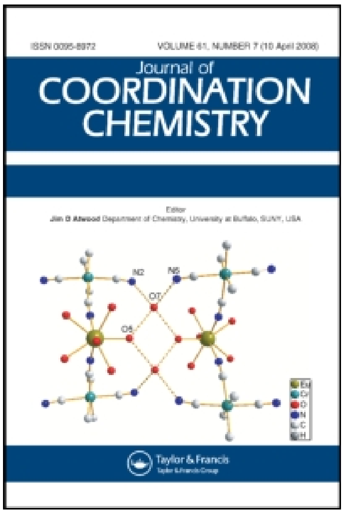

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MIXED-LIGAND COMPLEXES OF PALLADIUM(II) WITH DIETHYLENETRIAMINE

Mohamed M. Shoukry[a]; Ezzat M. Khairy[a]; Adel Saeed[b]
[a] Department of Chemistry, Faculty of Science, United Arab Emirates University, United Arab Emirates [b] Department of Chemistry, Faculty of Science, Cairo University, Egypt

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MIXED-LIGAND COMPLEXES OF PALLADIUM(II) WITH DIETHYLENETRIAMINE

MOHAMED M. SHOUKRY* and EZZAT M. KHAIRY

Department of Chemistry, Faculty of Science, United Arab Emirates University, United Arab Emirates

and ADEL SAEED

Department of Chemistry, Faculty of Science, Cairo University, Egypt

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Formation and equilibria of mixed-ligand Pd(II) complexes containing diethylenetriamine (dien) and other selected ligands (HL) have been investigated. Results of pH-titration measurements allowed the calculation of equilibrium constants, characteristic for binary and mixed-ligand complexes formed. The mode of chelation was ascertained by conductivity measurements.

Keywords: Palladium, diethylenetriamine, ternary complexes, stability constants

INTRODUCTION

Cis-dichloroplatinum(II) amine complexes have been extensively studied. Several of these complexes show distinct antitumour activity,[1] which function has recently received thorough attention in cancer research. Rosenberg *et al.*,[2,3] have prepared several mixed-ligand complexes, containing nucleic acid bases and related compounds, based on diaquaplatinum(II) amine complexes, which also exhibit potent antitumour properties, as well as being less toxic than the binary platinum(II)-amine species. The reaction of platinum(II) with ethylenediamine is known,[4] as is the biological activity of such platinum(II) and palladium(II) amine complexes. There is hardly any evidence to rule out the possibility that these platinum complexes owe their antitumour properties to interactions with enzymes associated with cell division.[5]

Because of the great affinity of palladium(II) toward diethylenetriamine, it would be of interest to study mixed-ligand complexes of dien with other selected ligands that may represent models for exploring the effective metal ion binding sites in biologically active systems. With this in mind, we have reported some studies along these lines,[6,7] some of which include an examination of complexes of Pd(II) with dien and amino acids[8,9] and peptides.[10]

The present report concerns the formation and characteristics of binary and ternary complexes of Pd(II) with dien and phosphate, carboxylate, ammonia, imidazole and pyridine ligands.

EXPERIMENTAL

Materials and reagents

The secondary ligands (HL) used were (sodium) dihydrogen phosphate, (potassium) hydrogen phthalate, formic acid, acetic acid, propionic acid, butyric acid, lactic

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* To whom all correspondence should be addressed.

acid, ammonium (chloride), as well as imidazole and pyridine (L). These materials were supplied by Fluka Chemical Co., and potassium tetrachloropalladate(II) was provided by Alfa Inorganics. The Pd content of solutions was estimated complexometrically.[11] Diethylenetriamine was of chemically pure grade, supplied by Aldrich. Dien.3HCl was prepared as described previously.[10] All solutions were prepared in deionised water. The concentrations of stock solutions of the ligands were checked potentiometrically.

TABLE I
Equilibrium and stability constants for the secondary ligands and their complexes.

System	*l*	*p*	*q*	*r*[a]	log B[b]	S[c]	Δ log K
Hydroxide	1	1	0	−1	−8.68(0.06)	1.0E-5	
Imidazole	0	0	1	1	6.82(0.01)	6.7E-7	−0.78
	1	0	1	0	6.40(0.00)	1.6E-8	
	1	1	1	0	5.62(0.01)	4.6E-8	
Formate	0	0	1	1	3.67(0.01)	5.9E-8	−0.08
	1	0	1	0	2.22(0.01)	4.2E-8	
	1	1	1	0	2.14(0.02)	3.1E-8	
Acetate	0	0	1	1	4.59(0.01)	3.5E-7	−0.21
	1	0	1	0	2.73(0.00)	1.9E-8	
	1	1	1	0	2.52(0.01)	8.2E-9	
Propionate	0	0	1	1	4.71(0.00)	2.0E-9	−0.34
	1	0	1	0	2.94(0.01)	9.0E-8	
	1	1	1	0	2.60(0.01)	7.3E-9	
Lactate	0	0	1	1	3.69(0.02)	3.8E-7	−0.13
	1	0	1	0	2.02(0.00)	1.1E-8	
	1	1	1	0	1.89(0.02)	3.3E-8	
Phthalate	0	0	1	1	5.08(0.02)	3.6E-7	−0.27
	1	0	1	0	3.31(0.01)	4.5E-8	
	1	1	1	0	3.04(0.01)	9.9E-8	
Phosphate	0	0	1	1	6.97(0.01)	9.4E-6	−0.47
	1	0	1	0	3.10(0.01)	3.0E-8	
	1	1	1	0	2.63(0.01)	4.7E-8	
Ammonia	0	0	1	1	9.12(0.01)	1.3E-9	−0.70
	1	0	1	0	6.06(0.00)	7.0E-9	
	1	1	1	0	5.36(0.01)	5.9E-8	
Butyrate	0	0	1	1	4.69(0.01)	4.9E-8	
	1	1	1	0	2.58(0.01)	1.3E-8	
Pyridine	0	0	1	1	5.24(0.00)	4.4E-8	
	1	1	1	0	4.04(0.03)	5.9E-7	

[a] The symbols *l*, *p*, *q* and *r* are the stoichiometric coefficients corresponding to Pd(II), dien, secondary ligand and H^+ respectively; [b] Standard deviations are given in parentheses; [c] Sum of square of residuals.

Apparatus and experimental techniques

The pH values were measured by means of a Schott 801 pH meter using a special vessel described elsewhere.[12] The pH meter and electrode were calibrated by using standard buffer solutions, prepared according to NBS specifications.[13] The electrolytic conductances were measured using a WTW LBR conductivity bridge.

The following mixtures (A–D) were prepared for the equilibrium constant determinations: (A): 10 cm^3 of 0.02M ligand (HL) + 30 cm^3 of 0.13M KNO_3; (B): 10 cm^3 of 0.05M Pd(II) + 5 cm^3 of 0.02M ligand (HL) + 5 cm^3 of 0.40M KNO_3; (C): 10 cm^3 of 0.02M Pd(II) + 10 cm^3 of 0.02M dien + 20 cm^3 of 0.20M KNO_3; (D): 10 cm^3 of 0.02M Pd(II) + 10 cm^3 of 0.02M dien + 10 cm^3 of 0.02M ligand (HL) + 10 cm^3 of 0.40M KNO_3. The mixture (E) was titrated conductometrically against 0.20M NaOH; (E): 10 cm^3 of 0.02M Pd(II) + 10 cm^3 of 0.02M dien + 10 cm^3 of 0.02M ligand (HL). In the case of imidazole and pyridine, their solutions were prepared in aqueous equimolar nitric acid solution.

The acid dissociation constants of the ligands were determined by titrating mixture (A) of each with standardized 0.20M NaOH. The stability constants for the binary complexes formed in solution were determined by titrating mixture (B) with standardized 0.10M NaOH. With the concentrations in mixture (B), the 1 : 1 complexes usually predominate,[14] so concentrations of $[Pd(L)_m]$ with $m \geqslant 2$, can be neglected. The stability constant for the complex $[Pd(dien)OH]^+$ was determined by titrating mixture (C) with standardized 0.20M NaOH. The stability constants $K^{Pd(dien)}_{Pd(dien)L}$ for the ternary complexes were determined by titration of mixture (D) with standardized 0.20M NaOH, utilising the data obtained within the pH range corresponding to the complete formation of the $[Pd(dien)]^{2+}$ complex and that prior to $[Pd(dien)OH^{2+}]$ formation.

All titrations were carried out at 25°C in a purified nitrogen atmosphere. The calculations were performed using the computer program[15] MINIQUAD 75 on an 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 residuals, as previously described.[15] The results obtained are shown in Table I.

RESULTS AND DISCUSSION

The acid dissociation constants of the ligands and the formation constants for their binary complexes with Pd(II) were calculated from the potentiometric data. Potentiometric equilibrium titration curves of the mixed-ligand complex of imidazole, taken as being representative, are depicted in Figure 1. The Pd(II)-dien (1 : 1) mixture titration curve starts at pH 2 and has a long low-pH buffer region followed by a sharp inflection at $a = 3$, (a = 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 $[Pd(dien)OH]^+$. The titration curve of the mixed Pd(II)-dien-imidazole (1 : 1 : 1) solution does not show the sharp inflection at $a = 3$, but reveals a sharp inflection at $a = 4$; the curve coincides with the Pd(II)-dien titration curve between $a = 0$ and $a = 3$. The formation of a mixed-ligand complex is ascertained by comparison of the mixed-ligand titration curve with the composite curve obtained by graphical addition of the imidazole 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. Based on the above findings and the fact that the 1 : 1 Pd(II)-dien complex is appreciably more stable than the 1 : 1 Pd(II)-ligand (L) complex,[16] it is evident that in the presence of both ligands, the dien is primarily ligated to the Pd(II) ion, and is followed by ligation of the secondary ligand. This is further confirmed by the conductivity measurements described below.

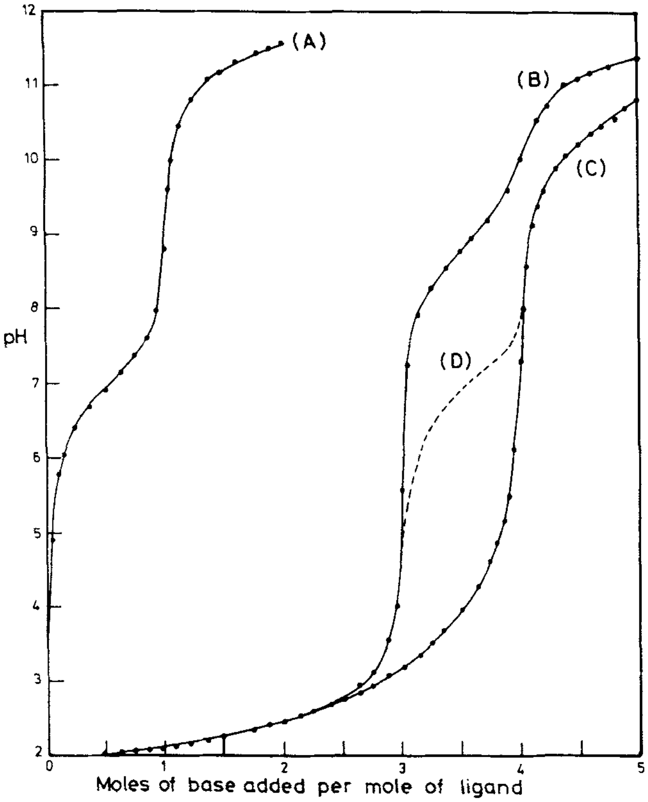

FIGURE 1 Potentiometric titration curves of Pd(II)-dien-imidazole system:(A) Imidazole; (B) 1 : 1 Pd (II)-dien; (C) Pd (II)-dien-imidazole and (D) Composite curve.

The relative stabilities of the ternary and binary complexes can be quantitatively expressed in a number of different ways. In a recent review[17] of the available methods, it has been argued that comparison can best be made in terms of Δ log K values. Based on our experimental data, Δ log K values were calculated using the relation (*1*). The values thus obtained are invariably negative. This means that the secondary ligands (L) form more stable complexes with the Pd(II) ion than with the Pd-dien complex. It is interesting to compare the Δ log K values (−0.08 to −0.78) obtained in this study with those found (−2.80 to −4.60) in a previous study[8] of the Pd(II)-dien-amino acid system. The great difference in the Δ log K values originates in the preferred bidentate coordination of an alpha amino acid; in $[\mathrm{Pd(dien)}]^{2+}$ only one coordination position remains.

$$\Delta \log K = \log K^{\mathrm{Pd(dien)}}_{\mathrm{Pd(dien)L}} - \log K^{\mathrm{Pd}}_{\mathrm{PdL}} \qquad (1)$$

The conductometric titration curve for the ternary complex containing imidazole, Figure 2, shows an initial decrease, then 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 slight increase of conductance is due to the formation of the ternary complex and is associated with the release of a proton ion from the secondary ligand. Beyond a = 4, the conductance increases more appreciably simply due to the presence of excess NaOH.

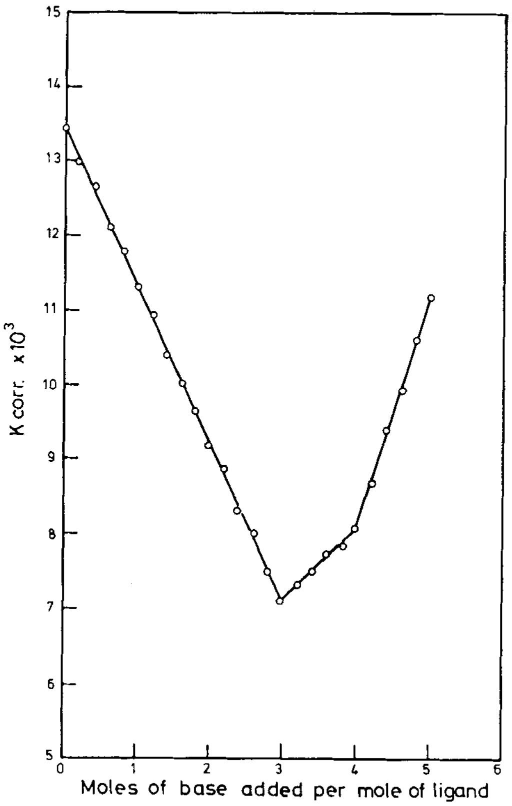

FIGURE 2 Conductometric titration of Pd (II)-dien-imidazole system.

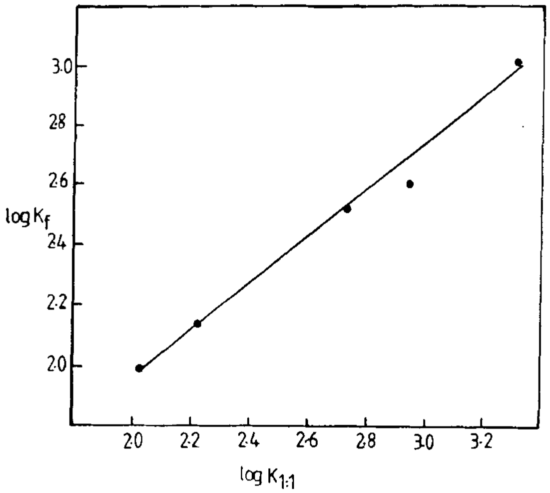

FIGURE 3 Relation between log K_f and log $K_{1:1}$.

It is well-known that for binary and ternary complexes with a series of structurally related ligands a linear relationship holds between the stability constant and the acid dissociation constant of the ligand.[18] However, in the case of ternary complexes a further dependence between the stability constant of the ternary complex and that of the corresponding 1 : 1 binary complex is found. This is shown by a plot of log K values for the mixed-ligand complexes studied here against corresponding values for the 1 : 1 binary complexes. The straight line obtained is shown in Figure 3. The importance of these plots is that they afford a means for estimating the stabilities of ternary complexes that have not yet been studied.

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