hydroxymethyl)- aminomethane	5·7[a]
PAR	0—3·5	green	4·7	acetate	5·9
	3·5—12	purple			
TAR	0—2·5	green	4·7	acetate	5·8
	2·5—11	purple			
TAMP	0—8	green	6·5	urotropine	6·0
	8—11	blue-green			
2-TAN-3·6—S	0—12	green	0	$HClO_4$	6·3[a]

[a] Colouration develops after about 1 minute.

solution during the study of mixed equilibria and finally the Pd(II) perchlorate. In strongly acidic media, the acidity was adjusted with $HClO_4$ after adding the metal solution. No buffers were used in the equilibrium studies. $HClO_4$ and sodium carbonate were employed for adjustment of the acidity of the medium, as the measuring reproducibility deteriorated when using sodium hydroxide $(10^{-3}M)$. For the study of equilibria in solutions with excess reagent, direct graphical and graphical logarithmic analysis of the absorbance curves was employed[34], using the previously-derived slope-intercept transformations of the equilibrium constant and the conditional stability constant for the following equilibria:

$$M + n H_xL \; \rightleftarrows \; ML_nH_z + q H^+, \qquad (A)$$

$$ML_nH_z + y H_xL \; \rightleftarrows \; ML_{n+y}H_s + q H^+. \qquad (B)$$
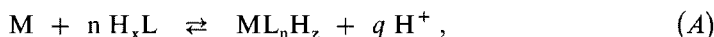
New transformations were developped for the formation of ternary complexes ML_nX_p and for the substitution equilibria:

$$ML_nX_mH_z + y H_xL \; \rightleftharpoons \; ML_{n+y}X_{m-p}H_s + q H^+ + p X^-, \qquad (C)$$

$$ML_nX_mH_z + y H_xL \; \rightleftharpoons \; ML_{n+y}H_s + q H^+ + m X^-, \qquad (D)$$

$$MX_mH_z \;\; + y H_xL \; \rightleftharpoons \; ML_yH_s + q H^+ + m X^-. \qquad (E)$$

For the study of equilibria in the Pd(II) Cl^-–heterocyclic azodye system, where H_xL is the ligand, X^- is the competing ligand and complexes MX_mH_z do not absorb in the visible spectral range, the following relationships are valid:

$$\Delta A = A - A_L = \varepsilon_1 c_M + \frac{(\varepsilon_2 c_M - \Delta A)\, c_L^y K}{[H]^q c_x^p}, \qquad (1)$$

$$\Delta A = A - A_L = \varepsilon_2 c_M + \frac{(\varepsilon_1 c_M - \Delta A)\,[H]^q\, c_x^p}{c_L^y K}, \qquad (2)$$

$$\log \frac{\Delta A - \varepsilon_1 c_M}{\varepsilon_2 c_M - \Delta A} = y \log c_L + q\, pH - p \log c_x + \log K \qquad (3)$$

assuming that $c_L \approx [H_xL]$, $c_x \approx [X^-]$, $c_M = [\text{complex}]_1 + [\text{complex}]_2$ in equilibria (C), (D) and (E) and that the free M^{2+} concentration is neglected. ε_1 and ε_2 are the molar absorption coefficients of the initial and newly-formed complex in the equilibria, respectively. In the presence of a greater number of acid–base ligand

species in the solution, the correction factor, $Z = 1 + [H^+]/K_a$ or $1 + K_a/[H^+]$, is introduced. If the ligand concentration bound in a complex cannot be neglected, then

$$[H_xL] = c_L - \frac{\varepsilon_1 c_M - \Delta A}{\varepsilon_1 - \varepsilon_2}.$$ (4)

In all cases, the solutions contained a constant concentration of an excess component and the concentration of the other component was varied (pH constant) or the pH was varied at constant concentrations of the other components.

   The reagent acid–base equilibria were interpreted numerically using the regression analysis method on a MSP2A computer with the PRCEK 1 program[27,35,36]. Some absorbance–pH curves for complexation equilibria were interpreted using the computation procedure according to the SPEKTFOT 4 program[28], which is derived from the general minimization program, LETAGROP[29], with the Fortran version adapted for the Tesla 200 computer. The program can be used if not more than four complexes and three acid–base reagent equilibria are present in the solution. The input data contain the experimental values, coefficients m, n and q for the assumed $M_mL_nH_q$ complexes, approximate values of their stability constants (accurate at most to $10^{\pm 0.5}$, in order that a large number of cycles should not be required for calculation of the accurate values), approximate values of the molar absorption coefficients and steps in which the p_i parameters are varied (*i.e.* constants and ε_i). The program looks for a combination of parameters according to the specified steps, for which the sum of the squares of the deviations attains a minimum value:

$$U = \sum(A_{\text{calculated}} - A_{\text{measured}})^2.$$ (5)

Then the minimum of the function $U = f(p_1, p_2, ..., p_i)$ is found and the best values of the varied parameters are calculated from this minimum. These values are then the input data for the next computing cycle. The computation can be repeated until U no longer changes. A gradual decrease in the U values confirms that the correct model has been selected for the complexation equilibrium.

   Some simple equilibria were investigated using the linear regression method with the above transformations according to the PRCEK program in the Fortran version on the Tesla computer[30]. The linearized form of the continuous variation curves for the formation of a complex with M : L = 1 : 1 is

$$\Delta A_i = \varepsilon(c_0 + \beta'^{-1}) + \frac{c_0^2 \varepsilon(x_{Li}^2 - x_{Li})}{\Delta A_i}$$ (6)

and yields the unknown values ε, $\beta'(\beta' = [ML]/[M]_t[L]_t)$ from the slope and the

intercept of the straight line. These values were calculated by the least squares method using the JOB program (ref.[30]) on the Tesla 200 computer. Only the molar absorption coefficient is calculated for systems with large β' values. The analytical curves, $\Delta A = f(c_{Pd})$, were evaluated by the least squares method on an MSP 2A computer[27] for various reagents.

Acid–Base Equilibria of TAR *in 30% and 50% v/v Dimethylformamide*

The absorbances were measured in a continuous apparatus in a nitrogen atmosphere at 485, 500, 520, 535 and 550 nm $(c_L = 3{\cdot}990 \,.\, 10^{-5}\text{M}, I \; 1{\cdot}0 \;(\text{NaClO}_4))$. The results, treated according to the PRCEK 1 program[27,35], are given in Table II.

TABLE II
Acid–Base Equilibria of TAR in Water–Dimethylformamide Medium

Equilibrium	pK_{an}		Chelate	λ_{max}, nm	
	30% (v/v)	50% (v/v)		30% (v/v)	50% (v/v)
$H_3L^+ \rightleftarrows H_2L + H^+$	$0{\cdot}84 \pm 0{\cdot}04$	$1{\cdot}06 \pm 0{\cdot}20$	H_3L^+	483	468
$H_2L \;\; \rightleftarrows HL^- + H^+$	$6{\cdot}56 \pm 0{\cdot}07$	$7{\cdot}25 \pm 0{\cdot}16$	H_2L	452	440—452
$HL \;\;\; \rightleftarrows L^{2-} + H^+$	$10{\cdot}42 \pm 0{\cdot}07$	$11{\cdot}52 \pm 0{\cdot}21$	HL^-	487	490
			L^{2-}	520	510

Complexation Equilibria of Pd(II) *with* TAR

In Pd(II) solutions with excess TAR, a green Pd(II) chelate is formed even in 5M-HClO$_4$ and is soluble in $\leq 30\%$ (v/v) dimethylformamide. A purple Pd(II) chelate is formed only at $pH_c > 2{\cdot}5$ and a red-brown precipitate separates slowly from the solution within $15-30$ min, even from 50% (v/v) dimethylformamide for $c_M \lessgtr \geq 4 \,.\, 10^{-5}\text{M}$, $c_L = 4 \,.\, 10^{-4}\text{M}$ and pH $2{\cdot}0-7{\cdot}0$. The absorbance of solutions in $0{\cdot}1-5\text{M-HClO}_4$ develops after 15 min and remains constant for $1-2$ h. The measurements were carried out 30 min after addition of the reagent.

The Absorbance–pH Curves

The green chelate $(\lambda_{max} \; 635 \text{ nm}, 465 \text{ nm})$ is formed practically quantitatively even in $6-8\text{M-HClO}_4$ in solutions with $c_L/c_M = 10$ and $c_L = 1{\cdot}995 \,.\, 10^{-4}\text{M}$ (isosbestic points lie on the absorption curves at 380 and 550 nm in 2M-HClO$_4$). Reproducible absorbance values were obtained in solutions with $> 3{\cdot}5\text{M-HClO}_4$ only when the

solutions were acidified with $HClO_4$ after the formation of the Pd(II) chelate in $<3.5\text{M-}HClO_4$, with intense cooling. In solutions with $c_H > 5\text{M}$, dimethylformamide decomposes and TAR is present in a differently absorbing protonated form other than H_3L^+. If Pd(II) is added last to a strongly acidic solution, dimethylformamide decomposition products and the formation of a new reagent which does not react with Pd(II) irreproducibly change the absorbance of the solution. The absorbance
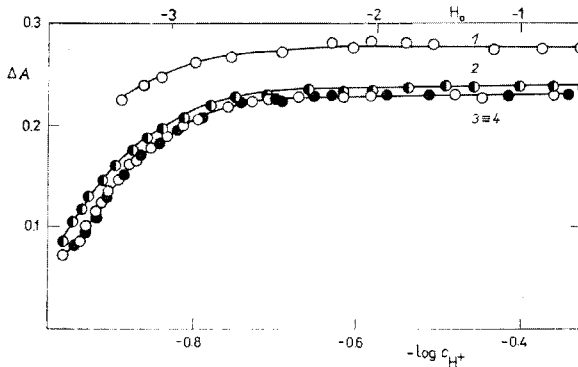

Fɪɢ. 1

Dependence of the Absorbance on the Acidity in a Strongly Acidic Medium in the Pd(II)–TAR System

$c_M = 3.970 \cdot 10^{-5}\text{M}$. 700 nm. Curve 1 $c_L/c_M = 10$, 30% (v/v) DMF; 2. $c_L/c_M = 10$, 10% (v/v) DMF; 3 $c_L/c_M = 10$, 5% (v/v) DMF; 4 $c_L/c_M = 20$, 5% (v/v) DMF.
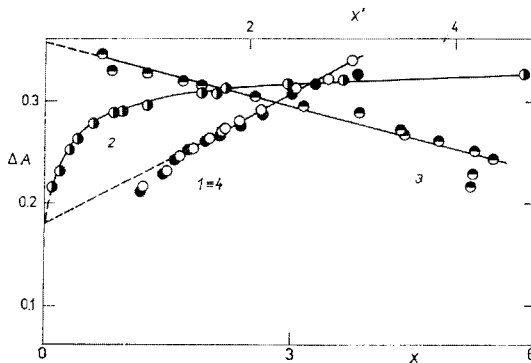

Fɪɢ. 2

Direct Graphical Analysis of the Dependence $A = f(H_0)$ Using Transformations (7) and (8)

Experimental conditions as in Fig. 1, $Z = 1$, curve 4, 670 nm. 1 $X = (A_{02} - \Delta A):[H]^2 \cdot 10^6$, $q = 1$ (first approximation); 2 $X = (A_{02} - \Delta A) \cdot 10^{10}/[H]^2$, $q = 2$; 3 $X' = (\Delta A - A_{01})$ [H] $\cdot 10^{-3}$, $q = 1$; 4 $X = (A_{02} - \Delta A) \cdot 10^6/[H]$, $q = 1$ (second approximation).

curves shifts to a more acidic region for acidities of $5-8\text{M-HClO}_4$ with increasing dimethylformamide concentrations, 5, 10, 30% (v/v) at 670 and 700 nm in the presence of excess reagent $(c_L/c_M = 10, c_L = 4 . 10^{-4}\text{M})$ and have the character of a transition between two complexes. The plateau of the second complex increases with increasing dimethylformamide content (Fig. 1). In strongly acidic HClO_4 media, the H_0 functions and antilog h were substituted into transformations (7), (8) and (9) for the transition between two mononuclear complexes instead of pH and H (ref.[26])

$$\Delta A = \varepsilon_1 c_M - \frac{kc_L^y (\Delta A - \varepsilon_2 c_M)}{Z^n [\text{H}]^q} , \tag{7}$$

$$\Delta A = \varepsilon_2 c_M - \frac{[\text{H}]^q Z^n (\Delta A - \varepsilon_1 c_M)}{kc_L^y} , \tag{8}$$

$$\log \frac{\Delta A - \varepsilon_1 c_M}{\varepsilon_2 c_M - A} + \log Z = q \, \text{pH} + y \log c_L + \log k . \tag{9}$$

Transformations (7) and (8) were linear for $y = 1$, $q = 1$, $Z = 1 + [\text{H}]/K_a = 1$ at 670 and 700 nm, with solutions 5 and 10% (v/v) in dimethylformamide. Curves $\Delta A = f(-\log c_H)$ have identical shapes for solutions with $c_M = 3\cdot972 . 10^{-5}\text{M}$ and various ligand excesses, $c_L = (3\cdot972 - 7\cdot944) . 10^{-4}\text{M}$ in 5% (v/v) dimethylformamide. This confirms a transition between two Pd(II) chelates with dissociation of a sin-
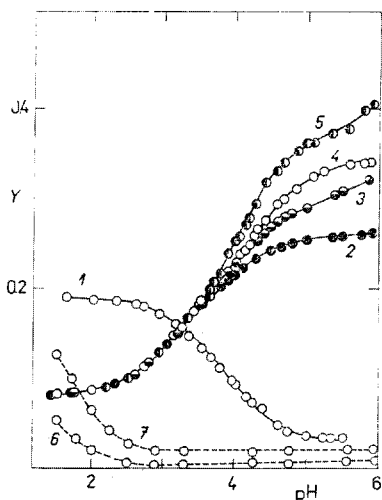

FIG. 3

The $\Delta A = f(\text{pH})$ Dependence in the Pd(II)–TAR System for Weakly Acidic Media

$c_M = 1\cdot986 . 10^{-5}\text{M}$; $c_L = 1\cdot995 . 10^{-4}\text{M}$; $Y = \Delta A$ (curves 1–5); $Y = A_L$ (curves 6 and 7); 50% DMF, $I = 1\cdot0$. Curve 1 670 nm, alkalized with Na_2CO_3; 2 570 nm, alkalized with Na_2CO_3; 3 555 nm, alkalized with Na_2CO_3; 4 570 nm, alkalized with NaOH; 5 555 nm, alkalized with NaOH; 6 ligand, 570 nm; 7 ligand, 555 nm.

gle proton in solutions with $c_H = 6-8M$ (Fig. 2); only the reaction

$$MLH_2(\varepsilon_{112}) \rightleftarrows MLH(\varepsilon_{111}) + H^+ , \quad K_{alk} \qquad (F)$$
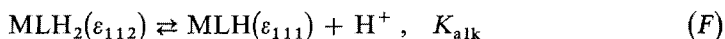
can take place. The ε_{112} and ε_{111} values are given in Table III.

A purple Pd(II) chelate with TAR (λ_{max} 520 nm, 400−425 nm) is formed at pH 2·2−5·5 in equimolar solutions and in solutions with excess ligand (an isosbestic point lies at 470 nm on absorption curves with various c_M/c_L values at pH 4·7). At pH > 6·5, where the *p*-hydroxyl proton of the reagent dissociates $(H_2L \rightarrow HL^-)$, another increase of $\Delta A = A - A_L$, occurs at 535−570 nm in dependence on the pH and is especially perceptible on alkalization of solutions with dilute sodium hydroxide. However, the absorption curves $(\lambda_{max}$ 525 nm) do not pass through the isosbestic point at pH 8·25, in dependence on a change in c_L/c_M. The absorbance–pH curves have different shapes at pH > 3·5 on neutralization with sodium carbonate (curves 2, 3 in Fig. 3). Transformations (7) and (8) are then linear in the whole pH range, 2·2−5·0, for $q = 1$, $Z = 1$ and $y = 1$ at 570, 555 and 535 nm. The extrapolated data, $A_{01} = \varepsilon_1 c_M$ and $A_{02} = \varepsilon_2 c_M$, were in good agreement with the experimental
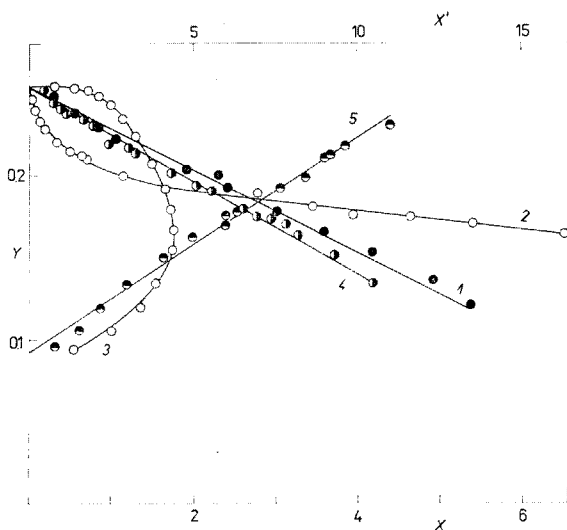

FIG. 4

Direct Analysis of the $A = f(pH)$ Dependence According to Transformations (7) and (8)

$c_L = 1·995 . 10^{-4}M$, $c_M = 1·986 . 10^{-5}M$; 50% (v/v) DMF, $I = 1·0M$-ClO_4^-, $Z = 1$, alkalized with Na_2CO_3; 570 nm, $Y = \Delta A$.

1 $X = (\Delta A - A_{01}) [H] 10^5$, $q = 1$ (first approximation); *2* $X' = (\Delta A - A_{01}) [H]^2 . 10^9$, $q = 2$; *3* $X = (\Delta A - A_{01}) [H]^{1/2} . 10^3$, $q = 0·5$; *4* $X = (\Delta A - A_{01}) [H] . 10^5$, $q = 1$ (second approximation); *5* $X = (A_{02} - \Delta A) . 10^{-2}/[H]$, $q = 1$.
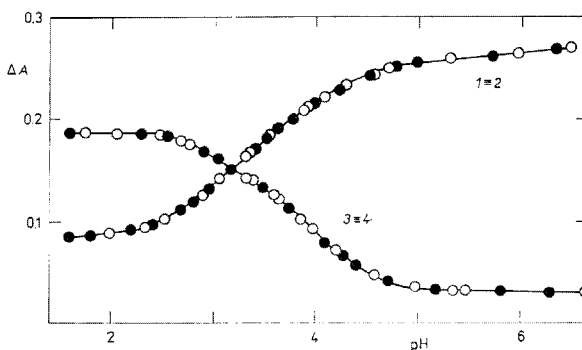
FIG. 5

Absorbance–pH Curves for Various Ligand Excesses in the Pd(II)–TAR System

$c_M = 1.986 \cdot 10^{-5}$ M, 50% DMF, $I = 1.0$, alkalized with Na_2CO_3. ○ $-c_L/c_M = 10$, $c_L = 1.996 \cdot 10^{-4}$ M; ● $c_L/c_M = 20$, $c_L = 3.970 \cdot 10^{-4}$ M; Curve 1, 2 570 nm; 3, 4 670 nm.
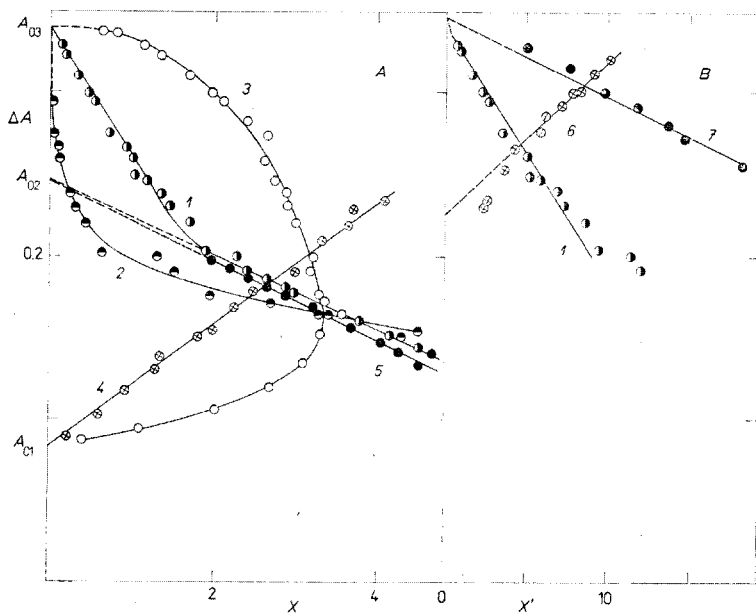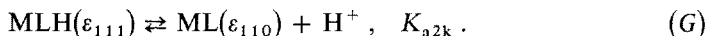

FIG. 6

Direct Analysis of the Absorbance–pH Curve Using Transformations (7) and (8)

$Z = 1$, $c_L = 1.995 \cdot 10^{-4}$ M, $c_M = 1.986 \cdot 10^{-5}$ M; 50% DMF, $I = 1.0$; alkalized with NaOH, 570 nm. Curve 1 $X = (\Delta A - A_{01}) \cdot [H] \cdot 10^5$, $q = 1$ (first approximation with measured A_0); 2 $X = (\Delta A - A_{01}) \cdot [H]^2 \cdot 10^9$, $q = 2$; 3 $X = (\Delta A - A_{01}) [H]^{1/2} \cdot 10^3$; $q = 0.5$; 4 $X = (A_{02} - \Delta A) \cdot 10^{-3}/[H]$; $q = 1$ (A_{02} obtained from curve 1 by extrapolation); 5 $X = (\Delta A - A_{01}) [H] \cdot 10^5$, second approximation, $q = 1$, A_0 obtained from curve 4); 6 $X' = (A_{03} - \Delta A) \cdot 10^{-3}/[H]$; $q = 1$ (A_{03} determined from the upper part of curve 1); 7 $X' = (\Delta A - A'_{02}) [H] \cdot 10^6$, $q = 1$ (A'_{02} obtained from curve 6).

TABLE III

The molar Absorption Coefficients of the Pd(II)-Chelates with TAR

Complex	PdLH$_2$		PdL			PdL(OH)		Mixture of PdL(OH)$_x$	PdLCl$_p$	
Method of determination	$A = f(H_0)$ graphically		$A = f(pH)$ calculation acc. to PRCEK SPEKTFOT4		calculation acc. to JOB program	continuous variations pH 5·25 JOB program	graphically from $A = f(pH)$	continuous variations pH 7·95 JOB program	$A = f(pH)$ PRCEK program	$A = f(c_{Cl})$ SPEKTFOT4 program
% (v/v) DMF	5%	10%	50%			50%		50%	50%	
nm 700	2 120	2 020								
670	4 540	4 400								
570			12 800	12 110 ± 18	11 905	15 596 ± 99	15 920	28 972 ± 223	11 300	10 950
555			14 200	13 819 ± 51	—	17 639 ± 171	17 980	32 144 ± 136	12 350	12 140
535			16 160	—	—	20 028 ± 181	—	27 326 ± 76	—	—

Complex	PdLH							PdLCl$_p$	
Method of determination	$A = f(H_0)$ 5%	10%	continuous variations 1M-H$^+$ (JOB)	Lambert-Beer dependence	$A = f(H_0)$ ternary Pd-Cl-L	$A = f(c_L)$ ternary Pd-Cl-L	$A = f(c_{Cl})$ ternary Pd-Cl-L	$A = f(pH)$ PRCEK program	SPEKTFOT4 program
% (v/v) DMF	5%	10%			30%			50%	
nm 700	5 000	5 280	7 366 ± 45	7 614 ± 18	7 210	7 130	6 980	—	
670	8 900	9 060	10 155 ± 23	10 155 ± 23	9 770	9 790	9 520	—	
635	9 720	9 870	10 885 ± 58	10 750 ± 17	10 470	10 700	10 430	10 470	
570			4 318 ± 23					4 280	3 960 ± 31
555								4 330	4 256 ± 41
535								5 290	4 075

data after the second approximation for $c_L/c_M = 10$. Identical subtracted absorbance –pH curves were obtained for 570, 555 and 535 nm in solutions with $c_L/c_M = 20$, $c_L = 3.990 \cdot 10^{-4} M$, at pH 2·1—4·5; consequently, the position and shape of the absorbance–pH curves is again independent of the ligand concentration and a single proton dissociates during the transition between the Pd(II) chelates (Figs 3—5). At pH 2·1—4·5, this transition corresponds to the following equilibrium alone:

$$ MLH(\varepsilon_{111}) \rightleftarrows ML(\varepsilon_{110}) + H^+ , \quad K_{a2k} . \qquad (G) $$

Interpretation of the absorbance–pH curves for solutions neutralized with dilute sodium hydroxide gave linear transformation (8) for $q = 1$, at pH 2·2—3·5, $c_L/c_M = = 10$, $c_L = 1.995 \cdot 10^{-4} M$ and at 570 nm (Fig. 6). The value found, $A_{02} = \varepsilon_2 c_M$, again gave a linear dependence for $q = 1$ with $A_{01} = \varepsilon_1 c_M$, identical with the measured value, on substitution into transformation (7). Hence the same equilibria are involved in this part of the absorbance–pH curve on neutralization with carbonate and with an alkali hydroxide. The equilibrium constant values, found by means of logarithmic analysis of the pH curve (transformation (9)), are practically identical for the two cases $\left(\log K = -3.38 \; (Na_2CO_3), \; -3.44 \; (NaOH)\right)$; the same is valid for the molar absorption coefficients (Table III).

At pH 3·8—5·5, a different equilibrium is encountered in solutions containing the alkali hydroxide than for those containing the carbonate, but a chelate with Pd : L = 1 : 1 is also formed and a single proton dissociates. If the graphical analysis is based on the last experimental plateau $\left(A_{03} = 0.340 \text{ at } 570 \text{ nm, curve } 4 \text{ in Fig. 3}\right)$, plateau A_{02} is obtained from transformation (7), which is identical with value A_{02} obtained from the lower branch. In this part of the pH-curve, the reaction

$$ ML(\varepsilon_{110}) + H_2O \rightleftarrows ML(OH)(\varepsilon_{11-1}) + H^+ , \quad k \qquad (H) $$
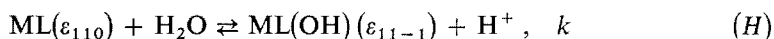
probably proceeds. Because of the small difference between the absorption coefficients of the two complexes, the reliability of the determination of equilibrium constant k is lower. The resultant ε_{11-1} values are also given in Table III.

Continuous variation plots in equimolar series confirm the stoichiometric ratio of the components in the complex, Pd : L = 1 : 1, in the whole acidity range from 3M-HClO$_4$ to pH 8, for measurement at 535—700 nm in a medium of 30—50% dimethylformamide. The molar absorption coefficients calculated from the variation curves in 50% (v/v) dimethylformamide at pH 5·25 and 7·95 (0·01M tetraborate buffer) for solutions alkalized with sodium hydroxide and those calculated from equation (6) have different values, due to the presence of various Pd(II) hydroxo complexes.
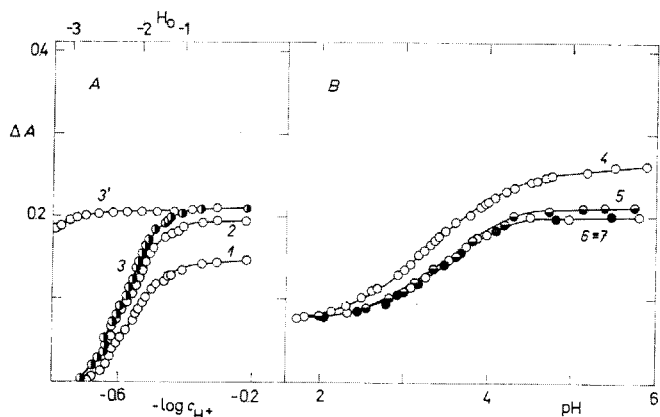
FIG. 7

Dependence of the Absorbance on the Solution Acidity in the Pd(II)–TAR–Cl System for Various
Cl^- Concentrations

$c_M = 1\cdot986 . 10^5 M$, $c_L = 2\cdot00 . 10^{-4} M$; A: 30% DMF, B: 50% DMF, $I = 1\cdot0$; alkalized with
Na_2CO_3. 1 700 nm, $c_{Cl} = 0\cdot114 M$; 2 670 nm, $c_{Cl} = 0\cdot114 M$; 3 635 nm, $c_{Cl} = 0\cdot114 M$; $3'$ 635 nm
without chloride; curves $4, 5, 6, 7$ at 570 nm; 4 without chloride, 5 0·03M-NaCl; 6 0·1M-NaCl,
7 0·3M-NaCl.
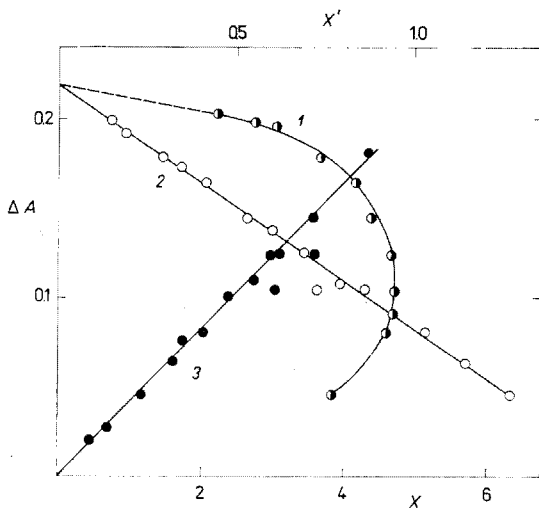
FIG. 8

Direct Analysis of the $A = f(H_0)$ Dependence Using Transformations (1) and (2) in the Presence
of Chloride

$c_M = 1\cdot986 . 10^{-5} M$, $c_L = 2\cdot00 . 10^{-4} M$, 30% DMF, $c_{Cl} = 0\cdot114 M$, 635 nm. 1 $X = (\Delta A -$
$- A_{01}) [H] . 10^5$, $q = 1$; 2 $X = (\Delta A - A_{01}) [H]^2 . 10^{-2}$, $q = 2$; 3 $X' = (A_{02} - \Delta A) . 10^4 / [H]^2$,
$q = 2$.

Complexation Equilibria in the Pd(II) *Chloride–TAR System*

The stoichiometric ratio, Pd : L = 1 : 1, also remains constant in the whole acidity range from 3M-HClO$_4$ to pH 5·2 in solutions with $\leq$0·114M-Cl$^-$. In solutions at pH $\leq$ 2 and with a constant excess of Cl$^-$ and of the ligand, the absorbance does not stabilize until after 3 h, but then remains constant. The absorbance–pH curves are shifted to lower acidities in the presence of Cl$^-$ (Fig. 7). In solutions with a constant excess of Cl$^-$ and in strongly acidic media, equilibrium (I) can be established:

$$\text{PdCl}_m + \text{H}_3\text{L}^+ \rightleftarrows \text{PdCl}_{m-p}\text{HL}(\varepsilon_2') + p\,\text{Cl}^- + 2\,\text{H}^+ . \qquad (I)$$
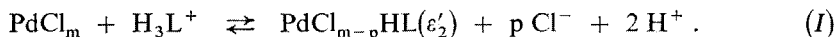
The number of protons dissociated $(q = 2\cdot03)$ was exactly confirmed by graphical analysis using transformations $(1)-(3)$, for $\text{H}_0 = -2\cdot1$ to $-1\cdot0$ and $30\%\,(\text{v/v})$ dimethylformamide (Fig. 8). The $A_{01} = \varepsilon_1 c_M$ and $A_{02} = \varepsilon_2 c_M$ values agree with the experimental data after the first approximation and the molar absorption coefficient found, ε_2', is identical with the ε_{111} value for the green binary complex (Table III). Analysis of the $A = \text{f}(c_{\text{Cl}})$ dependence at a constant acidity, 3·2M-HClO$_4$ at 635 to 700 nm, clearly indicated interaction of 3 Cl$^-$ with the green PdLH$^+$ complex $(\lambda_{\text{max}}$ 635 nm$)$, $p = 2\cdot96$, using transformations $(1)-(3)$, where ε_1 is the molar absorption coefficient of the PdCl$_3^-$ complex and ε_2 is that of PdHL (equilibrium (J)).

$$\text{PdCl}_3^- + \text{H}_3\text{L}^+ \rightleftarrows \text{PdHL}^+ + 3\,\text{Cl}^- + 2\,\text{H}^+ . \qquad (J)$$

As the $A_{01} = \varepsilon_1 c_M$ value found equals zero, no ternary complex is formed (Fig. 9). The curve of dependence $\Delta A = \text{f}(c_L)$ for $c_M = 3\cdot972 \cdot 10^{-5}\text{M}$ and 3·7M-HClO$_4$ in $30\%\,(\text{v/v})$ dimethylformamide, in the presence of a constant chloride concentration, 0·2M, at 635–700 nm, does not attain the maximum absorbance value even at a 20-fold ligand excess, compared with the binary system under the same conditions. However, the necessary TAR excess decreases with decreasing acidity and the absorbance on the plateau of the absorbance dependence increases. Graphical analysis considering equilibrium (E) and using transformations $(1)-(3)$ confirms coordination of a single dye molecule, even in the presence of chloride $(y = 1\cdot02$ for 635–700 nm, when the components do not absorb). The molar absorption coefficient found for the complex is identical with the value of ε_{111} for the binary complex, PdLH$^+$. The equilibrium constant, calculated from logarithmic dependence (3) for equilibrium (E) and the $A = \text{f}(c_L)$ dependence $(\log K = 4\cdot4)$, is also in agreement with the values found for the other absorbance curves in the presence of chloride (Table V). The absorption curves for the ternary system have identical λ_{max} and isosbestic points with the curves of the green binary Pd(II) complex with TAR. The results given confirm that no mixed-ligand ternary complex of Pd(II) is formed in acidic media in the presence of chloride.

At pH $2-6$, the solution absorbance in the presence of chloride stabilizes within 60 minutes and remains constant for $2-3$ h. The solubility of the red chelate in a medium of $50\%\,(v/v)$ dimethylformamide increases in the presence of chloride and λ_{max} is shifted from 570 nm to 550 nm, indicating the presence of a mixed Pd(II) chelate with TAR and chloride. Thus at pH $2-5$, reaction (K) occurs in addition to the basic reaction, (G):

$$MLH(\varepsilon_{111}) \;+\; p\,X^- \;\rightleftarrows\; MLX_p(\varepsilon_{11p}) \;+\; H^+ \quad k_p\,. \tag{K}$$
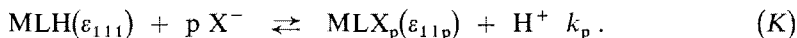
The absorbance–pH curves of solutions with $c_L/c_M = 10$, $c_L = 2\,.\,10^{-4}$M and various c_{Cl} equal to $0-0.3$M, at 570 and 550 nm (Fig. 7B) were interpreted assuming simultaneous reactions (K) and (G) and dissociation of TAR $(H_2L \rightleftarrows HL^- + H^+;\; K_{a2},\, \bar{\varepsilon}_L)$ using the following principal relationships:

$$A = \varepsilon_{11}[MLH) + \varepsilon_{110}[ML] + \varepsilon_{11p}[MLX_p]\,,$$

$$c_M = [MLH] + [ML] + [MLX_p] = [MLH]\,(1 + K_{alk}/[H]) + [MLX_p]$$

$$c_X = [X]$$

$$\Delta A = \varepsilon_{11p}c_M - \frac{[H]\,(Z_k\,\Delta A - \bar{\varepsilon}_K c_M)}{k_p c_X^p}\,, \tag{10}$$

$$\log\frac{Z_k\,\Delta A - \bar{\varepsilon}_K c_M}{\varepsilon_{11p}c_M - \Delta A} = pH + p\log c_X + \log k_p\,, \tag{11}$$

where $Z_k = 1 + K_{alk}/[H]$ and $\bar{\varepsilon}_k = \varepsilon_{111} + K_{alk}\varepsilon_{110}/[H]$. For K_{alk} the value calculated from the $A = f(pH)$ curves for the binary system was employed (Table V). Linearity of transformation (10) and the value, $q = 1.02$, obtained from the logarithmic dependence, (11) confirm that a single proton is dissociated in both equilibria (G) and (K). The molar absorption coefficients of the ternary complex with chloride are somewhat lower than those for the binary complex, ML (Table III). Only the chloride content in ternary complex $PdLCl_p$ is unknown. Analysis of the concentration dependence $A = f(c_{Cl})$ at pH 4·85 and at 555, 570 and 590 nm using transformations (10) and (11) gave $p = 2.09$, i.e. coordination of 2 Cl^- during formation of the ternary complex. However, this value is not entirely unambiguous because of experimental difficulties with solution preparation and the small difference between the values of limiting absorbances A_{01} and A_{02} at the optimum λ, although the values of the equilibrium constants obtained from the logarithmic analysis of the $A = f(c_{Cl})$ and $A = f(pH)$ curves under the given conditions are similar $(\log k_p = -0.4$ and -0.6, respectively$)$. However, this fact would indicate a deviation from the common coordination number of Pd(II), 4, or a decrease in the number of coordination bonds of TAR.

Complexation Equilibrium Constants

The constants for the complexation equilibria were calculated from the graphical logarithmic analysis ((*3*), (*9*) and (*11*)) and by the SPEKTFOT 4 procedure for equilibrium (*G*) (Tables IV and V). In Table IV, intermediate values of U, $\log \beta_{111}$, ε_{111} (complex MLH) and $\log \beta_{110}$, ε_{110} (complex ML) are given for the individual computing cycles. The data in the first line are the input data. The input coefficients for complex MLH were $m = 1$, $n = 1$ and $q = 1$, and for complex ML, $m = 1$, $n = 1$, $q = 0$.

Complexation Equilibria of Pd(II) *with* TAMP

A green Pd(II) chelate is formed in a wide acidity range; the equilibrium is established within $20-30$ minutes in $0.1\text{M}-1.0\text{M-HClO}_4$. The dependences of the absorption curves on the component concentrations confirm the formation of a single complex with λ_{max} $755-765$ and 367 nm and isosbestic points at 610 and 402 nm. At pH $2-7$, the absorbance of Pd(II) solutions with excess dye $(c_L/c_M = 2-20)$ in 30% (v/v) dimethylformamide stabilizes within 5 min. The absorption curves measured at pH 7.70 against a reagent solution of the same concentration indicate a mixture of complexes; for $c_M/c_L > 1$, a chelate with λ_{max} 760 nm predominates (the isosbestic point on the
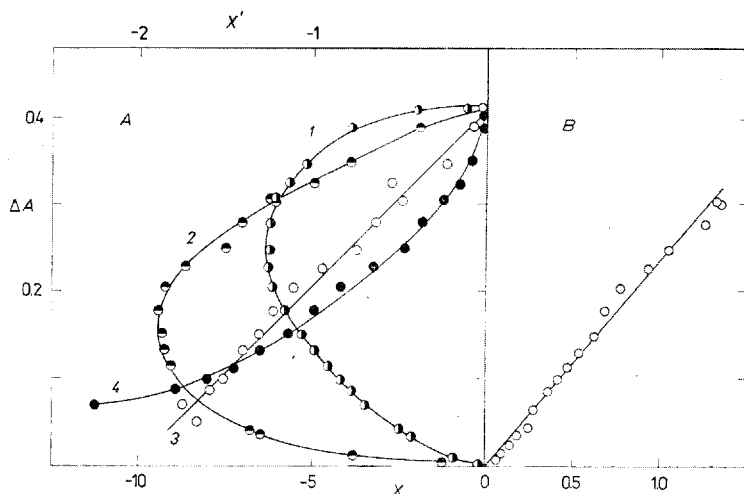

Fig. 9

Direct Analysis of the $A = f(c_{Cl})$. Dependence in Strongly Acidic Medium in the Pd(II)–TAR–Cl System According to Relationships (*1*) and (*2*)

$c_H = 3.215\text{M-HClO}_4$, $c_L = 3.990 . 10^{-4}\text{M}$, $c_M = 3.972 . 10^{-5}\text{M}$, 30% DMF, 635 nm; *A*: Curve *1* $X = (A_{01} - \Delta A) [\text{Cl}] . 10^2$, $p = 1$; *2* $X' = (A_{01} - \Delta A) [\text{Cl}]^2 . 10^2$, $p = 2$; *3* $X = (A_{01} - \Delta A) [\text{Cl}]^4 . 10^4$, $p = 4$; *B*: $X = (A_{02} - \Delta A) . 10/[\text{Cl}]^3$, $p = 3$.

absorption curves is at 610 nm) and for $c_L/c_M > 5$, a chelate with λ_{max} 600 – 710 nm is present, with an isosbestic point at 530 nm.

At pH 0 – 3 and 600 – 700 nm in a medium of 30% (v/v) dimethylformamide, the absorbance of solutions with excess ligand, $c_L/c_M = 10 - 30$ $(c_L = 4 . 10^{-4}$ to $1 \cdot 2 . 10^{-3}M)$, is constant. The continuous variation plots in 30% (v/v) dimethylformamide and 1M-HClO$_4$ at 790 – 610 nm confirm the formation of a single stable

TABLE IV

Changes in the U Values and the p_i Parameters During Computation According to the SPEKT-FOT 4 Program (Equilibrium (G))

Cycle	U	$\log \beta_{111}{}^a$	ε_{111}	$\log \beta_{110}{}^b$	ε_{110}
—	—	28·22	3 961	23·84	12 110
1	$0\cdot3825 . 10^{-1}$	28·02	3 961	24·04	12 110
2	$0\cdot6241 . 10^{-2}$	27·80	3 961	24·24	12 110
3	$0\cdot4808 . 10^{-3}$	27·80	3 961	24·44	12 110
4	$0\cdot5809 . 10^{-4}$	27·61	4 075	24·35	11 905

^{a} $\beta_{111} = [PdLH]/[Pd] [L] [H]$; ^{b} $\beta_{110} = [PdL]/[Pd] [L]$.

TABLE V

Constants for Some Pd(II) Equilibria with TAR $(I = 0 \cdot 1)$

K	$\log K$
$[PdHL][H]/[PdH_2L]$	4·12 (5% DMF); 4·24 (10% DMF)^d
$[PdL][H]/[PdHL]$	$-3\cdot44$ (50% DMF)^{e,k}; $-3\cdot38$ (50%) DMF)^{e,l}
$[PdHL][H]^2 [Cl]^3/[PdCl_3][H_3L]$	4·45^{a,f}; 4·39^{b,f}; 4·40^{c,f} (30% DMF)
$[PdHL]/[Pd][L][H]$	27·61^g (50% DMF)
$[PdHL]/[Pd][HL]$	20·42^i
$[PdHL]/[Pd][HL]$	16·16^h
$[PdL]/[Pd][L]$	24·35^g (50% DMF)
$[PdL(OH)][H]/[PdL]$	$-4\cdot64^{e,l}$
$[PdLCl_2][H]/[PdLH][Cl]^2$	$-0\cdot6^e$; $-0\cdot4^j$ (50% DMF)

^{a} From $\Delta A = f(H_0)$ at 635 nm; ^{b} from $\Delta A = f(c_{Cl})$ at 635 – 700 nm (average of 3 values); ^{c} from $\Delta A = f(c_L)$ at 635 and 700 nm; ^{d} calculated from $0 = q H_0 + \log K$ for 670 and 700 nm; ^{e} calculated from $0 = pH + \log K$; ^{f} calculated from $2 H_0 + \log c_L - 3 \log c_x + \log K$; ^{g} calculated according to SPEKTFOT 4; ^{h} $\beta_{1H} = \beta_{111} . K_{a3}$; ^{i} $\beta_{1H} = \beta_{111} . K_{a2}$; ^{j} from $\Delta A = f(c_{Cl})$, average for 590 and 570 nm; ^{k} alkalization with sodium carbonate; ^{l} alkalized with sodium hydroxide; ^{m} from $A = f(pH)$, average of values at 550 and 570 nm.
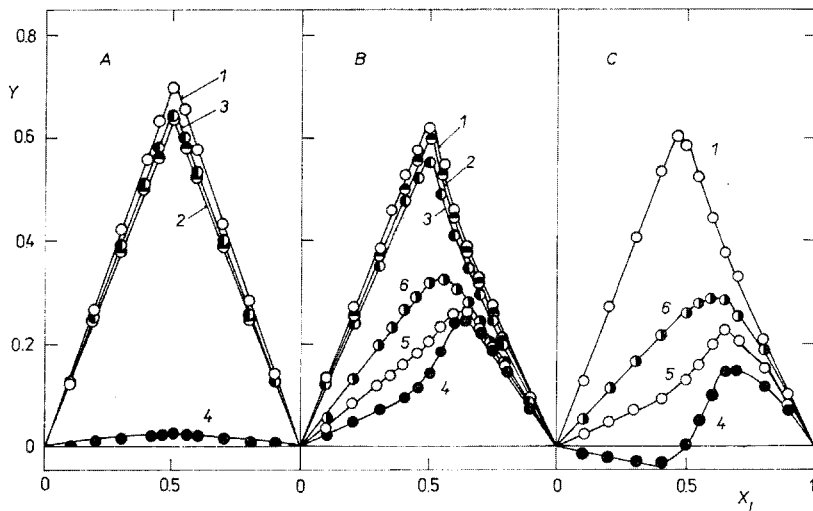
FIG. 10

Continuous Variation Plots in the Pd(II)–TAMP System

$c_0 = 1.60 \cdot 10^{-4}$M,   30% DMF, $Y = A - A_L$, A 1·0M-HClO$_4$; B pH 6·50, I 0·1M; C pH 7·95, 0·01M borate buffer. Curve (nm) 1 760, 2 730, 3 790, 4 610, 5 630, 6 650.
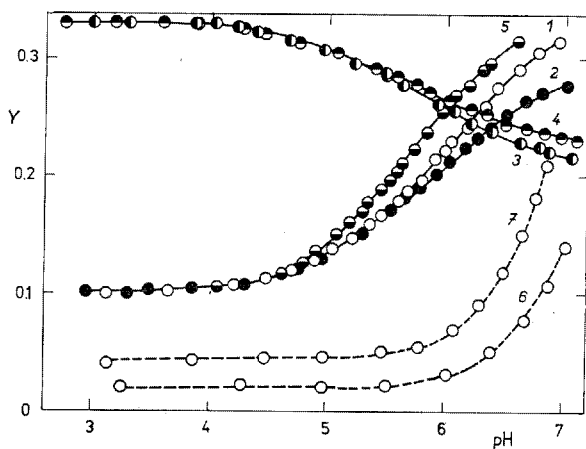

FIG. 11

The $\Delta A = \mathrm{f}(\mathrm{pH})$ Dependences in the Pd(II)–TAMP System

$c_M = 4.00 \cdot 10^{-5}$M, I 0·1, 30% DMF. Curves $1-5$: $Y = A - A_L$; $6, 7$: A_L. Curve 1 600 nm, $c_L/c_M = 20$, $c_L = 8.00 \cdot 10^{-4}$M; 2 600 nm, c_L/c_M m 10, $c_L = 4.0 \cdot 10^{-4}$M; 3 760 nm, $c_L/c_M = 20$; 4 600 nm, $c_L/c_M = 10$; 5 600 nm, $c_L/c_M = 30$, $c_L = 1.20 \cdot 10^{-3}$M; 6 600 nm, $c_L = 4.0 \cdot 10^{-4}$M; 7 600 nm, $c_L = 8.0 \cdot 10^{-4}$M.

1 : 1 complex (Fig. 10A). The absorbance curve of this complex cannot be measured at higher acidities, because of rapid decomposition of the reagent at pH $<$ 0, taking place both in $HClO_4$ and H_2SO_4. In this acidity range, the green PdL^+ chelate $(\lambda_{max}\ 760$ nm, $\varepsilon = 8610)$ is formed virtually quantitatively. Another complexation equilibrium is indicated at pH $> 4\cdot1$ in solutions with $c_L/c_M = 10-20\ (c_L = 4\ .\ 10^{-4}$ to $8\ .\ 10^{-3}$M) and is independent of the ligand concentration at pH $4\cdot1-5\cdot7$; however, at pH $> 5\cdot7$, the absorbance–pH curve shifts to lower pH with increasing ligand concentrations and the absorbance at $600-660$ nm increases for $c_L/c_M = 10-30$ and $c_L = 4\ .\ 10^{-4}-1\cdot2\ .\ 10^{-3}$M, while that at $730-790$ nm decreases. These changes indicate the presence of at least two complexation equilibria (Fig. 11). Transformations $(7)-(9)$ are linear for the pH–absorbance curve at 600 nm and c_L/c_M 20 $(c_L = = 4\ .\ 10^{-4}-8\ .\ 10^{-4}$M), for $q = 1\cdot0$ $(y = 1)$ in the pH region $4\cdot1-5\cdot8$, assuming a transition between two mononuclear Pd(II) chelates (Fig. 12). During the analysis, the measured $A_{01} = \varepsilon_1 c_M$ value for the PdL^+ chelate agree with the value calculated from transformation (7); the calculated value of $A_{02} = \varepsilon_2 c_M$ is, however, lower than the experimental value (Fig. 12) at pH 7 and 600 nm. In solutions with small ligand excesses equilibrium (L) probably predominates:

$$PdL^+ + H_2O \rightleftarrows PdL(OH) + H^+ . \qquad (L)$$
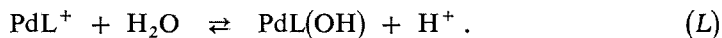
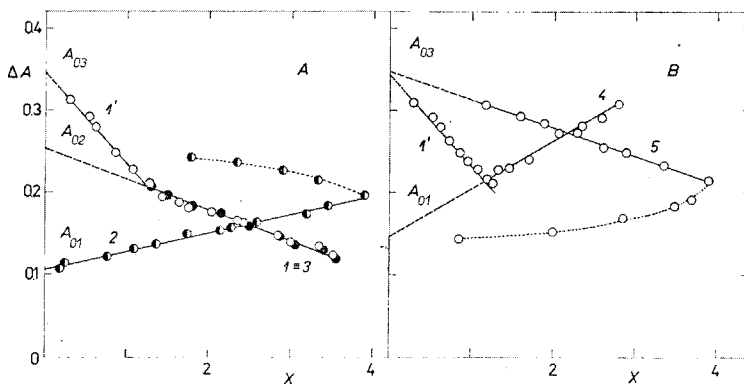At pH $> 5\cdot8$, the equilibrium also depends on dissociation of a single proton

FIG. 12

Direct Graphical Analysis of the Absorbance–pH Curve in the Pd(II)–TAMP System Using Transformations (7) and (8) at $Z = 1$

$c_L/c_M = 20$, $c_L = 8\cdot00\ .\ 10^{-4}$M, $c_M = 4\cdot00\ .\ 10^{-5}$M, 30% DMF, I 0·1; alkalized with Na_2CO_3, 600 nm. Curve $1, 1'$ $X = (\Delta A - A_{01})$ [H] . 10^7, $q = 1$; 2 $X = 10^{-4}(A_{02} - \Delta A)/$[H], $q = 1$; 3 $X = (\Delta A - A_{01})$ [H] . 10^7, $q = 1$ (second approximation); 4 $X = 10^{-5}(A_{03} - \Delta A)$ [H]$^{-1}$, $q = 1$; 5 $X = (\Delta A - A'_{01})$ [H] . $10^8, q = 1$.

and involves ligand participation (curves *4, 5*, Fig. 12B). The experimental A'_{01} value is different from A_{02} when the experimental A_{03} value is used in transformation (7) for $c_L/c_M \leqq 20$; the logarithmic analysis confirms these conclusions. If A_{02} determined from transformation (8) is used, then for $c_L/c_M = 10$ and 20, the slope *q* equals 1·03 only for pH $< 5·8$ (Fig. 13, curves *1* and *2*). The identity of the logarithmic straight lines for both ligand excesses again verifies that the ligand does not participate in the equilibrium in this pH region. If the A_{03} and A'_{01} values are used for the analysis of the upper parts of the pH–absorbance curves, then logarithmic transformation (9) is linear with a slope of $q = 1·05$ for $c_L/c_M = 10$ and 20 (Fig. 13, curves *4* and *5*). The straight line is shifted to a more acidic region for higher ligand excesses, confirming the participation of the ligand in this complexation equilibrium. With ligand excess $c_L = 1·2 . 10^{-3}$M, $c_L/c_M = 30$ and at pH $4·7 - 6·6$, equilibrium (*M*) entirely predominates:

$$ PdL^+ + HL \rightleftarrows PdL_2 + H^+ . \qquad (M) $$
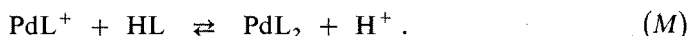
A single proton is dissociated in the reaction ($q = 1·02$, Fig. 13, curve *3*). Equilibrium (*L*) is indicated only at pH $4·1 - 4·7$, where the points are located outside linear dependence (9).
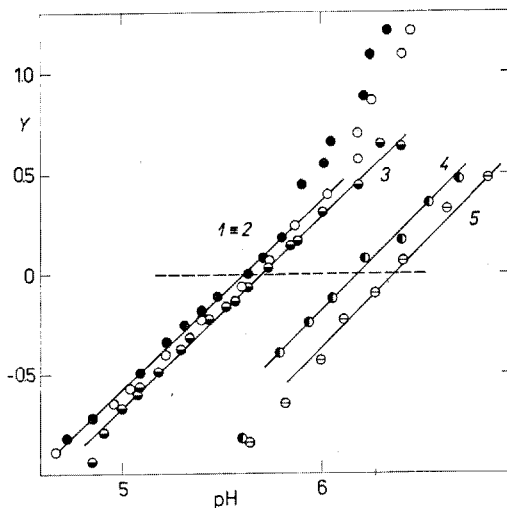

FIG. 13

Logarithmic Analysis of the $A = f(\text{pH})$ Dependence in the Pd(II)–TAMP System According to Relation (9), $Z = 1$

Experimental conditions as in Fig. 11. 600 nm. $Y = \log(\Delta A - A_{01})/(A_{02} - \Delta A)$; Curve *1* $c_L/c_M = 10$ (the A_{01}, A_{02} plateaux used); *2* $c_L/c_M = 20$ (the A_{01} and A_{02} plateaux used); *3* $c_L/c_M = 30$ (the A_{03} and A'_{01} plateaux used); *4* $c_L/c_M = 20$ (the A_{03} and $A'_{01} \neq A_{02}$ plateaux used); *5* $c_L/c_M = 10$ (the A_{03} and $A'_{01} \neq A_{02}$ plateaux used).

The continuous variation plots confirm the presence of a mixture of two complexes in solution at pH 6·5, one with a Pd : L stoichiometric ratio of 1 : 1 absorbing predominantly at 790−730 nm and the other with M : L = 1 : 2 absorbing at 610 to 650 nm (Fig. 10*B*). At pH 7·95 (0·01M tetraborate buffer), the complex formation is similar; at 540−610 nm, the maximum appears between $x_L = 0·60−0·67$ and at 760 nm at $x_L = 0·45$. Distortion of the curves indicates simultaneous hydrolysis of the complexes in solutions with excess metal (Fig. 10*C*).

Molar Absorption Coefficients and Equilibrium Constants

Graphical analysis yielded only orientative values for the constants and molar absorption coefficients. Simultaneous equilibria prevent the use of the PRCEK programs for equilibrium evaluation. The SPEKTFOT 4 procedure was successfully employed for the interpretation of the pH–absorbance curves. The molar absorption coefficient values, obtained by various procedures, are summarized in Table VI.

TABLE VI

Molar Absorption Coefficients of Pd(II) Complexes with TAMP in 30% (v/v) Dimethylformamide

Complex	790 nm	760 nm	730 nm	600 nm
PdL$^+$	7 980^a	8 610^a 8 400^b	7 740^a	2 525^b 3 823 ± 97^d
PdL(OH)	—	5 750^b	—	6 500^b 5 455 ± 475^d
PdL$_2$	—	—	—	8 250^c 8 706 ± 579^d

^{a} From the continuous variation plots in 1M-HClO$_4$; ^{b} from $A = f(pH)$ at $c_L/c_M = 10$ ($c_L = 4 . 10^{-4}$M; analysis of the part of the curve with predominating equilibrium (L)); ^{c} from $A = f(pH)$ for $c_L/c_M = 30$ ($c_L = 1·2 . 10^{-3}$M, for predominating equilibrium (M)); ^{d} computation according to the SPEKTFOT 4 program.

Interpretation of the pH–Absorbance Curves Using the SPEKTFOT 4 Procedure for pH 4·1−7·0 and 30% (v/v) Dimethylformamide in the Presence of Excess Ligand

The pH–absorbance curves were interpreted for solutions with $c_L/c_M = 20$ and 30, $c_L = 8 . 10^{-4}$M and 1·2 . 10^{-3}M. The calculation of the required stability constants was carried out using the equilibria and relationships summarized in Table VII.

TABLE VII

Equilibria of Pd(II) Chelates with TAMP and the Input Data for Some Constants in the SPEKTFOT 4 Procedure

Equilibrium	K	$\log K$
$PdL + OH^- \rightleftharpoons PdL(OH)$	K_{OH}	$-5 \cdot 64^a$
$Pd + HL \rightleftharpoons PdL + H^+$	k_1	
$PdL + HL \rightleftharpoons PdL_2 + H^+$	k_2	$-2 \cdot 76^b$
$Pd + L \rightleftharpoons PdL$	β_{110}	$6 \cdot 60^d$
$Pd + 2L \rightleftharpoons PdL_2$	β_{120}	
$Pd + L + OH^- \rightleftharpoons PdL(OH)$	β_{11-1}	
$HL \rightleftharpoons H^+ + L$	K^a_2	$-8 \cdot 39^c$
$\log \beta_{120} = \log k_2 + \log \beta_{110} + pK^a_2$		$12 \cdot 2$
$\log \beta_{11-1} = \log K_{OH} + \log \beta_{110}$		$1 \cdot 0$

[a] Logarithmic analysis of the lower part of the $A = f(pH)$ curve for $c_M/c_L = 1/10$ and 600 nm; [b] logarithmic analysis of the $A = f(pH)$ curve for $c_L/c_M = 30$ and 600 nm; [c] for 30% (v/v) dimethylformamide according to[31]; average value from the continuous variation plots for 1M-$HClO_4$ according to the JOB program.

TABLE VIII

The Input and Output Data for The Pd(II) Chelates with TAMP According to the SPEKTFOT 4 Procedure ($c_L/c_M = 20$, $c_L = 8 \cdot 0 . 10^{-4}$M)
$U = 2 \cdot 333 . 10^{-2}$ (after the first cycle); $U = 2 \cdot 015 . 10^{-3}$ (after the final and eleventh cycle).

Chelate	m	n	q	ε, 600 nm	$\log K$	$\varepsilon \pm 3s_\varepsilon$	$\log K \pm 3s_{\log K}$
PdL	1	1	0	2 525	$6 \cdot 60$	$3\ 823 \pm 94$	$7 \cdot 59 \pm 0 \cdot 11$
PdL(OH)	1	1	-1	6 500	$1 \cdot 00$	$5\ 455 \pm 475$	$1 \cdot 79 \pm 0 \cdot 03$
PdL_2	1	2	0	8 250	$12 \cdot 2$	$8\ 705 \pm 579$	$12 \cdot 12 \pm 0 \cdot 09$

As the input data for some constants, the approximate values determined by the graphical logarithmic analysis of particular parts of the absorbance–pH curves were employed. As the input data for the molar absorption coefficients were used the values found by graphical analysis of the absorbance curves. Because of the high stability of complex ML, the β_{110} value taken from the variation curve is only approximate $(\pm 1 - 2$ orders of magnitude). The more complex equilibria then do not permit sufficiently accurate determination of constants K_{OH} and K_2 and consequently also of the input $\log \beta_{120}$ and $\log \beta_{11-1}$ values. In Table VIII, the input m, n and q coef-

ficients and the stability constants and their final values are given. Because of the lower accuracy of the input data, eleven cycles were required for attaining the optimum U, ε and β values. The absorbance–pH curve calculated from the determined data is in good agreement with the absorbance–pH curve measured at 600 nm; $c_L/c_M = 20$ and $c_L = 8\cdot0 \cdot 10^{-3}$M (Table IX). The calculation also confirmed the correctness of the proposed composition of the Pd(II) chelates, which are in equilibrium at pH $4\cdot5 - 7\cdot0$ and $c_L/c_M = 20$. During the calculation from the absorbance curve data for solutions with $c_L/c_M = 30$ and $c_L = 1\cdot2 \cdot 10^{-3}$M, the results obtained according to the SPEKTFOT 4 program could be used only assuming that equilibrium $PdL^+ + L \rightleftarrows PdL_2$ predominates and the input data for complex $PdL(OH)$ $\left(\log \beta_{11-1}\right)$, obtained from the previous calculation for $c_L/c_M = 20$, do not change.

TABLE IX

Comparison of the Calculated and Experimental Absorbance–pH Curves in the Pd(II)–TAMP System ($c_L/c_M = 20$; $c_L = 8\cdot0 \cdot 10^{-4}$M)

pH	A_{meas}	A_{calc}	A
4·74	0·170	0·180	−0·010
4·90	0·179	0·189	−0·010
4·96	0·181	0·193	0·012
5·08	0·187	0·199	−0·012
5·20	0·195	0·206	−0·011
5·23	0·198	0·208	−0·010
5·25	0·205	0·216	−0·011
5·38	0·236	0·218	−0·013
5·40	0·207	0·219	−0·012
5·48	0·220	0·225	−0·005
5·56	0·222	0·231	−0·009
5·63	0·232	0·237	−0·005
5·75	0·250	0·249	+0·001
5·82	0·262	0·257	+0·005
5·90	0·269	0·266	+0·003
6·00	0·284	0·279	+0·005
6·07	0·296	0·290	+0·006
6·22	0·322	0·315	+0·007
6·30	0·341	0·332	+0·009
6·40	0·366	0·356	+0·009
6·44	0·370	0·367	+0·003
6·56	0·409	0·407	+0·002
6·62	0·429	0·430	−0·001
6·70	0·455	0·466	−0·011

Complexation Equilibria of Pd(II) *with* 2-TAN-3,6-S

The formation of a green chelate with Pd : L = 1 : 1 $\left(\lambda_{max} 432, 654, 706 \text{ nm}\right)$ in media of 6M-H_2SO_4 up to pH 6, whose absorbance is constant in this whole range, has already been described[16]. Also in perchloric acid media only 1 : 1 Pd(II) chelates are formed, even in the presence of excess ligand. The absorption curves of solutions with various c_M/c_L ratios for 1·0M-$HClO_4$ and pH 6·1 indicate the existence of at least two Pd(II) chelates with a 1 : 1 stoichiometric component ratio. The maximum at 700 nm, typical for the PdL complex in acidic solutions, is less pronounced at pH 6·1. The isosbestic points on the two curves are also substantially different (Table X and Fig. 14). In solutions with excess ligand ($c_L = 1·995 . 10^{-4}$M, $c_L/c_M = 10$), the absorbance is constant for $1·0-3·0$M-$HClO_4$ at $700-570$ nm; from pH 0 it slowly decreases at 700 nm but remains constant at 570 nm for pH $0-7$. The absorbance

TABLE X
Absorption Characteristics of the Pd(II) Complexes with 2-TAN–3,6-S

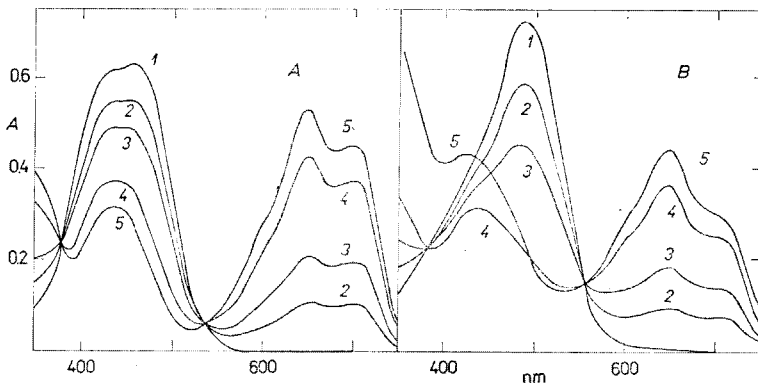| Medium	λ_{max}, nm	$\Delta\lambda_{max}$	$\lambda_{isos.point}$
1M-$HClO_4$	650, 705, 425—440	225	536, 377
pH 6·1	648, 700, 492, 425	223	552, 382

FIG. 14
Absorption Curves in the Pd(II)–2-TAN–3, 6-S System for Various c_L/c_M and a Constant Acidity
(A: 1·0M-$HClO_4$, B: pH 6·1 and I 0·1) $c_L = 4·0 . 10^{-5}$M; Curve *1* reagent; c_M/c_L: *2* 0·25; *3* 0·5; *4* 1·0; *5* 5·0.

of solutions in $2-5\text{M-HClO}_4$ increases for more than one hour at 25°C; the development time is shortened to 30 min at $70-80°C$ and the absorbance is then constant for up to 10 h in a 2M-HClO_4 medium at pH 7. The molar absorption coefficients, calculated for three wavelengths and three acidity values from the continuous variation plots using the JOB program[30], are given in Table XI.

TABLE XI

Molar Absorption Coefficients for the Pd(II) Complexes with 2-TAN–3,6-S, Computed According to the JOB Program

λ, nm	ε		
	$3 \cdot 0\text{M-HClO}_4$	$1 \cdot 0\text{M-HClO}_4$	pH $3 \cdot 0$
700	$13\,807 \pm 233$	$11\,830 \pm 162$	$10\,630 \pm 152$
645	$14\,268 \pm 114$	$13\,670 \pm 212$	$13\,240 \pm 234$
635	$12\,919 \pm 162$	$12\,290 \pm 93$	$12\,040 \pm 105$

### Assumed Structure of the Pd(II) Chelates with Heterocyclic Azodyes

Considering the equilibria encountered in the water–dimethylformamide medium in the TAR–Pd(II) and TAMP–Pd(II) systems, the following chelate structures can be assumed (see p. 1162).

The structure of PdH$^+$ with TAR and PdL$^+$ with TAMP agree with the proposal of Savransky and coworkers[32] for the Pd(II)-chelate with PAR and the structures of PdLH, PdL and PdL(OH) with TAR conform with the structural considerations of Yotsuyanagi and coworkers[21] for the Pd(II)-chelates with PAR; however, these authors assume a different proton dissociation mechanism. The pronounced change in the colouration from green to red-purple on dissociation of the p-hydroxyl proton from PAR and TAR in PdLH$^+$ chelates seems to be anomalous. The assumed structures cannot yet be differentiated for PdLH$_2^{2+}$.

Among the four stepwise-formed complexes, $PdCl_x^{2-x}$ ($e.g.$ ref.[37]), only $PdCl_3^-$ could be distinguished in the substitution equilibria with heterocyclic azodyes.

Spectrophotometric Determination of Palladium with TAR in $1 \cdot 0 - 1 \cdot 5\text{M-HClO}_4$ in the Presence of 30 % (v/v) Dimethylformamide
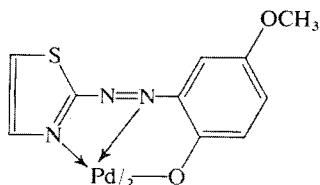
Procedure: To 5 ml of a 10^{-3}M reagent solution in dimethylformamide additional dimethylformamide is added to give a final concentration of 30% (v/v). 5M-HClO_4 is added after cooling and finally a Pd(II) solution is added. The solution is diluted with water to 25 ml. The measurement is performed after $15-30$ min at $635-700$ nm; the sensitivity is optimum at 635 nm and
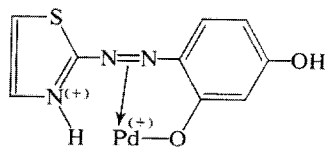
or
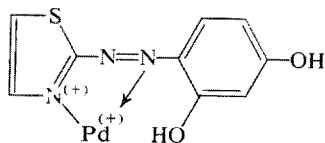
PdLH$_2^{2+}$ ($\geqq$8M-HClO$_4$)
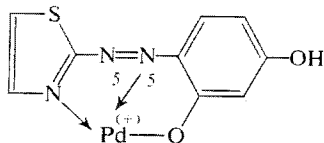
PdLH$^+$ ($\leqq$6M-HClO$_4$)
λ_{max} 635, 465 nm
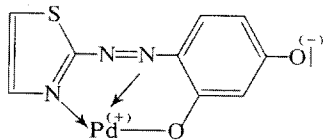
PdL (pH 2,2 – 5,0)
λ_{max} 520nm
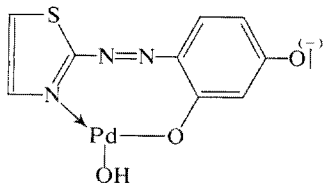
PdL(OH)$^-$ (pH >4)
λ_{max} 520 nm
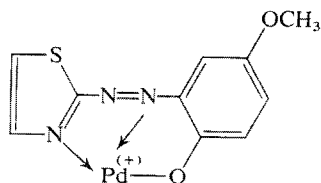
PdL$^+$ (3M-HClO$_4$, pH 3)
λ_{max} 760 nm
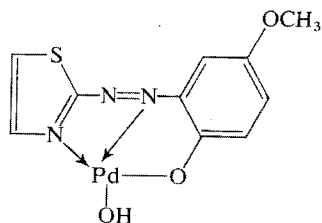
PdL(OH) (pH 4–7, $< c_L$)

PdL$_2$ (pH 5–8, $> c_L$)
λ_{max} 600–610 nm

the reagent solution does not absorb at these wavelengths. The conditions for the validity of the Lambert–Beer law are satisfied for concentrations of $\leqq 5$ µg Pd/ml. The permissible acidity is $1-3\text{M-HClO}_4$, but at $c_H > 1\cdot5\text{M-HClO}_4$ small chloride concentrations interfere. Chloride does not interfere up to a concentration of $0\cdot2\text{M}$ in a medium of $1-1\cdot5\text{M-HClO}_4$, if the absorbance is measured after $30-60$ minutes. At higher chloride concentrations, the resultant solution absorbances at $635-700$ nm are lower, but the absorbance dependence on the Pd(II) concentration is again linear. Nitrate does not interfere up to a concentration of $0\cdot1\text{M}$; at higher concentrations DMF decomposes with evolution of white fumes. Colloidal turbidity and later a precipitate are formed in the presence of $1\text{M-H}_2\text{SO}_4$ at concentrations of $\geqq 3$ µg Pd/ml; in $3\text{M-H}_2\text{SO}_4$ the resultant absorbances are identical with those in 1M-HClO_4, but even chloride concentrations below $5 . 10^{-3}\text{M}$ interfere. Numerical evaluation of the analytical curve by the least squares method using a small computer is given in Table XII.

The proposed procedure was compared with the procedure for the spectrophotometric determination of palladium with 4-(2-pyridylazo)resorcinol in $3\text{M-H}_2\text{SO}_4$ at 600 nm[5,14]. The results of the evaluation are given in Table XIII. It follows from the comparison that the determination of palladium with TAR at 635 nm is more sensitive and suitable, as Cl^- does not interfere, while the presence of chloride practically prevents the determination of palladium in $3\text{M-H}_2\text{SO}_4$ (ref.[14]). The following elements do not interfere in the determination of 1 µg Pd/ml in 1M-HClO_4

TABLE XII

Characteristic Parameters of the Method for the Determination of Palladium with TAR in $1\cdot0$ to $1\cdot5\text{M-HClO}_4$ and 30% (v/v) DMF

Parameters	635 nm	670 nm	700 nm
$r_k{}^a$	$1\cdot0000$	$0\cdot9999$	$0\cdot9999$
$\varepsilon_n \pm \Delta\varepsilon^b$	$10\ 750 \pm 17$	$10\ 030 \pm 23$	$7\ 614 \pm 10$
$s_{xy}{}^c$, A	$6\cdot939 . 10^{-4}$	$9\cdot808 . 10^{-4}$	$7\cdot568 . 10^{-4}$
$m_A{}^d$	$0\cdot002$	$0\cdot003$	$0\cdot002$
m_c, mol . $1^{-1\ e}$	$1\cdot937 . 10^{-7}$	$2\cdot934 . 10^{-7}$	$2\cdot982 . 10^{-7}$
m_c, µg . ml$^{-1\ f}$	$0\cdot0260$	$0\cdot0312$	$0\cdot0317$
Sensitivity index mol . 1^{-1} . cm ^{g}	$9\cdot302 . 10^{-7}$	$9\cdot9710 . 10^{-7}$	$1\cdot313 . 10^{-6}$
Sensitivity index µg/cm$^{2\ h}$	$0\cdot098$	$0\cdot106$	$0\cdot139$
U^i	$1\cdot479 . 10^{-5}$	$2\cdot956 . 10^{-5}$	$1\cdot760 . 10^{-5}$

[a] Correlation coefficient; [b] molar absorption coefficient and its $3s_\varepsilon$; [c] standard deviation of the scatter around the regression straight line; [d] determination limit in absorbance units; [e] determination limit in mol 1^{-1} Pd(II); $3s_{xy}(A)/\varepsilon_n$ (mol 1^{-1}); [f] determination limit in µg Pd(II)/ml, $3s_{xy}(A)/(\text{d}A/\text{d}c)$ (µg ml^{-1}); [g] concentration of Pd(II) for $A = 0\cdot010$ and $1 = 10$ mm in mol 1^{-1}; [h] concentration of Pd(II) in µg/ml; [i] $U = \sum(A_{\text{meas}} - A_{\text{calc}})^2$.

at 635 nm, for $c_L/c_A = 20$, $c_L = 2 . 10^{-4}$M, with an absorbance error of $\pm2\%$ rel.:
Pt(IV) (660 : 1), Os(VIII) (10 : 1), Ir(IV) (60 : 1), Rh(III) (100 : 1), Pb (2500 : 1),
Fe(III) (700 : 1), Co(II) (700 : 1), Zn(II) (2300 : 1), Fe(II) (450 : 1), Au(III) (650 : 1),
Ni(II) (60 : 1), Ag(I) (100 : 1), Cu (10 : 1), Hg(II) (2500 : 1) in the presence of
0·05M-Cl$^-$. Ag(I) (>100 : 1) interferes; even when it is precipitated as AgCl, the
negative error in the determination of palladium remains large (-8%).

Spectrophotometric Determination of Palladium with TAR *at* pH $5\cdot0-5\cdot5$
in a Medium of 50% (v/v) DMF *and* 0·2M *Acetate Buffer*

Procedure: To 5 ml of a 10^{-3}M solution of TAR in DMF in a 25 ml volumetric flask are added
7·5 ml DMF, 5 ml of a 1M acetate buffer (pH 4·7) and a chloride-free solution of Pd(II); the mix-
ture is diluted to the mark with water. The solution absorbance is measured after 20 minutes
at 555—570 nm against the blank under the same conditions. The reagent also strongly absorbs
at the optimum pH. The $\Delta A = f(c_{Pd})$ dependence is linear for $\leq 3\cdot2$ μg Pd/ml. In the presence
of $\geq 0\cdot2$M acetate, the molar absorption coefficient of the Pd(II) chelate increases ($\varepsilon = 18\,050$
with acetate, $\varepsilon = 14\,200$ without acetate at 555 nm). A ternary complex is probably formed,
Pd-TAR-ac, similar to the system, Pt(IV)–PAR-ac (ref.[33]). Chloride decreases the solution ab-
sorbance, but its effect becomes constant at $\geq 0\cdot5$M chloride concentration; hence the determina-
tion of palladium in the presence of chloride is possible, provided that the calibration curve
is evaluated under the same conditions. The determination of palladium with TAR at pH 5·0 to
5·5 is poorly selective in contrast to the determination with PAR at pH ~ 7 (ref.[14]). As even
10^{-3}M-EDTA interferes, it cannot be used for masking interfering ions. The evaluation of the
parameters by the method of linear regression of the $A = f(c_{Pd})$ dependence is given in Table
XIV.

TABLE XIII
Evaluation of the Parameters in the Method for the Determination of Palladium(II) with PAR
in 3M-H$_2$SO$_4$ According to Ref.[14]

Parameters	580 nm	600 nm	615 nm
r_k	0·9996	0·9998	0·0005
$\varepsilon_n \pm \Delta\varepsilon$	9 768 ± 68	9 278 ± 46	8 055 ± 62
s_{xy} (A)	$2\cdot306 . 10^{-3}$	$1\cdot564 . 10^{-3}$	$2\cdot095 . 10^{-3}$
m_A	0·007	0·005	0·006
m_c, mol l^{-1}	$7\cdot082 . 10^{-7}$	$5\cdot057 . 10^{-7}$	$7\cdot803 . 10^{-3}$
m_c, μg ml^{-1}	0·075	0·054	0·083
Sensitivity index mol cm/l	$1\cdot026 . 10^{-6}$	$1\cdot078 . 10^{-6}$	$1\cdot241 . 10^{-6}$
Sensitivity index μg/cm^2	0·109	0·115	0·132
U	$9\cdot335 . 10^{-5}$	$4\cdot295 . 10^{-5}$	$7\cdot707 . 10^{-5}$

TABLE XIV

Characteristic Parameters of the Methods for the Determination of Palladium with TAR and PAR

λ, nm	TAR (pH 5·5, 50% (v/v) DMF)			PAR (pH 7)		
	555^a	555	570	515	535	570
r_k	0·9988	0·9997	0·9991	0·9927	0·9921	0·9935
$\varepsilon_n \pm \Delta\varepsilon$	$17\,387 \pm 200$	$18\,057 \pm 111$	$16\,388 \pm 161$	$31\,239 \pm 907$	$28\,547 \pm 861$	$20\,404 \pm 560$
s_{xy}, A	$4{\cdot}213 \,.\, 10^{-3}$	$2{\cdot}311 \,.\, 10^{-3}$	$3{\cdot}360 \,.\, 10^{-3}$	$2{\cdot}042 \,.\, 10^{-2}$	$1{\cdot}939 \,.\, 10^{-2}$	$1{\cdot}261 \,.\, 10^{-2}$
m_A	0·013	0·007	0·010	0·006	0·006	0·006
m_c, mol l^{-1}	$7{\cdot}269 \,.\, 10^{-7}$	$3{\cdot}839 \,.\, 10^{-7}$	$6{\cdot}150 \,.\, 10^{-7}$	$1{\cdot}961 \,.\, 10^{-7}$	$2{\cdot}038 \,.\, 10^{-7}$	$1{\cdot}854 \,.\, 10^{-7}$
m_c, µg ml^{-1}	0·077	0·041	0·065	0·021	0·022	0·020
Sensitivity index mol cm l^{-1}	$5{\cdot}751 \,.\, 10^{-7}$	$5{\cdot}538 \,.\, 10^{-7}$	$6{\cdot}102 \,.\, 10^{-7}$	$3{\cdot}201 \,.\, 10^{-7}$	$3{\cdot}503 \,.\, 10^{-7}$	$4{\cdot}901 \,.\, 10^{-7}$
Sensitivity index µg/cm^2	0·061	0·059	0·065	0·034	0·037	0·052
U	$3{\cdot}117 \,.\, 10^{-4}$	$9{\cdot}37 \,.\, 10^{-5}$	$1{\cdot}982 \,.\, 10^{-4}$	$7{\cdot}320 \,.\, 10^{-3}$	$6{\cdot}607 \,.\, 10^{-3}$	$2{\cdot}791 \,.\, 10^{-3}$

^{a} In the presence of 0·5M-NaCl.

The method is less sensitive and exhibits a higher detection limit value than the method employing PAR at pH 7·0 (ref.[14]), although the reproducibility is better.

Spectrophotometric Determination of Palladium with TAMP

The optimum conditions for the determination employ the PdL^+ chelate with λ_{max} 760 nm in $0·4-0·8M$-$HClO_4$ and 30% (v/v) DMF. The reagent rapidly decomposes at acidities above $1M$-$HClO_4$. The solution absorbance is measured after 10 min at $700-760$ nm against water as the reference solution. The $\Delta A = f(c_{Pd})$ dependence is linear up to a concentration of 5·6 μg Pd/ml. The evaluation of the analytical curves by regression analysis on a computer according to ref.[27] is given in Table XV. Chloride does not interfere up to a concentration of $0·2M$ in $0·4-0·8M$-$HClO_4$; H_2SO_4 and $\leqq 0·1M$-HNO_3 and the following elements do not interfere: Os(VIII) (100 : 1), Ir (60 : 1), Rh(III) (100 : 1), Pt(IV) (300 : 1), Au(III) (600 : 1), Ni (60 : 1), Co(II) (350 : 1), Fe(III) (400 : 1), Fe(II) (200 : 1), Pb(II) (2 500 : 1), Zn(II) (2 300 : 1), Hg(II) (2 500 : 1) (in the presence of $0·05M$-Cl^-), Ag(I) (100 : 1); Cu(II) interferes.

Spectrophotometric Determination of Palladium with 2-TAN-3,6-S

The determination of palladium with 2-TAN-3,6-S in $3M$-H_2SO_4 at 655 nm ($\varepsilon = = 12000$) has already been proposed for a concentration range of $2-8$ μg Pd/ml (ref.[16]). For the determination of palladium using PdL (λ_{max} 645 nm), $1·0-1·5M$-$HClO_4$

TABLE XV
Characteristic Parameters in the Method for the Determination of Palladium with TAMP in 30% (v/v) DMF

Parameters	730 nm	760 nm
r_k	0·9997	0·9998
$\varepsilon_n \pm \Delta\varepsilon$	$7\,733 \pm 45$	$8\,762 \pm 36$
s_{xy}, A	$1·513 . 10^{-3}$	$1·052 . 10^{-3}$
m_A	0·005	0·004
m_c, mol l^{-1}	$5·871 . 10^{-7}$	$4·932 . 10^{-7}$
m_c, μg ml^{-1}	0·0625	0·0525
Sensitivity index mol cm/l	$1·293 . 10^{-6}$	$1·053 . 10^{-6}$
Sensitivity index μg/cm^2	0·138	0·122
U	$4·021 . 10^{-5}$	$3·245 . 10^{-5}$

TABLE XVI

Characteristic Parameters in the Method for the Determination of Palladium with 2-TAN–3,6-S in $1\cdot0 - 1\cdot5\text{M-HClO}_4$

Parameters	635 nm	645 nm
r_k	0·9999	1·0000
$\varepsilon_n \pm \Delta\varepsilon$	12 430 $\pm$ 30	13 655 $\pm$ 17
s_{xy}, A	$1\cdot143 \cdot 10^{-3}$	$6\cdot458 \cdot 10^{-4}$
m_A	0·003	0·002
m_c, mol l^{-1}	$2\cdot758 \cdot 10^{-7}$	$1\cdot419 \cdot 10^{-7}$
m_c, mg ml^{-1}	0·029	0·015
Sensitivity index mol cm/l	$8\cdot045 \cdot 10^{-7}$	$7\cdot324 \cdot 10^{-7}$
Sensitivity index $\mu g/cm^2$	0·086	0·078
U	$2\cdot867 \cdot 10^{-5}$	$9\cdot154 \cdot 10^{-6}$

is suitable in the presence of $c_L = 2 \cdot 10^{-4}\text{M}$, the components being added in the order: the reagent, $HClO_4$, the palladium-containing sample. The solution is diluted with water to 25 ml. The absorbance is measured after 20 min at 635 or 645 nm against water. The $\Delta A = f(x_{Pd})$ dependence is linear up to 5·2 μg/ml. The evaluation of the dependence by the linear regression method on a computer is given in Table XVI. The determination of palladium is not disturbed by $\leqq 0\cdot2\text{M-Cl}^-$, $\leqq 1\cdot5\text{M-NO}_3^-$ and $\leqq 0\cdot5\text{M-H}_2SO_4$. The presence of Cl^- makes it necessary to measure the absorbance after $60 - 90$ minutes; heating of the solution does not affect the absorbance development. The following elements do not interfere in the determination of 1 μg Pd/ml: Os(VIII) (100 : 1), Ir(III) (60 : 1), Rh(III) (100 : 1), Pt(IV) (360 : 1), Au(III) (600 : 1), Cu(II) (10 : 1), Ni(II) (60 : 1), Co(II) (150 : 1), Fe(III) (700 : 1), Fe(II) (1 000 : 1), Pb(II) (2 500 : 1), Zn(II) (2 300 : 1), Hg(II) (2 500 : 1 in the presence of $0\cdot05\text{M-Cl}^-$), Ag(I) (1 000 : 1), The error in the absorbance does not exceed $\pm 2\%$ rel.

Among the compared heterocyclic azodyes, TAR and 2-TAN–3,6-S in acidic media are the most suitable for the practical determination of palladium.

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