Spectroscopic studies on complex formation and non-covalent interactions in ternary palladium(II) systems involving spermidine and 2,3-diaminoproprionate or 2,4-diaminobutyrate

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Abstract

NMR and electronic absorption spectral studies have been carried out on complex formation and non-covalent interactions in ternary palladium(II) systems involving spermidine (Spd) and 2,3-diaminopropionate (Dpa) or 2,4-diaminobutyrate (Dba). ^{13}C NMR spectra indicated that Pd(Spd) and $Pd(Spd)_2$ with the N3 and N4 coordinations and $Pd(AA)_2$ with the N4 coordination were predominant species at neutral pH in the binary Pd(II)–Spd and Pd(II)–AA systems (AA = Dpa or Dba), respectively. $Pd(Spd)_2$ and $Pd(AA)_2$ were also found to be predominant in the 1:1:1 Pd(II)–AA–Spd systems, and in the 1:2:x Pd(II)–AA–Spd systems (x = 1–10), $Pd(AA)_2$ was the only complex species present with entire Spd uncomplexed. Circular dichroism (CD) spectral magnitudes as well as the NMR spectral shifts observed for the ternary systems and the CD magnitude dependence on solvent polarity indicated that the side chain carboxylate group of AA is involved in hydrogen bonds or electrostatic interactions with the protonated amino groups of Spd. The apparent stability constants, log K, for the 1:1 adduct $Pd(AA)_2 \cdot Spd$ at pH 7.5 (25 °C and I = variable) have been calculated from the CD magnitudes to be 2.4 and 2.6 for AA = Dpa and Dba, respectively.

Key words: Spectroscopic study; Palladium complexes; Biogenic amine complexes; Spermidine complexes

Introduction

Biogenic amines, putrescine ($NH_2(CH_2)_4NH_2$), spermidine ($NH_2(CH_2)_3NH(CH_2)_4NH_2$) and spermine ($NH_2(CH_2)_3NH(CH_2)_4NH(CH_2)_3NH_2$), (Scheme 1) are known to play essential roles in the process of genetic information transfer. They occur in bacteria, plants and animal tissues and act as growth factors [1]. Whereas a distinct increase in the biogenic amine concentration in cancer cells, the growth of which is stimulated by the polyamines, has been found, complex formation of the polyamines with copper(II) has been reported to inhibit the growth process [2]. Changes in the amine content in cells accompany also other diseases; for example, the spermine/spermidine concentration ratio changes in the blood of patients affected by cystic fibrosis [3].

$NH_2CH_2CH_2CH_2CH_2NH_2$ putrescine

$NH_2\overset{1}{C}H_2\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{N}H\overset{5}{C}H_2\overset{6}{C}H_2\overset{7}{C}H_2CH_2NH_2$ spermidine (Spd)

$^{-}OO\overset{1}{C}\overset{2}{C}H(NH_2)\overset{3}{C}H_2NH_2$ 2,3-diaminopropionate (Dpa)

$^{-}OO\overset{1}{C}\overset{2}{C}H(NH_2)\overset{3}{C}H_2\overset{4}{C}H_2NH_2$ 2,4-diaminobutyrate (Dba)

Scheme 1.

Although the results of recent studies unequivocally show the importance of biogenic amines in genetic processes [4], convincing information on the nature and mechanism of their involvement in the processes is still lacking. There have been reported data pointing to strictly specified structural requirements for the interactions between polyamines and other biomolecules, such as the necessity of the four-carbon atom chain for stabilization of α phage DNA [5] and the differences observed in the effect of spermine and synthetic 4,7-

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diazadodecane-1,10-diamine on the melting point of calf thymus DNA [6]. A correlation between the amine chain length and the stabilization of nucleic acids has also been found [7].

It is characteristic of biogenic amines that they occur in the physiological medium almost exclusively in the protonated cationic forms, and as such they show a considerable affinity for anionic fragments of bioligands, e.g. phosphate groups of nucleic acids, fatty acids, phospholipids and amino acids. They can form complexes with metal ions in biological systems [8]. In addition, stable metal complexes with negatively charged side groups may interact electrostatically with protonated polyamines without disruption of the complex structure. Weak interactions of this and other types are essential for the formation of adducts in a fast and reversible way in the processes of such biological reactions as molecular recognition, enzyme catalysis and information transfer [9]. Mixed ligand complexes with two interacting ligands have been studied as useful models for various biological processes with participation of metal ions [10–16].

We have been interested in non-covalent interactions in ternary metal complexes and in the systems with a ternary complex and an uncoordinated molecule. Intramolecular hydrogen bonds and electrostatic interactions [12, 17] and aromatic ring stacking [18] have been established by spectroscopic and crystallographic methods for Cu(II) and Pd(II) complexes involving acidic and basic amino acids, aromatic amino acids, and/or aromatic nitrogen ligands. The complexes with intramolecular interactions were found to be stabilized relative to those without such interactions. Intermolecular interactions in adducts of platinum(II) complexes such as $Pt(phen)(en)^{2+}$ with NMP^{2-} (=AMP, GMP, etc.), $Pt(phen)(en)^{2+} \cdot NMP^{2-}$, have been studied by spectroscopic and calorimetric methods [19]. Complex formation may cause conformational changes of side chain groups, placing them in a way suitable for intermolecular interactions with other molecules. An excellent example of specific interactions between metal complexes and biomolecules is the DNA sequence recognition by zinc finger proteins [20, 21], which bind DNA sequence-specifically through positively charged and highly polar side groups of arginine residues etc. arranged upon zinc complex formation [22].

This paper presents the results of spectral and equilibrium studies on palladium(II)–amino acid (AA)–spermidine systems (AA=2,3-diaminopropionate, 2,4-diaminobutyrate) and the evidence for the occurrence of weak intermolecular hydrogen bonds between the protonated amino groups of spermidine and the negatively charged side chain carboxylate group of AA in $Pd(AA)_2$ complexes.

Experimental

Reagents

Spd·3HCl, DL-Dpa·HCl, DL-Dba·2HCl and D_2O were purchased from Sigma, L-Dba·2HCl from Fluka, and L-Dpa·2HCl from Tokyo Kasei Kogyo. Pd(II) was used as Na_2PdCl_4 obtained from Nacalai Tesque. All other reagents were of analytical grade or of highest grade available and were used without further purification. Distilled and deionized water was used in all the experiments.

Spectral measurements

Absorption spectra were recorded at room temperature on a Hitachi 330 spectrophotometer in a 1 cm path length quartz cell, and circular dichroism (CD) spectra were obtained with a JASCO J-40 spectropolarimeter in 2 cm and 0.1 cm path length quartz cells. Samples were prepared by dissolving weighed amounts of Na_2PdCl_4 and a ligand in water, the concentrations of Pd(II) being 1 or 2 mM. After preliminary neutralization with aqueous NaOH, the solutions were allowed to stand for 1 h, and the pH value was adjusted by aqueous NaOH or HCl. Measurements were carried out after equilibrium was attained, when no change in pH associated with complex formation was observed. An Iwaki M-225 pH meter with an Iwaki IW-050 combined electrode was employed. The ionic strength (I) of the solutions was not adjusted (I=variable). ^1H and ^{13}C NMR spectra were recorded on a JEOL FX-100 and a Varian VXR-300S spectrometer with D lock using dioxane and tert-butanol as internal standards. Values of chemical shifts were converted to the TMS scale by adding 67.40 ppm [23]. Ligand concentrations of the sample solutions were adjusted to 0.02–1 M by concentrating the dilute solutions.

Results and discussion

Palladium(II)–spermidine systems

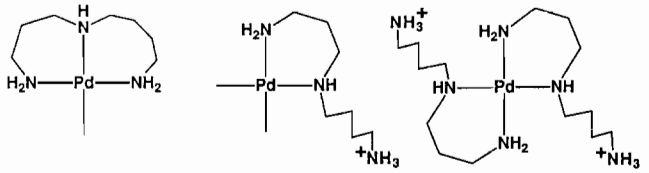
Palladium(II) complexes with nitrogen donors are inert on the NMR time scale, giving separate sets of NMR signals for free and coordinated ligands. Table 1 shows the ^{13}C NMR chemical shifts of free ligands, Spd, Dpa and Dba. The assignments of the signals were made on the basis of substituent effects, peak heights, and comparison of the chemical shifts of the coordinated ligands in binary and ternary systems (Tables 2 and 3) with the corresponding signals in the ligand-only systems (Table 1). Spd is an asymmetric biogenic amine (Scheme 1) having seven non-equivalent carbon atoms which give a set of seven ^{13}C NMR signals at 24–48 ppm. A detailed analysis of signal changes in

TABLE 1. ^{13}C NMR chemical shifts[a] for ligands

Ligand	pD	Chemical shifts (δ)						
		C-1	C-2	C-3	C-4	C-5	C-6	C-7
DL-Dpa·HCl	4.3	173.67	52.90	41.43				
L-Dba·2HCl	3.9	175.86	55.16	39.18	30.78			
Spd·3HCl	5.3	39.55	26.71	47.36	49.88	25.45	26.57	39.55

[a]Lower field shifts relative to TMS.

the 1:1 Pd(II)–Spd system showed formation of the Pd(Spd) complex (**1**) with Spd as a terdentate ligand (N3 coordination) (Table 2). The carbons C(1), C(3), C(4) and C(7) located next to the donor atoms exhibited downfield shifts (complex shifts, $\Delta\delta$, defined as the shifts from the corresponding values of Spd·3HCl), which were significantly larger than those for the other carbon atoms. For N3 coordination the $\Delta\delta$ value for C(1) is characteristically smaller than the values for C(3), C(4) and C(7). In the pH range 5–8 complex **1** was concluded to be the major complex species present in the 1:1 Pd(II)–Spd system. However, when the pH value was lowered to *c.* 3, the Pd(Spd) complex with N2 coordination (**2**) was formed. The $\Delta\delta$ value for C(7) was smaller (1.6 ppm) at pH 3, which indicates that the nitrogen at C(7) remained uncoordinated. About 40% of Spd was estimated to be uncoordinated at pH



1 **2** **3**

3 from the NMR spectrum, whereas at pH 5.5 it was nearly completely bound to Pd(II). The NMR spectrum for the 1:2 Pd(II)–Spd system indicated that, besides Pd(Spd), $Pd(Spd)_2$ with N4 coordination (**3**) was formed. The nitrogen atom at C(7) does not take part in the coordination, since the chemical shift difference between the signal for C(7) in the free ligand and in the complex was *c.* 2 ppm (Table 2). The existence of **1** and **3** was detected from the spectrum at pH c. 5.5, which revealed three separate sets of signals, one attributable to

TABLE 2. ^{13}C NMR chemical shifts[a] and complex shifts ($\Delta\delta$)[b] for binary Pd(II)–ligand systems

System	pD	Population	Chemical shift ($\Delta\delta$)[b]						
			C-1	C-2	C-3	C-4	C-5	C-6	C-7
1:1 Pd(II)–Spd	5.3		42.76	28.85	52.57	55.72	27.48	27.92	45.23
			(3.21)	(2.14)	(5.21)	(5.84)	(2.03)	(1.35)	(5.68)
	7.4		42.77	28.84	52.58	55.72	27.43	27.92	45.23
			(3.22)	(2.13)	(5.22)	(5.84)	(1.98)	(1.35)	(5.68)
1:2 Pd(II)–Spd	5.4		42.71	28.80	52.52	55.67	27.43	27.92	45.23
			(3.16)	(2.09)	(5.16)	(5.79)	(1.98)	(1.35)	(5.68)
			41.98	28.16	50.76	53.04	25.83	27.38	41.62
			(2.43)	(1.45)	(3.40)	(3.16)	(0.38)	(0.81)	(2.07)
	7.5		41.98	28.17	50.81	53.04	25.83	27.43	41.62
			(2.43)	(1.46)	(3.45)	(3.16)	(0.38)	(0.86)	(2.07)
1:1 Pd(II)–DL-Dpa	3.0	major	175.62	64.54	52.41				
			(1.95)	(11.64)	(10.98)				
		minor	176.36	63.07	50.95				
			(2.69)	(10.17)	(9.52)				
				63.18	51.03				
				(10.28)	(−9.60)				
1:2 Pd(II)–DL-Dpa	8.0	major	177.15	63.64	51.31				
			(3.48)	(10.74)	(9.88)				
		minor		63.56	51.21				
				(10.66)	(9.78)				
1:1 Pd(II)–DL-Dba	3.6	major	178.81	56.18	42.05	33.92			
			(2.95)	(1.02)	(2.87)	(3.14)			
		minor		56.28	42.17	33.55			
				(1.12)	(2.99)	(2.77)			
1:2 Pd(II)–DL-Dba	5.3	major (65%)	179.97	57.47	42.56	34.07			
			(4.11)	(2.31)	(3.38)	(3.29)			
		minor (35%)	179.90	57.55	42.46	34.07			
			(4.04)	(2.39)	(3.28)	(3.29)			

[a]Lower field shifts relative to TMS. [b]Values in parentheses denote $\Delta\delta$; $\Delta\delta = \delta_{complex} - \delta_{ligand}$ (Table 1).

TABLE 3. ^{13}C NMR chemical shifts[a] and differences of corresponding shifts[b] for ternary 1:2:1 Pd–L-Dba–Spd systems at pD 5.3

Component	Population (%)	Chemical shifts (differences of corresponding shifts)						
		C-1	C-2	C-3	C-4	C-5	C-6	C-7
Spd·3HCl	100	49.87 (0.01)	47.36 (0.00)	41.84 (0.06)	39.63 (0.08)	26.70 (−0.01)	26.54 (−0.03)	25.41 (−0.04)
$Pd(L\text{-}Dba)_2$	65	180.00 [0.03]	57.54 [0.07]	42.60 [0.04]	34.10 [0.03]			
	35	179.91 [0.01]	57.51 [−0.04]	42.49 [0.03]	34.10 [0.03]			

[a]Lower field shifts relative to TMS. [b]The values in parentheses are $\Delta\delta$ values and those in brackets are the chemical shift differences between $Pd(L\text{-}Dba)_2$ in the binary system and the ternary system with Spd.

Pd(Spd) and two to $Pd(Spd)_2$. At pH 7.5 the only detectable complex species was **3** with N4 coordination.

The conclusions based on the ^{13}C NMR data were confirmed by the electronic spectral data summarized in Table 4. For the 1:1 Pd(II)–Spd system at pH *c.* 5.5 and 7.5, the absorption peaks were observed at 322 and 320 nm, respectively, corresponding to N3 coordination. However, for the 1:2 Pd(II)–Spd system at pH 5.5, a band centered at 305 nm with a shoulder at ~320 nm corresponding to a mixture of **1** and **3** was observed, and at pH 7.5 only a peak at 292 nm characteristic of N4 coordination was observed [24]. Very recently the Pd(II) complexes of spd, putrescine and spermine were isolated, and formation of dimeric complexes has been indicated by ^1H NMR spectra [25]. Structure **2** was revealed for $[PdCl_2(Spd)_2]^+$ by X-ray analysis [25a].

TABLE 4. Absorption and CD spectral data for $Pd(L\text{-}AA)_2$–Spd systems

System	pH	Absorption		CD	
		λ_{max} (nm)	ϵ	λ_{max} (nm)	$\Delta\epsilon$
1:1 Pd(II)–Spd	5.5	322	150		
	7.5	320	120		
1:2 Pd(II)–Spd	5.5	305	290		
		320 sh			
	7.5	292	420		
1:2 Pd(II)–L-Dpa	5.9	287	330	282	0.68
	7.4	285	350	280	0.66
1:2 Pd(II)–L-Dba	5.9	290	420	288	0.55
	7.4	288	430	287	0.53
1:1:1 Pd(II)–L-Dpa–Spd	5.9	293	370	283	0.20
	7.5	290	400	282	0.15
1:1:1 Pd(II)–L-Dba–Spd	5.9	294	360	290	0.34
	7.2	290	400	290	0.34

Palladium(II)–diaminocarboxylate systems

^{13}C NMR measurement (Table 2) for the 1:1 Pd(II)–Dpa system showed that Pd(Dpa) and $Pd(Dpa)_2$ were present in the molar ratio of 3 to 2, whereas in the 1:2 system $Pd(Dpa)_2$ was virtually the only species present. Chemical shift differences from Dpa·HCl were less than 11.6 ppm. Downfield shifts due to Pd(II) binding indicate that Dpa coordinates to Pd(II) through both amino nitrogens, forming the complex of N4 coordination. $Pd(Dpa)_2$ in the 1:2 Pd(II)–Dpa system gave the electronic absorption peak at 285 nm at pH 7.4 corresponding to N4 coordination [18b, 26]. The complex shift of the carboxylate carbon (*c.* 3 ppm), when compared with that of the Pd(II)–amino acid complexes [17c, 27], shows that this group is not involved in complex formation.

The ^{13}C NMR spectrum of the 1:1 Pd(II)–Dba system exhibited the predominant signals due to the 1:1 complex and, contrary to the Dpa systems, $Pd(Dba)_2$ was not the major species. The spectrum of the 1:2 Pd(II)–Dba system, however, showed that $Pd(Dba)_2$ was predominant. Two closely related groups of peaks were observed as a result of *cis–trans* isomerism (Table 2). Participation of the four nitrogen atoms in coordination was confirmed by the electronic spectra, which were similar to those for Dpa (Table 4).

Non-covalent interactions in palladium(II)–diaminocarboxylate–spermidine systems

Detailed analysis of the NMR spectral data indicates that mixed complexes were not formed in the Pd(II)–AA–Spd ternary systems at least in amounts detectable by the NMR and electronic spectra. A comparison of ^{13}C NMR spectra and absorption spectra for binary and ternary systems points to $Pd(Spd)_2$ and $Pd(AA)_2$ as the main species in 1:1:1 Pd(II)–AA–Spd systems. The only detectable complex in the 1:2x Pd(II)–AA–Spd systems with $x \leqslant 10$ was $Pd(AA)_2$ irrespective of x, and Spd remained uncoordinated. This is typically seen from the ^{13}C NMR spectrum for 1:2:1 Pd(II)–Dba–Spd shown in Fig. 1. The $\Delta\delta$ values for

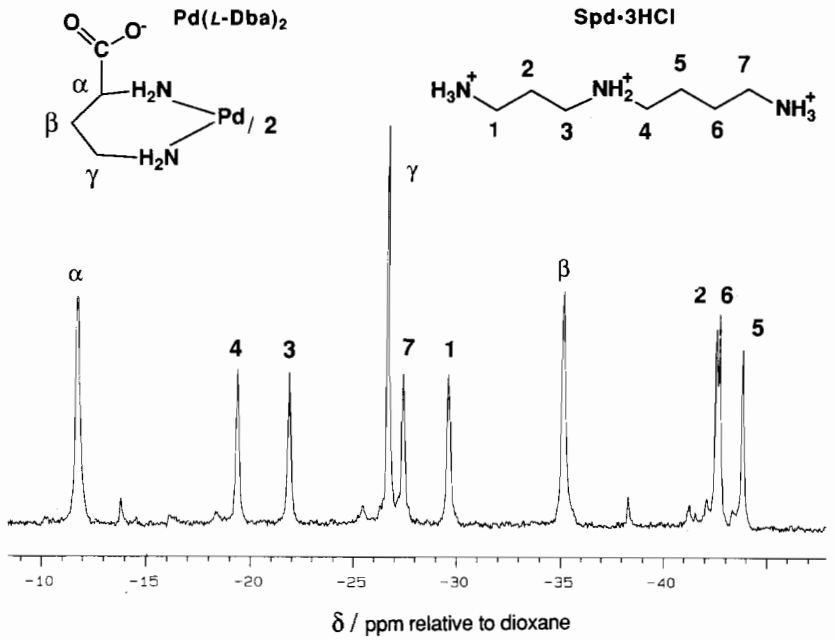


Fig. 1. ^{13}C NMR spectrum of the 1:2:1 Pd(II)–L-Dba–Spd system at pD 5.3.

all carbons of Spd at pH 5.3 are nearly the same as those observed for metal-free Spd·3HCl (Table 1). Analogous changes have been observed for the Pd(II)–Dpa–Spd systems.

On the other hand, the Pd(L-AA)$_2$ systems gave a positive CD peak due to the $d_{xy} \rightarrow d_{x^2-y^2}$ transition in the d–d region (280–290 nm) by the vicinal effect of the asymmetric carbon atom of L-AA. The CD spectral magnitudes exhibited a clear dependence on the Spd concentration (Fig. 2), although the latter was not involved in coordination. The absorption spectra of Pd(L-AA)$_2$ were not affected by addition of Spd. On the basis of a substantial body of evidence showing that the changes in the CD magnitude reflect the conformational changes of AA due to ligand–ligand interactions [12, 17a–17d, 18a, 27], the observed CD magnitude dependence establishes that Spd affects the conformation of L-AA as a result of hydrogen bonds or electrostatic interactions between the polar or negatively charged groups of Pd(L-AA)$_2$ and the protonated amino groups of Spd. In accordance with these observations, the CD spectral magnitude decreased with the decrease in solvent polarity, further supporting the existence of such electrostatic interactions (Fig. 3). The ^{13}C NMR spectra of the above systems showed no

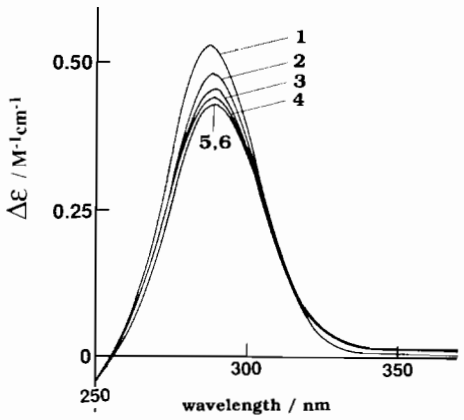


Fig. 2. CD spectra of the 1:2:x Pd(II)–L-Dba–Spd system at pH 7.5. Curves (number (x)): 1 (0), 2 (2), 3 (4), 4 (6), 5 (8), 6 (10). Total conc. of Pd(II) = 2.0 mM.

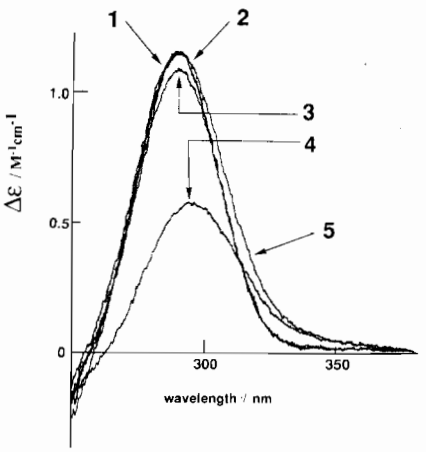


Fig. 3. Solvent and ionic strength dependences of the CD spectra for Pd(L-Dba)$_2$ and Pd(L-Dba)$_2$–Spd systems at neutral pH. Systems: Pd(L-Dba)$_2$, curves 1 (I = var. and 1 M $NaClO_4$) and 5 (in 50 vol./vol.% dioxane–water (I = var.)); Pd(L-Dba)$_2$–Spd, curves 2 (I = 1 M $NaClO_4$), 3 (I = var.), and 4 (in 50 vol./vol.% dioxane–water (I = var.)).

appreciable chemical shift changes due to intermolecular interactions at pH 5.3. Small $\Delta\delta$ values have been experienced previously with the Pd(II) complexes involving acidic and basic amino acids, where intramolecular electrostatic ligand–ligand interactions have been concluded from the CD spectra [17c]. Therefore, the ^{13}C chemical shifts appear to be rather insensitive to such weak interactions.

Evaluation of $Pd(AA)_2 \cdot Spd$ adduct stability

Assuming that $\Delta\epsilon$ changes are proportional to the adduct concentration, we can determine the degree of adduct formation (α) by eqn. (1):

$$\alpha = \frac{\Delta\epsilon_x - \Delta\epsilon_0}{\Delta\epsilon_{max} - \Delta\epsilon_0} \quad (1)$$

where $\Delta\epsilon_0$, $\Delta\epsilon_{max}$, and $\Delta\epsilon_x$ are the CD magnitudes for $Pd(AA)_2$, $Pd(AA)_2$ with a large excess of Spd, and $Pd(AA)_2$ with a given intermediate amount of Spd, respectively. The equilibrium constant for the adduct formation is given by eqn. (2):

$$Pd(AA)_2 + Spd \overset{K}{\rightleftharpoons} Pd(AA)_2 \cdot Spd$$

$$K = \frac{[Pd(AA)_2 \cdot Spd]}{[Pd(AA)_2][Spd]} \quad (2)$$

Since it was concluded from the NMR spectra that AA is completely bound to Pd(II) as $Pd(AA)_2$ in the 1:2x Pd(II)–AA–Spd systems, we may assume formation of the 1:1 $Pd(AA)_2 \cdot Spd$ adduct only. Thus, K is calculated from α for each 1:2x system by eqn. (3):

$$K = \frac{\alpha C_{Pd}}{(C_{Pd} - \alpha C_{Pd})(C_{Spd} - \alpha C_{Pd})} \quad (3)$$

where C_{Pd} and C_{Spd} are the total analytical concentrations of Pd(II) and Spd, respectively. The $\Delta\epsilon_x$ and $\Delta\epsilon_{max}$ values were obtained from the plots of $\Delta\epsilon$ against the Spd concentration for the 1:2x Pd(II)–Dba–Spd system at pH 7.5 (Fig. 4) and used for calculation of α (eqn. (1)). The log K value was calculated by eqn. (3) for each α value obtained and the values obtained for high Spd concentrations were excluded from averaging, because they may have been affected by formation of 1:2 or higher adducts. The log K values have thus been determined to be 2.4 for $Pd(Dpa)_2 \cdot Spd$ and 2.6 for $Pd(Dba)_2 \cdot Spd$ at pH 7.5. Considering that the measurements were made at I = var., these values should be regarded as an approximation. In this connection, a potentiometric study of the interactions between pyrophosphate and protonated polyamines revealed that the log K value for 1:1 Spd–pyrophosphate is 2.5 at I = 0.50 [28].

The species distributions calculated as a function of Spd concentration in the 1:2:1 $Pd(AA)_2$–Spd system (C_{Pd} = 2 mM) indicate that $Pd(Dpa)_2 \cdot Spd$ (Fig. 5) and $Pd(Dba)_2 \cdot Spd$ amount to 27 and 34% of C_{Pd}, respectively.

Modes of intermolecular interactions and concluding remarks

The binary complexes Pd(L-AA)$_2$ are present in *cis* and *trans* forms. We have previously studied the *cis–trans* isomerism of Pd(L-His)$_2$ (His = histidinate) and ternary Pd(II) complexes with L-His and an L-amino acid [27] and assigned the ^1H NMR signals to the *cis* and *trans* forms on the basis of the spectra for *cis*-Pt(L-His)$_2$ [29] and *cis*-Pd(imidazole)Cl$_2$ [26d]. Assuming that this signal assignment also holds for Pd(L-Dba)$_2$, we assigned the signal at 180.0 ppm to the *trans* form and that at 179.9 ppm to the *cis* form and estimated the population of each isomer from the peak areas to be 53% (*trans*) and 47% (*cis*) at 22 °C. In the 1:1 Pd(L-Dba)$_2$–Spd system, the populations were estimated to be 56% (*trans*) and 44% (*cis*) at 22 °C, and at 60 °C the differences between the *cis* and *trans* isomers (4%) were smaller in both systems. These results suggest that the *trans* form is favorable for the interactions, and the adduct structure may be schematically described as **4**, which involves hydrogen bonds between the carboxylate oxygens located on the same side of the coordination plane and two protonated amino groups

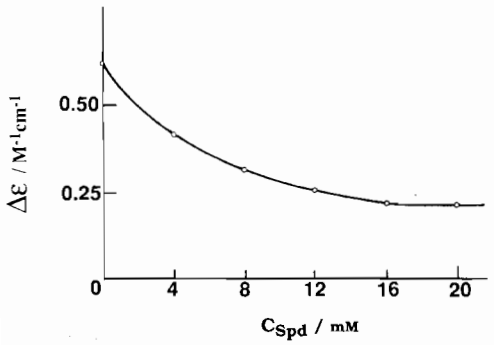


Fig. 4. CD spectral magnitudes of Pd(L-Dba)$_2$ as a function of Spd concentration. C_{Pd} = 2.0 mM; pH 7.5 (I = var.); wavelength 290 nm.

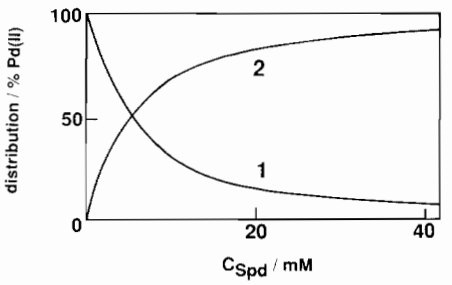


Fig. 5. Species distributions for the Pd(L-Dpa)$_2$–Spd system as a function of Spd concentration. C_{Pd} = 2.0 mM; pH 7.5. Curves: 1, Pd(L-Dpa)$_2$; 2, Pd(L-Dpa)$_2 \cdot$ Spd.

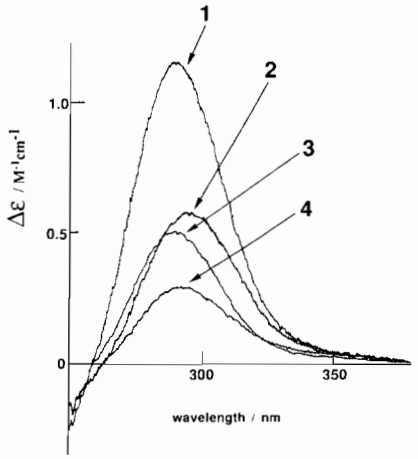
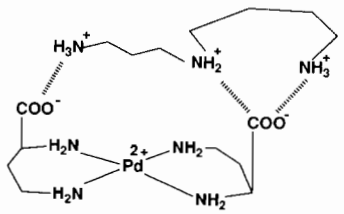


Fig. 6. CD spectral magnitude dependences of Pd(L-Dba)$_2$ on amines present in 50 vol./vol.% dioxane–water at pH 5–6. C_{Pd} = 2.0 mM; conc. of amines, 60 mM. Curves: 1, no amine; 2, Spd; 3, putrescine; 4, 1,3-diaminopropane.

of Spd. It is interesting to note in this connection that diamines, putrescine and 1,3-diaminopropane, affect the CD magnitude of Pd(L-Dba)$_2$ more than Spd (Fig. 6), indicating that they interact with the complex more strongly probably owing to two neighboring NH_3^+ groups.



4

Taken together, these findings give a clear picture of the complex formation in the Pd(II)–amino acid–biogenic amine systems and provide evidence for adduct formation through intermolecular hydrogen bonds. Biogenic amines thus show an intrinsic affinity for negatively charged groups, such as the phosphoester groups of RNA and DNA. The X-ray structural analyses of sperminium diphosphate [30] and tRNA with bound Mg(II) and spermine [31] demonstrate that such is the case for tRNA·polyamine adducts, where polyamines probably stabilize the RNA structure by neutralizing the negative charges of the neighboring phosphoester groups.

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