

EQUILIBRIUM STUDIES OF BINARY AND TERNARY COMPLEXES OF PALLADIUM(II) INVOLVING AMINO ACIDS

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The formation constants of the binary and ternary complexes of palladium(II) with diethylenetriamine and amino acids as ligands have been determined potentiometrically at 25 °C in 0.1 M NaNO₃ solution. The relative stability of each ternary complex was compared with that of the corresponding binary complexes in terms of $\Delta \log K$ values. The mode of chelation was ascertained by conductivity measurements.

Interest in the study of reactions of the palladium(II) ion with amino acids and other ligands of biological importance began with the discovery of Rosenberg et al.¹ that certain platinum complexes exhibit carcinostatic activity. In view of the great affinity of palladium(II) for diethylenetriamine, it seemed worthwhile to study the binary and ternary complexes with some amino acids²⁻⁴, we present an investigation which traces the formation and equilibria of the binary and ternary complexes of palladium(II) with diethylenetriamine (dien) and amino acids.

EXPERIMENTAL

Materials and Reagents

The amino acids used were ornithine hydrochloride, lysine hydrochloride, glutamine, methionine, proline, hydroxyproline and β -phenylalanine (Fluka, Germany). Diethylenetriamine (Aldrich, U.S.A.) was converted to the hydrochloride (dien . 3 HCl) as described previously⁵. Potassium tetrachloropalladate(II) was provided by Alfa Inorganics (U.S.A.).

Apparatus

Potentiometric measurements were made by using a Metrohm 686 Titroprocessor (Switzerland) equipped with a 665 Dosimat. The pH meter and electrode were calibrated with standard buffer solutions prepared according to NBS specifications⁶. Conductance of solutions were measured on a WTW LBR conductivity bridge (Germany).

Procedures and Measuring Techniques

All solutions were prepared in deionized water. The Pd content of solutions was estimated complexometrically⁷. The following mixtures A – D were prepared for the study and their composition is given in Table I.

Mixture A – D were potentiometrically titrated against a standardized NaOH solution (0.25 M). The titrations were performed in a special vessel described previously⁸ at 25 °C in a purified N₂ atmosphere. The titrations were terminated when either the pH-meter readings became unstable showing a continuous downward drift or visual precipitations occurred. The acid dissociation constants of the amino acids were determined by titrating mixture A. The formation constants for the binary complexes formed in solution were determined by titrating mixture B and C. With the concentrations in mixture B, the 1 : 1 complexes usually predominate⁹, so concentrations of [PdL_m], where $m \geq 2$, can be neglected. The stability constants $K_{Pd(dien)L}^{Pd(dien)}$ for the ternary complexes were determined by titration of mixture D, utilising the data obtained within the pH range corresponding to the complete formation of [Pd(dien)]²⁺ complex.

The experimental pH titration data were analyzed using the computer program¹⁰ MINIQUAD loaded on a IBM-4331 computer. The model selected was that which gave the best statistical fit to, and proved chemically consistent with the titration data, and without any systematic bias in the residuals, as previously described¹⁰. The results obtained are shown in Table II.

RESULTS AND DISCUSSION

The acid dissociation constants of the ligands have been reported¹¹. We redetermined them under the experimental conditions ($T = 25$ °C, $I = 0.1$ M NaNO₃) used for determining the formation constants of the palladium(II) complexes. The determined values are in good agreement with literature values.

Binary Complexes

Difficulties are encountered in the study of aqueous solutions of [Pd(H₂O)₄]²⁺ due to its slow hydrolysis in solutions of pH ≈ 1 to give insoluble oxo compounds of uncertain stoichiometry¹². As a result, water-soluble complex ions of palladium as [PdCl₄]²⁻ are used in stability constants experiments. As a result, calculated constants are conditional constants appropriate to ligand exchange reactions in which the exchanged ligand is not water.

TABLE I
Composition of solution mixtures of Pd-dien–amino acid system (c , mol l⁻¹/V, ml)

Mixture	Pd ²⁺	Amino acid	Dien	NaNO ₃
A	–	0.02/10	–	0.13/30
B	0.05/10	0.02/5	–	0.20/10
C	0.02/10	–	0.02/10	0.20/20
D	0.02/10	0.02/10	0.02/10	0.40/10
E ^a	0.02/10	0.02/10	0.02/10	–

^a Titrated conductometrically.

The palladium(II)-diethylenetriamine complex was investigated previously by Rasmussen et al.¹³. They detected the formation of 1 : 1 complex and reported a rough estimation of stability constant as $\log K \approx 34$. Based on our study the determined stability constant of the 1 : 1 complex formed is $\log K = 22.40 \pm 0.05$.

TABLE II
Formation constants of the binary and ternary complexes of amino acids

System	<i>l</i>	<i>p</i>	<i>q</i> ^a	$\log B^b$	$S \cdot 10^7$ ^c	$\Delta \log K$
Binary complexes						
Ornithine	0	1	1	10.73		
	0	1	2	19.71		
	1	1	0	16.01 (0.08)	4.0	
	1	1	1	20.29 (0.08)		
Lysine	0	1	1	10.53		
	0	1	2	19.48		
	1	1	0	15.36 (0.03)	8.0	
	1	1	1	19.81 (0.07)		
Glutamine	0	1	1	8.91		
	1	1	0	8.10 (0.02)	3.5	
Methionine	0	1	1	9.17		
	1	1	0	8.94 (0.01)	0.6	
Proline	0	1	1	10.58		
	1	1	0	10.17 (0.03)	15	
β -Phenylalanine	0	1	1	9.61		
	1	1	0	9.54 (0.08)	8.8	
Ternary complexes						
Ornithine	1	1	0	6.83 (0.02)	1.5	-9.18
	1	1	1	15.76 (0.02)		
Lysine	1	1	0	5.47 (0.04)	2.8	-9.89
	1	1	1	15.10 (0.03)		
Glutamine	1	1	0	4.54 (0.08)	20	-3.56
Methionine	1	1	0	3.81 (0.08)	28	-5.13
Proline	1	1	0	5.82 (0.02)	2.2	-4.35

^a *l*, *p* and *q* refer to the $\text{Pd}_l(\text{amino acid})_q \text{H}_r$ for the binary complexes and *l* refers to $\text{Pd}(\text{dien})$ for the ternary complexes; ^b standard deviations in parentheses; ^c sum of square of residuals.

The binary complexes of palladium(II) with amino acids were studied under conditions, where 1 : 1 complexes predominate. With leucine and lysine the protonated complexes are formed together with the deprotonated complexes. It is noted that, the stability constants of the deprotonated complexes formed with leucine and lysine are higher than those of the other amino acids. This may be due to the presence of an extra amino group and its participation in complex formation. The acid dissociation constant of the protonated complex is given by Eq. (1):

$$pK_{Pd(L)_{(II)}}^H = \log K_{Pd(L)_{(II)}}^{Pd} - \log K_{Pd(L)}^{Pd}. \quad (1)$$

The values of pK^H are 4.45 and 4.28 for ornithine and lysine binary complexes, respectively. These values are much lower than the pK^H values of NH_3^+ group of ornithine and lysine. This is explained by considering the acidification of the NH_3^+ group caused by its participation in bonding to Pd(II).

Ternary Complexes

Potentiometric titration curve of the Pd(II)-dien (1 : 1) mixture (C) starts at pH \approx 2 and has a long-low pH buffer region followed by a sharp inflection at $a = 3$, (a is number of moles of base added per mole of ligand), corresponding to complete formation of the 1 : 1 complex. Beyond $a = 3$ and above pH 8 the titration curve shows an inflection at $a = 4$, which is due to the formation of $[\text{Pd}(\text{dien})(\text{OH})]^+$ complex. Its stability constant was determined previously¹⁴. The titration curve of the mixed Pd(II)-dien-amino acid (D) solution does not show the sharp inflection at $a = 3$, but reveals an inflection at $a = 4$; the curve coincides with the Pd(II)-dien titration curve between $a = 0$ and $a = 3$. The formation of a ternary complex is ascertained by comparison of the mixed-ligand titration curve with the composite curve obtained by graphical addition of the amino acid titration data to that of the 1 : 1 Pd(II)-dien titration. It is obvious that the mixed ligand system deviates considerably from the resultant composite curve, indicating the formation of a stable ternary complex species. In case of ornithine and lysine the deviation from the composite curve is in the region $a = 3$ to $a = 5$ indicating the formation of the $[\text{Pd}(\text{dien})\text{HL}]^+$ complex and its dissociation to the $[\text{Pd}(\text{dien})\text{L}]$ species.

The conductometric titration curve for the ternary complex of proline, taken as a representative, shows initial decrease and an inflection at $a = 3$. This probably corresponds to the neutralization of H^+ ions resulting from the formation of the Pd(II)-dien complex. Between $a = 3$ and $a = 4$, the conductance increases slightly, supposedly due to the formation of a ternary complex associated with the release of a hydrogen ion from proline. Beyond $a = 4$, the conductance increases more appreciably due to the presence of an excess of NaOH.

Based on the above findings and since the 1 : 1 Pd(II)-dien complex is appreciably more stable than the 1 : 1 Pd(II)-amino acid complex (Table I), it is evident that in

presence of both ligands, the dien is primarily ligated to the Pd(II) ion, occupying three coordination positions. This is followed by ligation of the amino acid, occupying the coordination position remained, i.e. the ternary complex formation could be considered in stepwise equilibria.



The acid dissociation constant value of the protonated ternary complex species, given by Eq. (1), is 8.93 for ornithine and 9.63 for lysine. These values compare favourably with the acid dissociation constant of the ω -amino group. This indicates that one amino group is bound to Pd(II) ion in ternary complex formation and the ω -amino group is free. It should be duly noted that the stability constant values of the deprotonated ternary complexes of ornithine and lysine are in fair agreement with the stability constant values obtained for the other amino acids, if the difference in the basicity of the amino acids would be considered. This provides further support to the view that ornithine and lysine coordinate to the Pd(II) ion in mixed-ligand complex as a monodentate ligand.

In order to assess the significance of the stability of the ternary complex species in relation to those of the parent binary complex¹⁵, the parameter, $\Delta \log K$, the difference in stability between the binary and ternary complexes was calculated:

$$\Delta \log K = \log K_{\text{Pd}(\text{dien})\text{L}}^{\text{Pd}(\text{dien})} - \log K_{\text{PdL}}^{\text{Pd}}. \quad (2)$$

In general one expects to observe negative values for $\Delta \log K$, because more coordination positions are available for bonding of amino acid in the binary complex than in the ternary complex. Based on our study, $\Delta \log K$ values are invariably negative. This means that the amino acids form more stable complex with the Pd(II) ion than with the $[\text{Pd}(\text{dien})]^{2+}$ complex. It is interesting to compare $\Delta \log K$ values of ornithine and lysine with those of the other amino acids. The great difference in the $\Delta \log K$ values is due to the presence of more coordination sites in ornithine and lysine than in the other amino acids.

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