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Equilibrium study of Pd(dmen)(H2O)22+ complexes with bio-relevant ligands

Mohamed R. Shehata, Mohamed M. Shoukry* and Sara A. Mohamed

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

Correspondence to: Mohamed M. Shoukry; e.mail: shoukrymm@hotmail.com

Summary: $Pd(dmen)Cl_2$ complex, was synthesized and characterized, where dmen= N,N-dimethylethylenediamine. Stoichiometry and stability constants of the complexes formed between $[Pd(dmen)(H_2O)_2]^{2+}$ and various biologically relevant ligands as amino acids, peptides and dicarboxylic acids are investigated at 25°C and at constant 0.1 M ionic strength. Amino acids and dicarboxylic acids form 1:1 complexes. Peptides form two complex species Pd(dmen)L and $Pd(dmen)(LH_{-1})$ The concentration distribution diagrams of the various species formed are evaluated.

Introduction

The use of platinum coordinatuion compounds in cancer chemotherapy has been extensively studied following the fortuitous discovery of the therapeutic properties of cisplatin [cis-diamminedichloroplatinum(II)] by Rosenberg et.al. [1,2]. First approved for the treatment of testicular cancer in 1978, cisplatin is one of the most widely utilized antitumour drugs, exhibiting high efficacy against solid tumors, particularly testicular and ovarian cancer [3-8]. Despite the remarkable success of cisplatin, several problems have been found in clinical use. First, cisplatin treatment is often accompanied by severe side effects, including cumulative toxicities of nephrotoxicity, neurotoxicity, and emetogenesis [5,6,9-11]. In addition, cisplatin activity is limited to a relatively narrow range of tumors as a result of inherent or treatment – induced tumor resistance [6,12]. In the search for new platinum anticancer drugs, great efforts are devoted to the design of complexes more efficient and less toxic than the reference drugs already in clinical use. For this purpose, the rational design of complexes and the study of relevant structure-activity relationships have been extended to families of new compounds having high structural diversity.

Pd(II) and Pt(II)-amine complexes have the same general structures and thermodynamic properties. However, the former complexes are five orders of magnitude more reactive than their platinum counterparts. Therefore, Pd(II) complexes are good models for the analogous Pt(II) complexes in solution. Recent work in our laboratories focused on the equilibria of complex-formation reactions of (diamine)palladium(II) complexes with biorelevant ligands as amino acids, peptides and dicarboxylic acids and esters [13-17]. As an extension of the research conducted in our laboratory, the Palladium(II) complex with N,N-dimethylethylenediamine (dmen) was investigated. The ligand dmen has two methyl groups attached to one nitrogen atom of ethylenediamine. The two methyl groups will create steric hinderence with the incoming ligand. This will slow down the reactivity of the complexes to the same level as for its platinum-amine analogues. Also, the methyl groups substituents may undergo hydrophobic interaction with DNA, such effect may favor the interaction with DNA, which is the main target for the antitumor agent.

Experimental

Materials

The complex [Pd(dmen)Cl_2] was prepared by heating $PdCl_2$ (0.177 g; 1.0 mmol) and KCl (0.149 g; 2.0 mmol) in the least amount of water to 70ºC with stirring. The solution of $[PdCl_4]^{2-}$ solution was cooled to 25ºC, filtered and N,N-dimethylethylenediamine (0.088 g; 1.0 mmol), was added to the stirred solution. The pH of the solution was adjusted to 2-3 by addition of HCl. The solution was evaporated to a small volume (20 ml) under vacuum then an orange crystalline precipitate of [Pd(dmen)Cl_2] was formed on cold. The precipitate was filtered off and washed with cold water. An orange crystalline precipitate was obtained; yield 92%. Anal. Calc, for $C_4H_{12}N_2PdCl_2$ (F.wt=265.48): C, 18.08; H, 4.52; N, 10.55 %. Anal. Found: C, 18.04; H, 5.40; N, 10.29%.

The complex was converted in solution into the diaqua form by treating it with 2 equivalents of $AgNO_3$, as described elsewhere [18]. The ligands in the hydrochloride form were converted to the corresponding hydronitrate form using the same way as described before. The amino acids used were glycine, alanine, β -alanine, β-phenylalanine, proline, valine, isoleucine, serine, theronine. histidine, histamine

dihydrochloride, lysine.2HCl, ornitine.2HCl ethanolamine.HCl, imidazole, S-methylcysteine, methionine and glutamic acid. The peptides studied are glycinamide, glycylglycine, asparagines and glutamine. The dicarboxylic acids investigated are cyclobutane dicarboxylic acid, malonic acid, oxalic acid, succinic acid, adipic acid. The amino acid esters investigated are glycine methyl ester, histidine methyl ester and methionine methyl ester. These materials were all obtained from Sigma Chem. Co.

Potentiometric measurements

Potentiometric measurements were performed using a Metrohm 751 Titroprocessor. The electrode and titroprocessor were calibrated with standard buffer solutions prepared according to NBS (the US National Bureau of Standards) specifications [19]. pH meter readings were converted to hydrogen ion concentration by titrating a standard HNO_3 solution (0.01 M), the ionic strength of which was adjusted to 0.1 M with $NaNO_3$, with standard NaOH (0.05M) at 25°C. The pH was plotted against p[H]. The relationship pH–p[H] = 0.05 was observed.

The acid dissociation constants of the ligands were determined by titrating 0.625 mmol samples of each with standard NaOH solutions. The acid dissociation constants of the coordinated water molecules in $[Pd(dmen)(H_2O)_2]^{2+}$ were determined by titrating 0.625 mmol of the complex with standard 0.05M NaOH solution. The formation constants of the complexes were determined by titrating solution mixtures of $[Pd(dmen)(H_2O)_2]^{2+}$ (0.625 mmol) and the ligand in the concentration ratio of 1 : 1 for amino acids, peptides and dicarboxylic acids. Imidazole was converted into their protonated form with standard HNO_3 solutions. The titrated solution mixtures each had a volume of 40 ml and the titrations were carried out at 25°C and 0.1 M ionic strength (adjusted with $NaNO_3$). A standard 0.05M NaOH solution was used as titrant. The equilibrium constants evaluated from the titration data are defined by Eq. (1) and (2).

$$pM + qL + rH \rightleftharpoons (M)_p(L)_q(H)_r \qquad (1)$$

$$\beta_{pqr} = [(M)_p(L)_q(H)_r] / [M]^p [L]^q [H]^r \qquad (2)$$

Where the charges are omitted for simplicity.

M, L and H represent $[Pd(dmen)(H_2O)_2]^{2+}$, ligand and proton, respectively. The calculations were performed using the program MINIQUAD-75 [20]. Stoichiometric and stability constants of the complexes were determined by fitting various possible composition models. The selected model gave the best statistical fit and was chemically consistent with the titration data without giving any systematic drift in the magnitude of various residuals, as described elsewhere [20]. The stability constants of the complexes formed in solution are given in Tables 1–3. Distribution diagrams were obtained using the program SPECIES [21].

Table 1. Formation constants for complexes of $[Pd(dmen)(H_2O)_2]^{2+}$ with amino acids at 25°C and 0.1M ionic strength.

System	M L H[a]	logβ[b]	pK_a[c]
Pd(dmen)-OH			
	1 0 -1	-5.29(0.02)	5.29
	1 0 -2	-14.74(0.02)	9.45
	2 0 -1	-2.12(0.07)	
Glycine			
	0 1 1	9.61(0.02)	9.61
	0 1 2	12.02(0.03)	2.41
	1 1 0	10.25(0.02)	
Alanine			
	0 1 1	9.71(0.01)	9.71
	0 1 2	11.89(0.02)	2.18
	1 1 0	10.30(0.01)	
β-Alanine			
	0 1 1	10.11(0.02)	10.11
	0 1 2	13.75(0.03)	3.64
	1 1 0	9.72(0.04)	
	1 1 1	11.02(0.07)	1.30
β-Phenylalanine			
	0 1 1	9.12(0.01)	9.12
	0 1 2	11.01(0.03)	1.89
	1 1 0	9.81(0.03)	
Valine			
	0 1 1	9.58(0.01)	9.58
	0 1 2	11.71(0.02)	2.13
	1 1 0	10.14(0.02)	
Proline			
	0 1 1	10.52(0.01)	10.52
	0 1 2	12.35(0.05)	1.83
	1 1 0	11.14(0.05)	
Isoleucine			
	0 1 1	9.76(0.02)	9.76

	0 1 2	11.89(0.03)	2.13
	1 1 0	10.15(0.04)	
Ethanolamine			
	0 1 1	9.45(0.01)	9.45
	1 1 0	7.11(0.02)	
	1 2 0	13.69(0.09)	
	1 1-1	2.51(0.02)	4.60
Serine			
	0 1 1	9.14(0.01)	9.14
	0 1 2	11.40(0.02)	2.26
	1 1 0	9.89(0.01)	
	1 1-1	1.37(0.01)	8.52
Threonine			
	0 1 1	9.06(0.01)	9.06
	0 1 2	11.03(0.02)	1.97
	1 1 0	9.37(0.02)	
	1 1-1	0.66(0.02)	8.71
Histidine			
	0 1 1	9.15(0.01)	9.15
	0 1 2	15.30(0.02)	6.15
	0 1 3	17.81(0.06)	2.51
	1 1 0	11.52(0.02)	
	1 1 1	17.58(0.03)	6.06
Histamine			
	0 1 1	9.59(0.01)	9.59
	0 1 2	15.65(0.02)	6.06
	1 1 0	11.24(0.01)	
	1 1 1	15.13(0.03)	3.89
Imidazole			
	0 1 1	6.85(0.02)	6.85
	1 1 0	6.42(0.02)	
	1 2 0	12.68(0.01)	
Ornithine			
	0 1 1	10.58(0.02)	10.58
	0 1 2	19.43(0.02)	8.85
	1 1 0	11.13(0.02)	
	1 1 1	19.65(0.01)	8.52
Lysine			
	0 1 1	10.44(0.02)	10.44
	0 1 2	19.66(0.03)	9.22
	1 1 0	10.82(0.03)	
	1 1 1	20.83(0.02)	10.01
S-Methylcysteine			
	0 1 1	8.65(0.02)	8.65
	0 1 2	10.61(0.03)	1.96
	1 1 0	9.73(0.03)	
Methionine			
	0 1 1	9.12(0.02)	9.12
	0 1 2	11.39(0.03)	2.27
	1 1 0	9.42(0.04)	
Cysteine			
	0 1 1	10.36(0.01)	10.36
	0 1 2	18.61(0.01)	8.25
	0 1 3	20.62(0.01)	2.01
	1 1 0	16.33(0.03)	

Glutamic Acid	1 1 1	20.59(0.03)	4.26
	0 1 1	9.54(0.01)	9.54
	0 1 2	13.65(0.02)	4.11
	1 1 0	9.06(0.01)	
	1 1 1	13.27(0.02)	4.21

[a]M, L and H are the stoichiometric coefficients corresponding to *[Pd(dmen)(H$_2$O)$_2$]$^{2+}$*, amino acid, and H$^+$, respectively; the coefficient –1, refers to a proton loss; [b]log β of Pd(dmen)-amino acids. Standard deviations are given in parentheses; sum of square of residuals are less than 5E-7; [c] the pK$_a$ of the ligands, the protonated species or the aqua complexes.

Results and discussion

Acid-base equilibria of the ligands and [Pd(dmen)(H$_2$O)$_2$]$^{2+}$ complex

The acid dissociation constants of the ligands were determined under the same experimental conditions of ionic strength and temperature used to study the PdII complexes. The acid–base equilibria of [Pd(dmen)(H$_2$O)$_2$]$^{2+}$ given in Eq. (3a, 3b and 3c) were investigated and the equilibrium constants were determined and given in Table 1. These values were taken into account in determining the stability constants of the PdII complexes.

$$\underset{100}{[Pd(dmen)(H_2O)_2]^{2+}} \rightleftharpoons \underset{10\text{-}1}{[Pd(dmen)(H_2O)(OH)]^{+}} + H^{+} \qquad (3a)$$

$$\underset{10\text{-}1}{[Pd(dmen)(H_2O)(OH)]^{+}} \rightleftharpoons \underset{10\text{-}2}{[Pd(dmen)(OH)_2]} + H^{+} \qquad (3b)$$

$$\underset{100}{[Pd(dmen)(H_2O)_2]^{2+}} + \underset{10\text{-}1}{[Pd(dmen)(H_2O)(OH)]^{+}} \overset{\log K_{dimer}}{\rightleftharpoons}$$

$$\underset{20\text{-}1}{[(H_2O)Pd(dmen)(OH)Pd(dmen)(H_2O)]^{3+}} + H_2O \qquad (3c)$$

The pK_{a1} and pK_{a2} values for $[Pd(dmen)(H_2O)_2]^{2+}$ are 5.29 and 9.45, respectively, which are comparable with the literature values of similar systems [22,23]. The equilibrium constant for the dimerization reaction (3c) can be calculated [24] by equation (4) and amounts to 3.17

$$\log K_{dimer} = \log \beta_{20-1} - \log\beta_{10-1} \quad (4)$$
$$= -2.12-(-5.29) = 3.17$$

Table.2. Formation constants for complexes of $[Pd(dmen)(H_2O)_2]^{2+}$ with peptides at 25°C and 0.1M ionic strength.

System	M L H[a]	log β[b]	pK_a[c]
Glycinamide			
	0 1 1	7.88(0.02)	7.88
	1 1 0	7.27(0.02)	
	1 1-1	4.11(0.03)	3.16
Glycylglycine			
	0 1 1	7.94(0.01)	7.94
	0 1 2	11.01(0.02)	3.07
	1 1 0	7.98(0.01)	
	1 1-1	3.72(0.02)	4.26
Aspargine			
	0 1 1	8.56(0.01)	8.56
	0 1 2	10.79(0.03)	2.23
	1 1 0	9.02(0.03)	
	1 1-1	0.86(0.04)	8.16
Glutamine			
	0 1 1	9.50(0.01)	9.50
	0 1 2	13.61(0.02)	4.11
	1 1 0	11.86(0.03)	
	1 1-1	1.94(0.03)	9.92

[a]M, L and H are the stoichiometric coefficients corresponding to *$[Pd(dmen)(H_2O)_2]^{2+}$*, peptides, and H^+, respectively; the coefficient –1, refers to a proton loss; [b]log β of Pd(dmen)-peptides. Standard deviations are given in parentheses; sum of square of residuals are less than 5E-7; [c] the complex pK_a of the peptides or of the peptide NH ionization.

Table. 3. Formation constants for complexes of $[Pd(dmen)(H_2O)_2]^{2+}$ with dibasic acids at 25° C and 0.1M ionic strength.

System	M	L	H[a]	log β[b]	pK_a[d]
Cyclobutane-1,1-dicarboxylic acid					
	0	1	1	5.57(0.01)	5.57
	0	1	2	8.57(0.01)	3.00
	1	1	0	6.53(0.04)	
	1	1	1	9.19(0.05)	2.66
Malonic acid					
	0	1	1	5.25(0.02)	5.25
	0	1	2	7.85(0.03)	2.60
	1	1	0	5.66(0.03)	
	1	1	1	8.81(0.05)	3.15
Oxalic acid					
	0	1	1	3.96(0.02)	3.96
	0	1	2	6.24(0.03)	2.28
	1	1	0	4.76(0.04)	
	1	1	1	6.85(0.05)	2.09
Succinic acid					
	0	1	1	5.54(0.02)	5.54
	0	1	2	9.57(0.03)	4.03
	1	1	0	4.17(0.01)	
	1	1	1	8.20(0.02)	4.03
Adipic Acid					
	0	1	1	5.45(0.03)	5.45
	0	1	2	8.57(0.04)	3.12
	1	1	0	3.80(0.03)	
	1	1	1	9.06(0.04)	4.87
Fumaric Acid					
	0	1	1	4.21(0.03)	4.21
	0	1	2	6.07(0.03)	1.86
	1	1	0	3.27(0.03)	
	1	1	1	7.72(0.04)	3.45

[a]M, L and H are the stoichiometric coefficients corresponding to Pd(N-N), dibasic acids, and H^+ respectively; [b]log β of Pd(dmen)-dibasic acids. Standard deviations are given in parentheses; sum of square of residuals are less than $5e^{-7}$, [c]The pK_a of the protonated species ($\log \beta_{111} - \log \beta_{110}$).

Amino acid complexes

Fitting of the potentiometric data for [Pd(dmen)]-amino acid equilibria indicated the formation of 1 : 1 complexes. Histidine is a tridentate ligand having amino, imidazole and carboxylate groups as binding sites. With $[Pd(dmen)(H_2O)_2]^{2+}$, only two of the three binding sites are involved in complex formation, hence histidine coordinates in either a glycine-like or a histamine-like mode. The stability constant of the histidine complex is in fair agreement with that of histamine and higher than those of amino acids. This indicates that histidine interacts with the Pd^{II} complex in the same way as histamine coordinates. The analysis of the titration results for imidazole complex reveals the formation of 1:1 and 1:2 complexes. The stability constant of

1:1 complex with imidazole has a smaller value than those of amino acids. This gives a further support that amino acids are coordinating as bidentate ligands. The stability constant values ($\log\beta_{110}$) of simple amino acid complexes are compared. The proline complex has the highest value. This may be due to the highest basicity of the proline amino group as reflected by highest pKa value. The stability constant of the alanine complex ($\log\beta_{110}$ =9.22) is lower than that of glycine ($\log\beta_{110}$ = 9.72), although pK_a of alanine (9.69) is higher than that of glycine (9.60). This may be due to the steric interaction between the alkyl groups in the DME and the methyl group in the alanine. The stability constant of the complex with lysine ($\log\beta_{110}$ = 11.63) is little bit higher than those of α- amino acids. This may be taken to indicate that lysine most likely chelates through the α-amino and carboxylate groups (N, O-donor set). There is another way for coordination of lysine, where the two amino groups are bound to the Pd^{II} ion. However, such assumption is ruled out as formation of such a complex will involve formation of less stable 8-membered chelate ring, which is thermodynamically unfavored. The stability constant value of methionine complex ($\log\beta_{110}$ = 8.77) is lower than those of most simple amino acids. This may be explained on the premise that the amino group of methionine is less basic than those of other amino acids as reflected by pK_a values, Table 1.

Peptide complexes

The potentiometric data of the peptide (HL) complexes were fitted assuming the formation of the species $[Pd(dmen)(L)]^+$ (110) and $[Pd(dmen)(LH_{-1})]$ (11−1). The former species is formed by coordination through the amino group and carbonyl oxygen atom. On increasing the pH, the coordination site should switch from the carbonyl oxygen to the amide nitrogen with release of the amide hydrogen, forming the complex $[Pd(dmen)(LH_{-1})]$. Such changes in coordination centers are now well documented [25]. The pK^H of the coordinated amide group was calculated using Eq. (5) and is given in Table 2. The pK^H for the glycinamide complex is lower that the pK^H of the other peptides. This may be explained on the premise that the more bulky substituent group on the peptide may serve to hinder the structural change in going from protonated to deprotonated complexes [26,27]. Asparagine complex has the highest

stability constant value, most probably due to the presence of α-amino group that can coordinate firstly as glycine does. The α-amino group of asparagine is more basic than those of other peptides, which result in an increase of stability constant of its complex.

$$pK^{H} = \log \beta_{110} - \log \beta_{11-1} \qquad (5)$$

The concentration distribution diagrams of peptide complexes, indicate that all peptides form the complex species (110) at low pH, and thus prevents the hydrolysis of Pd^{II} ion i.e. the hydrolysed species (10-1) and (10-2) are either not formed or formed in very low concentration. The induced ionization of the peptide hydrogen of glycinamide and glycylglycine starts at pH ~ 3. However asparagine ionization starts above pH ~ 8. Therefore, under normal physiological condition (pH 6-7), the peptides would coordinate to $[Pd(dmen)(H_2O)_2]^{2+}$ in entirely different ways. Glycinamide and glycylglycine are present entirely in the deprotonated form (11-1), whereas asparagine exists solely in the protonated form.

Dicarboxylic acid complexes

In case of dicarboxylic acids complexes, the potentiometric data were fitted based on the basis of the formation of 110 and monoprotonated complex species (111), Table 3. The formation constants of the (110) complexes with oxalic, CBDCA and malonic acids, where five- and six- membered chelate rings are higher than those involving seven-membered, as in succinic, and nine-membered chelate rings as in adipic acid. This may be explained on the premise that the five- and six- membered rings are more favored energetically than the seven and the nine-membered rings.

It is interesting to note that CBDCA has a higher stability constant than malonic acid, although both form 6-membered chelate rings. This may be due to the higher pK_a values of the former than the latter dicarboxylic acid. The pK_a value of the protonated complex species of [Pd(dmen)CBDCA] is 2.13. This value is lower than that of free CBDCAH-, which indicates acidification of the seconed carboxylic group upon coordination of $[Pd(dmen)(H_2O)_2]^{2+}$ with the first carboxylate group. The pKa value of this protonated species in case of $[Pd(en)HCBDCA]^{+}$ was estimated before from u.v./vis measurements to be ca.2.5 at 25°C and 0.1M ionic strength [28]. The concentration distribution diagram of CBDCA complex, taken as an example and

given in Fig. 1, shows that the protonated species (111) is stable only at low pH and the species (110) is predominating in the physiological pH. The hydrolysed species for all dibasic acid complexes predominates only at high pH.

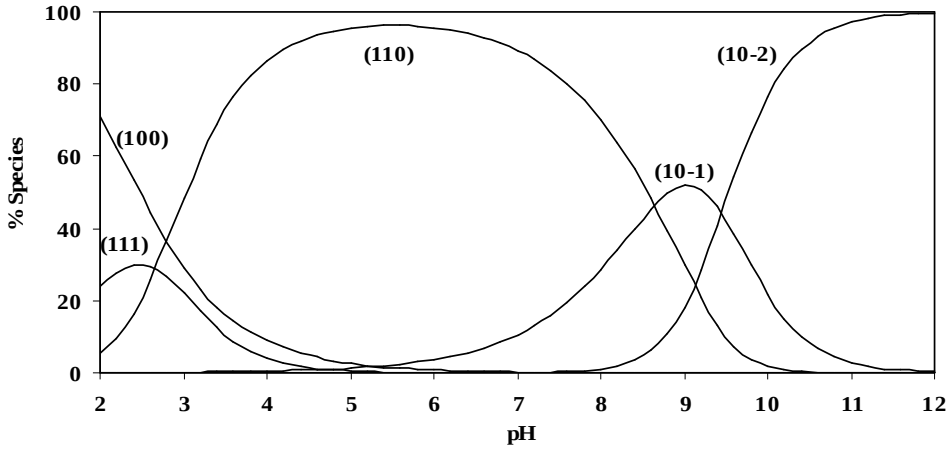

Figure 1. Concentration distribution of various species as a function of pH in the Pd(dmen)-CBDCA system.(at concentration of 1.25 mmole/liter for $[Pd(dmen)(H_2O)_2]^{2+}$ and CBDCA).

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