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Substitution Reaction of Palladium (II) Complexes With Some Amino Acids

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التفاعلات الاستبدالية لمعقدات البلاديوم الثنائي مع بعض الأحماض الامينية

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Abstract:
A new set of palladium (II) complexes with sodium salts of the following amino acids have been investigated: L-arginine (argH), L-serine (serH2), L-glutamic acid (gluH2), L-glutamine (glnH), L-asparagine (asnH) and L- threonine (thrH2). The isolated complexes have been characterized by their elemental analyses, solubility, conductivity measurements, IR, electronic absorption and ^{13}C-NMR spectra.

Keywords: Palladium (II) complexes, 2,6-diaminopyridine, Amino acids.

الملخص
تعتبر معقدات ثنائي امينو بايردين من المعقدات المهمة في مجالات مختلفة اهمها الصناعات الدوائية. تم في هذه الدراسة تحضير معقدات املاح الصوديوم للأحماض الامينية بواسطة 6,2-ثنائي امينو بايردين بتفاعل *cis*-$[Pd(dap)Cl_2].H_2O$ مع املاح الاحماض الامينية : الارجنين، سيرين، حمض الجلوتامين، الجلوتامين، اسبارجنين، الثايرونين. وتم الحصول على ست معقدات مختلفة, $Na[Pd(dap)(glu)Cl].2H_2O$, $Na[Pd(dap)(ser)Cl].HCl.H_2O$, $Na[Pd(dap)(arg)Cl_2].HCl$, $Na_2[Pd_2(dap)(gln)_2Cl_4]$, $[Pd(dap)(asn)]Cl.HCl.\ 0.5H_2O$ and $Na_2[Pd(dap)(thr)Cl_2].0.5H_2O$.

الكلمات المفتاحية: معقدات البلاديوم، 2,6- ثنائي امين باردين، الاحماض الأمينية.

Introduction

Complexes of palladium(II) with nitrogen-donor ligands have received great attention because of their biological, photochemical and catalytic properties as well as their interesting structures (Zaghal, 2007).The compound 2,6-diaminopyridine (dap) seems to be a suitable ligand for palladium (II) which shows preferences for nitrogen-donor ligands and for square planar geometry (Cotton;1999).The 2,6-diaminopyridine ligand is an N-donor chelating agent which combines the properties of both primary aromatic and N-heterocyclic amines as shown below. It has three coordination sites: the pyridine nitrogen and the two amino (NH_2) groups.

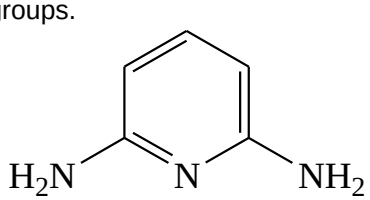
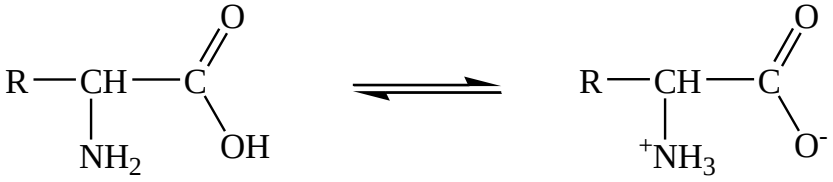


Figure 1. Structure of 2,6-diaminopyridine

In 2004, further investigated the substitution reactions of *cis*-[Pd(dap)Cl_2].H_2O with the following ligands: SCN^-, CN^-, N_3^-,thiourea, 4,4`-bipyridine, 8-aminoquinoline, imidazole and oxalate (Mhaidat;2004). In 2007, Zaghal and co-workers prepared and characterized some complexes of dap with Pd(II), Rh(III) and Hg(II) and studied the bonding modes of 2,6-diaminopyridine through ^{1}H- and ^{13}C-NMR (El-Qisairi, 2007). The Pd(II) complexes, [Pd(NN)Cl_2], where NN= bpy or phen, have been reacted with the anions (Jin et al;2000). The resulting complexes $[Pd(NN)(NO)]^{n+}$, where NN= bpy, phen; NO= anion of the amino acid and n= 0 or 1 have been found to be more biologically active than the parent compounds (Jin et al;2000). Amino acids are the building blocks of proteins (Mcmurry;2004). They contain both basic amino and acidic carboxyl groups and exist in aqueous solutions primarily in the form of dipolar ions or zweitterions as shown in Figure 2.



(a) (b)

Figure 2. An amino acid: (a) uncharged form (b) zweitterionic form.

Manar Bani Saeed has prepared mixed-ligand and bis-chelated complexes of Pd (II) with the anions. These complexes were characterized by conductivity measurements, IR, UV-visible and ^{1}H- and ^{13}C-NMR spectral measurements (Bani Saeed; 2013).The aim of this work has, therefore, been to further investigate the substitution reactions of *cis*-FPd(dap)Cl_2].H_2O with amino acids in order to prepare mixed-ligand (dap-amino acid) complexes that might have interesting structures as well as important biological properties. The following amino acids were used: L-arginine, L-serine, L-glutamic acid, L-glutamine, L-asparagine and L-threonine. Their names, abbreviations and linear structures are shown in Table 1. We focused our attention on the anions of the amino acids, i.e. the deprotonated ones in basic solutions as shown below:

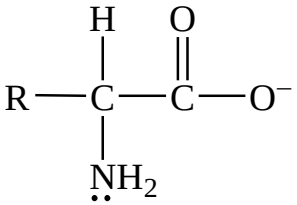


Figure 3. Anion of the amino acids in basic solution.

These anions prefer to bind to Pd(II) through the $–COO^-$ and $–NH_2$ groups and thus acting as bidentates (Bani Saeed, 2013) forming a 5-membered ring or they bind to Pd(II) as monodenate ligands through the $–COO^-$ or through the $–S^-$ and $–NH_2$ groups in amino acids having sulfur donor atoms.

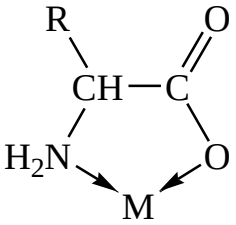


Figure 4. Coordinated amino acid anions in pladium.

Material and methods

The solvents used were analytical reagent grade and were used as purchased unless otherwise mentioned. The ligand 2,6-diaminopyridine, ($C_5H_7N_3$), palladium(II) chloride ($PdCl_2$) were purchased from Fluka A. G., Buchs, Switzerland. L-Glutamic acid ($C_5H_9O_4N$), L-glutamine ($C_5H_{10}N_2O_3$) and United Kingdom.

Potassium bromide (KBr), benzonitrile (C_6H_5CN), L-serine ($C_3H_7O_3N$), L-asparagine ($C_4H_8O_3N_2$) and L-arginine ($C_6H_{14}O_2N_4$) were purchased from BDH, Poole, United Kingdom. L-Threonine ($C_4H_9O_3N$) was purchased from Sigma, U.S.A.The starting complexes *cis*-dichlorobis(benzonitrile) palladium(II), *cis*-[$Pd(PhCN)_2Cl_2$, and *cis*-dichloro(2,6-diaminopyridine)palladium (II) monohydrate, *cis*-[$Pd(dap)Cl_2$].H_2O, were prepared as described in the literature according to the following procedures:

Preparation of *cis*-[$Pd(PhCN)_2Cl_2$] (i)

A mixture of $PdCl_2$ (0.50 g) and excess benzonitrile (20 ml) was heated to about 100°C until $PdCl_2$ dissolved. The resulting red solution was filtered while hot and the filtrate was poured into low boiling (40-60°C) petroleum ether (200 ml). The light-yellow precipitate formed was filtered off, washed with light petroleum ether and then dried under vacuum at 35°C.

(ii) Preparation of *cis*-[$Pd(dap)Cl_2$].H_2O

A methanolic solution (10 ml) containing 2,6-diaminopyridine (0.07 g; 0.66 mmol) was dropwise added to a filtered methanolic solution (10 ml) of [$Pd(PhCN)_2Cl_2$] (0.25 g; 0.66 mmol). Turbidity developed immediately. The solution was stirred for 4 hours. The orange precipitate was filtered off, washed with methanol and dried at room temperature.

Reactions of *cis*-Dichloro(2,6-diaminopyridine) palladium(II) Monohydrate, *cis*-[$Pd(dap)Cl_2$].H_2O, with Amino Acids

The starting complex *cis*-dichloro(2,6-diaminopyridine) palladium (II) monohydrate (hereafter referred to as complex A) was reacted with the sodium salts of the following amino acids: L-arginine (argH), L-serine ($serH_2$), L-glutamic acid ($gluH_2$), L-glutamine (glnH), L-asparagine (asnH) and L-threonine ($thrH_2$). All of the isolated complexes were dried at 40°C. They were obtained by the following procedures:

(i) Na[Pd(dap)(arg)Cl_2]. HCl

A concentrated aqueous solution of the sodium salt of L-arginine [argH (0.058 g, 0.32 mmol) and $NaHCO_3$ (0.027 g, 0.32 mmol) was added dropwise to a stirred solution of complex A (0.10g, 0.32 mmol) in deionized water (20 ml). The reaction mixture was refluxed at 85°C for 18 hours. The reaction mixture was filtered then the solvents were evaporated completely under reduced pressure. The reddish-brown precipitate formed was washed with ethanol, acetone and diethyl ether by centrifuge. The yield is 0.099 g (58 %). The complex decomposes at 220°C.

(ii) Na[Pd(dap)(ser)Cl]. HCl.H_2O

To a stirred suspension of complex A (0.10 g, 0.32 mmol) in deionized water (20 ml) was added dropwise a concentrated aqueous solution of the sodium salt of L-serine [$serH_2$ (0.034 g, 0.32 mmol) and $NaHCO_3$ (0.027 g, 0.32 mmol)]. No immediate change was observed. The reaction mixture was refluxed at 85°C for 18 hours and then filtered. The filtrate was evaporated to dryness under reduced pressure. The reddish-brown precipitate obtained was washed very well with ethanol, acetone and diethyl ether by centrifuge. The yield is 0.082 g (58 %). The complex decomposes at 187°C.

(iii) Na[Pd(dap)(glu)Cl].2H_2O

A concentrated aqueous solution of the sodium salt of L-glutamic acid [$gluH_2$ (0.048 g, 0.32 mmol) and $NaHCO_3$ (0.027 g, 0.32 mmol)] was added dropwise to a stirred suspension of complex A (0.10 g, 0.32 mmol) in deionized water (20 ml). The reaction mixture was refluxed at 85°C for 16 hours. The reaction mixture was filtered then the solvents were evaporated completely under reduced pressure. The reddish-brown precipitate formed was washed with ethanol, acetone and diethyl ether by centrifuge. The yield is 0.10 g (69 %). The complex decomposes at 208°C.

(iv) $Na_2[Pd_2(dap)(gln)_2Cl_4]$

To a stirred suspension of complex A (0.10 g, 0.32 mmol) in deionized water (20 ml) was added a concentrated aqueous solution of the sodium salt of L-glutamine [glnH (0.048 g, 0.32 mmol) and $NaHCO_3$ (0.027 g, 0.32 mmol)]. No immediate change was observed. The reaction mixture was refluxed at 85°C for 16 hours and then filtered. The filtrate was evaporated to dryness under reduced pressure. The reddish-brown precipitate obtained was washed with ethanol, acetone and diethyl ether by centrifuge. The yield is 0.18 g (68 %). The complex decomposes at 207°C.

(v) [Pd(dap)(asn)]Cl.HCl.0.5H_2

A concentrated aqueous solution of the sodium salt of L-asparagine [asnH (0.049 g, 0.32 mmol) and $NaHCO_3$ (0.027 g, 0.32 mmol)] was added dropwise to a stirred suspension of complex A (0.10 g, 0.32 mmol) in deionized water (20 ml). The reaction mixture was refluxed at 80°C for 16 hours and filtered. The filtrate was evaporated to dryness under reduced pressure. The reddish-brown precipitate formed was washed with ethanol, acetone and diethyl ether by centrifuge. The yield is 0.11 g (86%). The complex decomposes at 231°C.

(vi)- Na_2[Pd(dap)(thr)Cl_2].0.5H_2O

To a stirred suspension of complex A (0.10 g, 0.32 mmol) in deionized water (20 ml) was added dropwise a concentrated aqueous solution of the sodium salt of L-threonine [$thrH_2$ (0.039 g, 0.32 mmol)

and $NaHCO_3$ (0.027 g, 0.32 mmol)]. No immediate change was observed. The reaction mixture was refluxed at 85°C for 16 hours. It was then filtered and the solvents were evaporated completely under reduced pressure. The reddish-brown precipitate obtained was washed well with ethanol, acetone and diethyl ether by centrifuge. The yield is 0.098 g (65 %). The complex decomposes at 211°C.

Results and discussion

Physical Measurements

The elemental analyses for C, H, N, and S for the isolated complexes were run by the Jordan University of Science and Technology Laboratories, Jordan and Nanyang Technological University, Singapore.

Melting points were determined on an electrothermal melting point apparatus and were uncorrected. Conductivity measurements were carried out on a BC 3020 digital conductivity meter at 25°C using $1x10^{-3}$ M solutions in water. The infrared absorption spectra were recorded on an FT-IR Tensor 27 spectrometer, Bruker spectrum 2000 over the range 4000-300 cm^{-1}. Potassium bromide pellets were used.

Electronic absorption spectra were recorded on a double beam spectrometer "Shimadzu Corporation" UV-2401 (PC), using $1x10^{-5}$ M solutions in dimethyl sulfoxide at 25°C. The ^{1}H- and ^{13}C- NMR spectra were recorded on a 400 and 100 MHz Bruker Avanced III spectrometer. Deuterated dimethyl sulfoxide (DMSO-d_6) was used as a solvent with tetramethylsilane (Me_4Si) as an internal standard. The palladium(II) complexes were prepared by the reactions of *cis*-$[Pd(dap)Cl_2].H_2O$ with the sodium salts of the following amino acids: L-cysteine ($cysH_2$), L-tyrosine (tyrH), L-phenylalanine (pheH), L-aspartic acid ($aspH_2$), L-alanine (alaH), glycine (glyH), L-arginine (argH), L-serine ($serH_2$), L-glutamic acid ($gluH_2$), L-glutamine (glnH), L-asparagine (asnH) and L- threonine ($thrH_2$) using 1:1 molar ratios.

The isolated amino acid complexes are all colored, stable in air with relatively high decomposition points between 187-231° C as shown in (Table 1). They are insoluble to slightly soluble in water and common organic solvents while they are all soluble in DMSO and slightly soluble in DMF (Table 2). The results of the elemental analyses are reported in (Table 3). Conductivity measurements were carried out using 10^{-3} M solutions in H_2O. The molar conductance values obtained are shown in (Table 4) and they were assigned by comparison with those reported for similar systems (Girolami et al.,1999).

Table 1. Some physical properties of the isolated complexes.

Complex	Yield (%)	Color	Decomp. Point (oC)
$Na[Pd(dap)(arg)Cl_2]$. HCl	58	reddish brown	220
$Na[Pd(dap)(ser)Cl]$. $HCl.H_2O$	58	reddish brown	187
$Na[Pd(dap)(glu)Cl].2H_2O$	69	reddish brown	208
$Na_2[Pd_2(dap)(gln)_2Cl_4]$	68	reddish brown	207
$[Pd(dap)(asn)]Cl.HCl.\ 0.5H_2O$	86	reddish brown	231
$Na_2[Pd(dap)(thr)Cl_2].0.5H_2O$	65	reddish brown	211

Table 2. Solubility of the complexes.

Compound	ETOH	H_2O	Acetone	DMSO	DMF
$Na[Pd(dap)(arg)Cl_2]$. HCl	-	+	-	+	+
$Na[Pd(dap)(ser)Cl]$. $HCl.H_2O$	-	+	-	+	+
$Na[Pd(dap)(glu)Cl].2H_2O$	-	+	-	+	+
$Na_2[Pd_2(dap)(gln)_2Cl_4]$	-	+	-	+	±
$[Pd(dap)(asn)]$ $Cl.HCl.0.5H_2O$	-	+	-	+	±
$Na_2[Pd(dap)(thr)Cl_2].0.5H_2O$	-	+	-	+	+

(+) Soluble, (±) Slightly soluble, (-) Insoluble.

Table 3. Elemental analysis of the complexes.

Compound	Analysis	Calculated (found) %		
	C	H	N	S
$Na[Pd(dap)(arg)Cl_2]$. HCl	25.45 (24.32)	4.08 (4.17)	18.89 (18.62)	
$Na[Pd(dap)(ser)Cl]$. $HCl.H_2O$	22.27 (22.05)	3.50 (3.23)	12.98 (12.52)	
$Na[Pd(dap)(glu)Cl].2H_2O$	26.39 (26.47)	3.99 (3.78)	12.31 (12.30)	
$Na_2[Pd_2(dap)(gln)_2Cl_4]$	22.52 (23.46)	3.15 (2.99)	12.26 (12.93)	

[Pd(dap)(asn)]Cl.HCl. $0.5H_2O$	25.82 (23.93)	3.61 (3.58)	16.94 (16.60)	
Na_2[Pd(dap)(thr)Cl2].$0.5H_2O$	23.57 (23.35)	3.30 (3.70)	12.22 (12.53)	

Table 4. Conductivity measurements of the complexes.

Complex	Λ^a_m (omh^{-1} cm^2 mol^{-1})
Na[Pd(dap)(arg)Cl_2]. HCl	263
Na[Pd(dap)(ser)Cl]HCl.H_2O	179
Na[Pd(dap)(glu)Cl].$2H_2O$	148
Na_2[Pd_2(dap)$(gln)_2Cl_4$]	303
[Pd(dap)(asn)]Cl.HCl. $0.5H_2O$	135
Na_2[Pd(dap)(thr)Cl2].$0.5H_2O$	198

Λ^a_m stands for molar conductance of $1x10^{-3}$ M solutions in H_2O at 25°C.

IR Spectra

The infrared spectra of 2,6-diaminopyridine, *cis*-[Pd(dap)Cl_2].H_2O, amino acids and the complexes were measured in the range 4000-300 cm^{-1} using KBr pellets. They were assigned on the basis of earlier studies made on complexes of 2,6-diaminopyridine and amino acids and their derivatives [Mhaidat ;2004 , El-Qisari et al ;2007, El-Sherif;2011, Nagy et al;2003,Nakamoto ;2009, Akat·eva et al ;2004, Krylova et al ;2005, Krylova et al ;2006, Dokken et al ;2009, Krylova et al ; 2011, Sallam et al ; 2011].

The IR spectra of the reported coordinated amino acid anions in the Pd(II) and Pt(II) complexes show the ν(NH) mode in the area 3100-3200 cm^{-1} and the ν(COO^-) in region 1620-1690 cm^{-1}. This shift in both stretching vibrations was reported to confirm the bidentate coordination of the amino acid anion to the metal through $–NH_2$ and $–COO^-$ groups forming a 5-membered chelate ring, as shown below:

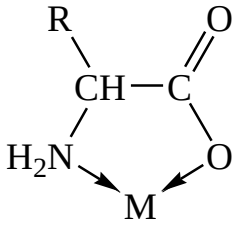


Figure 5. Coordinated amino acid anions with pd(ii) and pt(ii).

Recently, Bani Saeed has found that the tyrosinate and phenylalaninate behave as monodentates through the carboxylate groups in both [Pd(biq)$(tyr)_2$] and [Pd(biq)$(phe)_2$].$2.5H_2O$, respectively. The presence of very strong bands at 1643 and 1666 cm^{-1}, respectively, which may be assigned to ν(COO), confirmed the involvement of the carboxylate ($–COO^-$) groups in bonding. It has also been reported that even the simplest amino acid, such as glycine, can coordinate to metal ions as a monodentate through either nitrogen or oxygen or a bidentate through N- and O- atoms forming a five-membered ring or a four-membered ring through the two oxygen atoms of the carboxylate group . It can also bridge between two metal ions through N and O, or through the carboxylate oxygen atoms. For more complex amino acid, with more potential donor atoms, there are many more possibilities (Bani-saeed ; 2013).

In addition, our complexes prepared in this study have 2,6-diaminopyridine also as a ligand. This seems to complicate the spectral measurements. The ligand 2,6-diaminopyridine is known to coordinate to transition metal ions through either the $–NH_2$ groups or the pyridine nitrogen. Moreover, it was reported that coordination of the amino group significantly shifts ν(NH_2) and δ(NH_2) bands to lower frequencies while bonding to the pyridine nitrogen shifts ν(C=C) and ν(C=N) bands to higher frequencies (Mhaidat al., 2004, El-Qisari et al., 2007).

In the present work, we observe slight changes to lower or higher frequencies in addition to changes in the intensity and / or number of these bands upon complexation. These changes may also be explained by the decrease in H-bonding between the ligands upon coordination. Therefore, a detailed comparison between free and bonded dap cannot be made since both do not have the same degree of H-bonding. Moreover, 2,6-diaminopyridine and the amino acid anions used in this study have similar functional groups in common. Both have the $–NH_2$ groups and some have aromatic rings.

Therefore, the assignment of the peaks of our IR spectra was not that simple. The spectrum of each Pd(II)-dap-amino acid complex was compared with the reported data for mixed-ligand complexes mentioned above, starting complex A, free dap and free amino acids. The main points are given below:

(i) The IR spectrum of $Na[Pd(dap)(arg)Cl_2].HCl$ shows a very strong broad band centered at 3397 and another strong broad band at 3182 cm^{-1}, which may be assigned to v(N–H) of free $–NH_2$ of both free ligands, free –NH and =N–H of arginine as well as protonated $–NH_2$ or =NH groups. The presence of a very strong band at 1672 cm^{-1} indicates that the carboxylate group of argininate is bonded to Pd(II). The bands at 580, 503 and 426 cm^{-1}, which are absent in the free ligands, may be assigned to v(Pd–N) and v(Pd–O).

(ii) The IR spectrum of $Na[Pd(dap)(ser)Cl].HCl.H_2O$ shows two strong bands at 3435 and 3420 cm^{-1}, which may be assigned to v(O–H) of the hydroxyl group of serinate and of water of hydration. The presence of many bands in the v(N–H) region at 3314, 3268, 3179 and 3109 cm^{-1}, may indicate that dap is not symmetrically bonded, like the starting complex A. The presence of a very strong broad band at 1630 cm^{-1} suggests that the carboxylate group is bonded to Pd(II). The presence of many bands in the low-frequency region which are very close to these of the ligands made it difficult to assign the v(Pd–N) and v(Pd–O).

(iii) The IR spectrum of $Na[Pd(dap)(glu)Cl].2H_2O$ shows a strong very broad band with peaks at 3417, 3319, 3182 and 3090 cm^{-1} which may be assigned to v(O–H) of water of hydration and v(N–H) of all the $–NH_2$ groups present in the complex from both ligands. The presence of a very strong broad band at 1640 with a strong shoulder at 1633 cm^{-1} indicates that one $–COO^-$ group is bonded to Pd(II) and the other one is ionized and not protonated. The peaks at 558, 502, 452 and 415 cm^{-1}, which are absent in the free ligands, may be assigned to v(Pd–N) and v(Pd–O).

(iv) The IR spectrum of $Na_2[Pd_2(dap)(gln)_2Cl_4]$ shows a strong broad band with peaks at 3407, 3316, 3226 and 3182 cm^{-1} in the region of the N–H stretching frequency. These bands are shifted to lower frequencies and reduced in number as compared to both free dap and glutaninate anion. This observation suggests that some $–NH_2$ groups are coordinated to Pd(II) and the complex is somehow symmetrical. Later, NMR data will confirm this conclusion and indicate that dap is symmetrically bonded through the two $–NH_2$ groups. The very strong broad bands at 1648 and 1632 cm^{-1} confirm the coordination of the carboxylate group to Pd(II) and the presence of the carbonyl (C=O) of the amide group of the amino acid anion. The bands at 609 and 531cm^{-1}, which are absent in the free ligands, may be assigned to v(Pd–N) and v(Pd–O).

(v) The IR spectrum of $[Pd(dap)(asn)]Cl.HCl.0.5H_2O$ exhibits a very strong and very broad band with peaks at 3403, 3387, 3335 and 3180 cm^{-1} due to v(O–H) of water of hydration and v(N–H) of the many $–NH_2$ groups present in the complex. The band at 1669 cm^{-1} may be assigned to the carbonyl (C=O) stretching vibration while the band at 1639 cm^{-1} is assigned $v(COO^-)$ of a coordinated group. The bands at 534, 504, 489 and 459 cm^{-1} may be assigned to v(Pd–N) and v(Pd–O). The starting complex *cis*-$[Pd(dap)Cl_2].H_2O$ has two bands due to v(Pd–N) at 505 and 489 cm^{-1}. The presence of these two bands in the above complex confirms the coordination of Pd(II) to one of the $–NH_2$ groups and pyridine nitrogen like the starting complex A.

(vi) The IR spectrum of $Na_2[Pd(dap)(thr)Cl_2].0.5H_2O$ shows a strong very broad band with peaks at 3415, 3319 and 3186 cm^{-1} which may be assigned to v(O–H) of water of hydration and v(N–H) of $–NH_2$ groups. The reduction in the number of bands in this region may indicate that the complex is symmetrical. The presence of a strong split band centered at 1630 cm^{-1}, which may be assigned to $v(COO^-)$, with some contribution of $\delta(NH_2)$, confirms the coordination of the carboxylate group to Pd(II). The bands in the low-frequency region which appear at 531, 494 and 438 cm^{-1} are assigned to v(Pd–N) and v(Pd–O).

Electronic Spectra

The electronic absorption spectra for the isolated complexes were carried out using $1x10^{-5}$ M solutions in dimethyl sulfoxide (DMSO). The results obtained are given in (Table 5) . The bands were assigned by comparing them with those reported for complexes of 2,6-diaminopyridine as well as amino acids and their derivatives (Mhaidat et al.,2004, El-Qisari et al., 2007, Jin et al., 2000, El-Sherif et al., 2011, Akat̀eva et al., 2004, Nijasure et al.,1999).

The electronic absorption spectra of 2,6-diaminopyridine, the starting complex $[Pd(dap)Cl_2].H_2O$ and the new Pd(II) –dap-amino acid complexes were measured in DMSO using 10^{-5} M solutions. The results are presented in Table 7. The spectra were assigned by comparing them with the reported mixed-ligand complexes $[M(NN)(NO)]^{n+}$ where NN= bpy, phen and biq; NO= various amino acid anions (listed in the IR section), n= 0,1 (Jin et al., 2000; Bani Saeed et al., 2013; El-Sherif al,2011); in addition to the spectra of free and coordinated 2,6-diaminopyridine (Mhaidat, 2004; El-Qisari et al., 2007). The spectrum of free dap shows three strong ligands centered (LC) bands due to π-π^* or n-π^* transitions at 256, 322 and 326 nm. However, its complex $[Pd(dap)Cl_2].H_2O$ shows only two bands at 280 and 314 nm. The latter one is assigned to a metal-ligand-charge-transfer (MLCT) or ligand-metal-charge-transfer (LMCT) transitions. The first band is assigned to LC and MLCT transitions. Moreover, we found out that the square planer d^8 complexes of Pd(II) and Pt(II) show four charge transfer bands from the metal (HOMO,

σ*) to the ligand (LUMO, π*, σ*). For example, $PdCl_4^{2-}$ has the following MLCT bands at: 226, 245, 267 and 280 nm. The electronic spectra of our mixed dap-amino acid complexes. Table 5 shows LC bands that are characteristic of 2,6-diaminopyridine (dap), as well as LMCT from both ligands to Pd(II) and / or MLCT from Pd(II) to both donor sites. The first LC band which is in the range 253-257 nm appears in the spectra of Pd(II)-dap with cy, argininate, serinate . The second LC band which is mixed with MLCT that appears in the range 270-299 nm is present in the spectra of Pd(II)-dap with argininate, glutamate, asparaginate and threoninate. The third LC band which is also mixed with MLCT from Pd(II) to both ligands that appears in the range 326-337 nm is found in the spectra with serinate, asparaginate and threoninate. Almost all complexes are characterized by the presence of broad bands in their spectra either in the range 304-312 nm or 348-361 nm which are assigned to MLCT and / or LMCT from Pd(II) to both ligands and vice versa.

However, bands due to d-d transitions are not observed since they are forbidden and should be very weak. Thus, they may be hidden under the strong broad MLCT bands. The colors (yellow to reddish brown) of all our complexes (Table 2) are in the range expected for Pd(II) complexes [Cotton et al.,1999).

Table 5. Electronic spectra of dap and the complexes.

Complex	λ_{max} (nm)	ε x10^{-3} ($1mol^{-1}$ cm^{-1})	Assignment
dap*	256 322 326	2.68 2.80 2.90	LC[b]
$[Pd(dap)Cl_2].H_2O$*	280 314br	8.76 12.8	LC[b] / MLCT[b] MLCT / LMCT[b]
$Na[Pd(dap)(arg)Cl_2]$. HCl	257 281 311br	6.32 2.66 3.75	LC[b] LC[b] / MLCT[b] MLCT / LMCT[a,b]
$Na[Pd(dap)(ser)Cl]HCl.H_2O$	253 334 352br	26.0 5.49 5.82	LC[b] LC[b] / MLCT[a,b] MLCT / LMCT[a,b]
$Na[Pd(dap)(glu)Cl].2H_2O$	287 310br	10.72 13.2	LC[b] / MLCT[b] MLCT / LMCT[a,b]
$Na_2[Pd_2(dap)(gln)_2Cl_4]$	326 361br	4.69 6.03	LC[b] / LMCT[a,b] MLCT / LMCT[a]
$[Pd(dap)(asn)]Cl.HCl.\ 0.5H_2O$	257sh 286br 310br 337 349br	7.81 3.54 4.31 2.73 2.82	LC[b] LC[b] / MLCT[b] MLCT / LMCT[a,b] LC[b] /MLCT[a,b] MLCT / LMCT[a]
$Na_2[Pd(dap)(thr)Cl_2].\ 0.5H_2O$	290 304br 334 351br	6.78 6.90 5.60 5.88	LC[b] / MLCT[b] MLCT / LMCT[a,b] LC[b] / MLCT[a,b] MLCT / LMCT[a]

* Refs. [Mhaidat al;2004] and references therein.

In DMSO using 1x10^{-5} M solutions; br, broad; sh, shoulder, [a] to amino acid, [b] to dap

NMR Spectra

The reported ^1H- and ^{13}C-NMR spectra for amino acid complexes and the mixed-ligand complexes $[M(NN)(NO)]^{n+}$ where NN= bpy, phen, biq; NO= various amino acid anions , n= 0, 1 [Mhaidat al;2004, El-Qisari et al;2007, Jin et al ;2000, Bani Saeed al;2013, El-Sherif al;2011, Nijasure et al; 1999, Erickson et al;2003] . that the ^1H-NMR spectra were very difficult to analyze due to the presence of many $-NH_2$ groups from both ligands, dap and the amino acid anion, in addition to other functional groups such as hydroxyl, carboxylate, amide … etc, which complicate the proton signals. Therefore, in the present study only the ^{13}C-NMR spectral measurements will be examined. Fortunately, the ^{13}C-NMR spectra of both dap and $[Pd(dap)Cl_2].H_2O$ have been reported by our group [El-Qisari et al;2007]. Their results are shown in Table 6 with the new isolated complexes. Free dap shows only 3 signals at 157.59, 140.79 and 99.06 ppm due to C_2, C_6; C_4 and C_3, C_5.

This result indicates the symmetrical nature of dap. However, when dap is bonded to Pd(II), it shows 5 signals at 158.40, 157.47, 139.55, 97.10 and 96.70 due to C_2, C_6, C_4, C_3 and C_5, respectively. The

spectra of all our complexes were measured in DMSO-d_6. Therefore, its ^{13}C-NMR spectrum was carried out in D_2O. the ^{13}C-NMR spectra of our mixed dap-amino acid complexes of Pd(II) were assigned by comparing them with the reported data for the mixed ligand complexes (Mhaidat et al.,2004; El-Qisari et al., 2007; Jin et al.,2000; Bani Saeed et al., 2013; El-Sherif et al., 2011; Nijasure et al., 1999; Erickson et al;2003] as well as with free dap and also with the starting complex *cis*-[Pd(dap)Cl_2].H_2O (El-Qisari et al., 2007). The main points are given below:

The ^{1}H- and ^{13}C- NMR spectra of free amino acids in D_2O and the isolated complexes were measured in DMSO-d_6 using Me_4Si as a reference, Table 6. However, the ^{1}H-NMR spectra were very difficult to analyze due to the presence of many –NH_2 groups, which complicate the proton signals. Therefore, in the present study emphasis will be on ^{13}C-NMR spectra. The results are shown in Table 6. Band assignments were made by comparison with spectra reported for complexes of 2,6-diaminopyridine and amino acids and their derivatives (Mhaidat et al, 2004, El-Qisari et al.,2007; Jin et al., 2000; Bani Saeed et al., 2013; El-Sherif et al., 2011; Nijasure et al., 1999; Erickson et al., 2003).

Table 6. ^{13}C-NMR data (in DMSO-d_6, 100 MHz) for dap and the complexes.

Compound	NMR chemical shift; δ, ppm
2,6-diaminopyridine	157.59, 140.79, 99.06
[Pd(dap)Cl_2].H_2O	158.40, 157.47, 139.55, 97.10, 96.70
Na[Pd(dap)(arg)Cl_2]. HCl	182.46, 181.51, 171.97 158.40, 157.20, 157.11, 156.18, 140.60, 139.84, 96.30, 94.98, 57.49, 55.85, 53.15, 40.34, 40.17, 30.34, 30.11, 27.75, 24.80, 24.38
Na[Pd(dap)(ser)Cl]HCl.H_2O	180.16, 158.35, 156.45, 140.38, 139.79, 96.46, 95.03, 62.19, 62.06, 61.96, 60.40, 60.27, 60.16, 58.82, 55.97
Na[Pd(dap)(glu)Cl].2H_2O	181.97, 180.90, 174.20, 174.06, 158.47, 138.34, 95.10, 57.31, 55.88, 29.92, 29.72, 28.51
Na_2[Pd_2(dap)$(gln)_2Cl_4$]	182.12, 181.57, 176.99, 174.05, 173.92, 158.20, 156.79, 138.63, 95.11, 57.57, 56.20, 55.15, 31.12, 30.97, 29.20, 29.12, 24.72
[Pd(dap)(asn)]Cl.HCl. 0.5H_2O	181.36, 180.44, 172.35, 172.27, 172.03, 158.43, 155.63, 141.28, 94.93, 55.05, 53.74, 50.20, 37.91, 35.08
Na_2[Pd(dap)(thr)Cl_2]. 0.5H_2O	181.30, 180.62, 158.41, 155.85, 141.03, 94.96, 66.19, 63.25, 20.20

[(a)] In D_2O because it is insoluble in DMSO-d_6.

Conclusion

In the present study we managed to prepare some mixed-ligand complexes of Pd(II) with 2,6-diaminopyridine and amino acids. These reactions resulted in the formation of the following types of complexes:

(i) Mononuclear complexes namely: Na[Pd(dap)(arg)Cl_2].HCl, Na[Pd(dap)(ser)Cl]HCl.H_2O , Na[Pd(dap)(glu)Cl].2H_2O, [Pd(dap)(asn)]Cl.HCl. 0.5H_2O and Na_2[Pd(dap)(thr)Cl_2]. 0.5H_2O.

(ii) Binuclear complexes namely: Na_2[Pd_2(dap)$(gln)_2Cl_4$].

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