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ORIGINAL ARTICLE

Substitution reactions of *cis*-dichloro(2,2′-biquinoline)palladium(II) with amino acids

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Abstract The substitution reactions of the 2,2′-biquinoline (biq) complex *cis*-[Pd(biq)Cl_2] with different amino acids, namely, glycine (glyH), L-serine (serH), L-tyrosine (tyrH), L-phenylalanine (pheH) and L-alanine (alaH) have been investigated. The new complexes [Pd(biq)(gly)]Cl, [Pd(biq)(ser)]PF_6·0.5H_2O, [Pd(biq)(tyr)$_2$], [Pd(biq)(tyr)]PF_6·H_2O, [Pd(biq)(phe)$_2$]·2.5H_2O, [Pd(biq)(phe)]PF_6·H_2O and [Pd(biq)(ala)]Cl.1·5H_2O have been characterized by elemental analysis, conductivity measurements, IR, electronic absorption and ^{1}H and ^{13}C NMR spectra. Based on these data all amino acid anions are found to act as bidentates except tyrosinate and phenylalanilate which behave also as monodentates.

1. Introduction

The discovery of cisplatin and its use as one of the most effective drugs in the treatment of various types of cancer (Gao et al., 2009; Zhang et al., 2010; El-Sherif, 2011) have led to the development of second generation of platinum complexes formed by replacing the two ammonia molecules by other N-donor ligands (Gao et al., 2009; Zhang et al., 2010; El-Sherif, 2011; Kumar et al., 1982; Mital et al., 1991; Jin and Ranford, 2000; Casas et al., 2003). However, cisplatin and the second generation of platinum drugs have major drawbacks such as high toxicity, low water solubility and relative inactivity against gastrointestinal tumors (Gao et al., 2009; Zhang et al., 2010; El-Sherif, 2011). To overcome such drawbacks, research continues in this field in order to prepare new platinum and other transition metal complexes with less toxicity and higher activity (Gao et al., 2009; Zhang et al., 2010; El-Sherif, 2011; Kumar et al., 1982; Mital et al., 1991; Jin and Ranford, 2000; Casas et al., 2003). Among the other transition metal complexes are those of palladium(II) (Gao et al., 2009; Zhang et al., 2010; El-Sherif, 2011; Mital et al., 1991; Jin and Ranford, 2000; Casas et al., 2003). Interest in Pd(II) comes from the fact that both Pd(II) and Pt(II) are in the same group and complexes of both are expected to

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show somehow similar structural properties (El-Sherif, 2011; Cotton et al., 1999). Numerous Pd(II) complexes with other aliphatic amines and aromatic N-heterocyclic ligands such as ethylenediamine, pyridine, quinoline, 2,2′-bipyridine, 1,10-phenanthroline as well as with amino acids, amino acid esters, DNA units, peptides and related compounds have been synthesized and their anticancer activity was examined (Gao et al., 2009; Zhang et al., 2010; El-Sherif, 2011; Kumar et al., 1982; Mital et al., 1991; Jin and Ranford, 2000; Casas et al., 2003; Puthraya et al., 1986; El-Medani et al., 1998; Battistuzzi et al., 1998; Nijasure et al., 1999; Karkali and Bugari, 2000; Nagy and Sóvágó, 2001; Mohamed and Shoukry, 2001; Nagy et al., 2003; Krylova et al., 2008).

The synthesis, characterization, DNA binding and cytotoxic studies of some Pd(II) complexes of 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) (Mital et al., 1991; Puthraya et al., 1986) with amino acids having the general formula $[Pd(NN)(NO)]^{n+}$ where NN is bpy, phen; NO is an anion of an amino acid such as L-cysteine, L-aspartic acid, L-glutamic acid, L-methionine, L-histidine, L-arginine, L-phenylalanine, L-tyrosine, glycine, L-alanine, L-leucine, L-tryptophan, L-valine, L-proline or L-serine; $n = 0$ or 1 have been reported (Mital et al., 1991; Jin and Ranford, 2000; Casas et al., 2003; Cotton et al., 1999; Puthraya et al., 1986). These mixed-ligand complexes proved to be more biologically active than the parent compounds $[Pd(NN)Cl_2]$ (Mital et al., 1991; Puthraya et al., 1986).

Although many derivatives formulated as $[Pd(NN)(NO)]^{n+}$ (NN = bpy, phen; NO = amino acid anions) have been isolated and studied, no similar complexes have been reported with the structurally related but sterically hindered 2,2′-biquinoline ligand. Free biq is known to have a *trans* configuration while upon complexation it adopts a *cis* one (Fig. 1). Moreover, its complex *cis*-$[Pd(biq)Cl_2]$ has been reported to show high mutagenic activity (Kana'n et al., 2002).

The above state of affairs prompted us to study the substitution reactions of *cis*-$[Pd(biq)Cl_2]$ with various amino acids in order to prepare mixed-ligand complexes that might have better biological properties. We, herein, report the isolation of some Pd(II)-biq complexes containing various amino acids.

2. Experimental

2.1. Materials

2,2′-Biquinoline ($C_{18}H_{12}N_2$; biq), ammonium hexafluorophosphate (NH_4PF_6), L-phenylalanine ($C_9H_{11}O_2N$) and palladium(II) chloride ($PdCl_2$) were purchased from Fluka while other reagents were obtained from BDH. All solvents used were of AR grade. The *cis*-$[Pd(biq)Cl_2]$ starting complex (hereafter referred to as complex A) was prepared according to the literature method (Zaghal and Qaseer, 1991).

2.2. Physical measurements

Melting points were determined on an electrothermal digital melting point apparatus (uncorrected). Conductivity measurements were carried out for 1×10^{-3} M DMSO solutions on a BC 3020 digital conductivity meter at 25 °C. IR spectra were recorded on an FT-IR Tensor 27 spectrometer, Bruker spectrum 2000 over the range 4000–300 cm^{-1} using KBr and CsI pellets. ^1H and ^{13}C NMR spectra were recorded on a 400 and 100 MHz, respectively, Bruker Avance III spectrometer in *DMSO–d_6* using Me_4Si as internal standard. Electronic absorption spectra were recorded on a double beam spectrometer "Shimadzu Corporation" UV-2401 (PC) using 1.5×10^{-5} M solutions in DMSO. Elemental analyses for C, H and N were carried out by the Jordan University of Science and Technology Laboratories, Jordan.

2.3. Preparation of the complexes

The *cis*-dichloro(2,2′-biquinoline)palladium(II) (complex A) was reacted with the sodium salts of the following amino acids: glycine (glyH), L-serine (serH), L-tyrosine (tyrH), L-phenylalanine (pheH) and L-alanine (alaH), as described below. The metal: ligand molar ratio used is almost 1:1 with slight excess of the ligand. All complexes were filtered off, washed several times with deionized H_2O, Me_2CO and Et_2O by centrifugation and dried under vacuum at room temperature.

2.3.1. Synthesis of [Pd(biq)(gly)]Cl

To a stirred suspension of complex A (0.10 g, 0.23 mmol) in deionized water (20 ml) was added dropwise a concentrated aqueous solution of glyH (0.022 g, 0.29 mmol) and $NaHCO_3$ (0.024 g, 0.29 mmol). The reaction mixture was refluxed for 18 hours, and then it gave a yellow solid. Yield: 0.085 g, 77%; decomp. p. 170 °C.

2.3.2. Synthesis of [Pd(biq)(ser)]PF_6·0.5H_2O

A concentrated aqueous solution of serH (0.032 g, 0.30 mmol) and $NaHCO_3$ (0.025 g, 0.30 mmol) was added dropwise to a stirred suspension of complex A (0.10 g, 0.23 mmol) in deionized water (20 ml). The reaction mixture was refluxed for 12 hours until a clear yellow solution was obtained. The

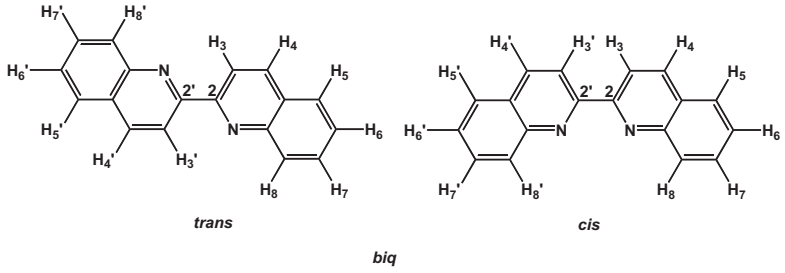

Figure 1 Structure of biq (*cis* and *trans* conformations) and atom numbering scheme.

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solution was allowed to cool to room temperature and filtered. A saturated aqueous solution of NH_4PF_6 was then added and a yellow solid was obtained. Yield: 0.070 g, 48%; decomp. p. 190 °C.

2.3.3. Synthesis of [Pd(biq)(tyr)$_2$]

To a stirred suspension of complex A (0.10 g, 0.23 mmol) in deionized water (20 ml) was added dropwise a concentrated aqueous solution of tyrH (0.052 g, 0.29 mmol) and $NaHCO_3$ (0.024 g, 0.29 mmol). The color of the reaction mixture changed from orange to yellow and a yellow precipitate appeared immediately. It was stirred for 10 hours at room temperature then a dark yellow solid was formed. Yield: 0.072 g, 43%; decomp. p. 174 °C.

2.3.4. Synthesis of [Pd(biq)(tyr)]$PF_6 \cdot H_2O$

To the filtrate of the reaction mixture obtained in part (2.3.3), a saturated aqueous solution of NH_4PF_6 was added and a deep yellow solid was formed immediately. Yield: 0.082 g, 51%; decomp. p. 210 °C.

2.3.5. Synthesis of [Pd(biq)(phe)$_2$]$\cdot 2.5H_2O$

To a stirred suspension of complex A (0.20 g, 0.46 mmol) in deionized water (20 ml) was added dropwise a concentrated aqueous solution of pheH (0.092 g, 0.56 mmol) and $NaHCO_3$ (0.047 g, 0.56 mmol). The clear reaction mixture was refluxed for 16 hours. Upon heating, the color of the mixture changed from orange to yellow and a yellow solid resulted. Yield: 0.15 g, 44%; yellow; decomp. p. 162 °C.

2.3.6. Synthesis of [Pd(biq)(phe)]$PF_6 \cdot H_2O$

To the filtrate of the reaction mixture obtained in part (2.3.5), a saturated aqueous solution of NH_4PF_6 was added and a yellow solid was formed immediately. Yield: 0.11 g, 35%; decomp. p. 178 °C.

2.3.7. Synthesis of [Pd(biq)(ala)]Cl.1$\cdot 5H_2O$

A concentrated aqueous solution of alaH (0.033 g, 0.37 mmol) and $NaHCO_3$ (0.031 g, 0.37 mmol) was added dropwise to a stirred suspension of complex A (0.10 g, 0.23 mmol) in deionized water (20 ml). The mixture was refluxed for 12 hours. Upon heating, the color of the mixture changed from orange to yellow and then a yellow solid was obtained. Yield: 0.065 g, 55%; decomp. p. 160 °C.

3. Results and discussion

The Pd(II) complexes were prepared by the reaction of *cis*-[Pd(biq)Cl_2] with the sodium salts of glycine, L-serine, L-tyrosine, L-phenylalanine and L-alanine amino acids using 1:1 molar ratios. The new isolated complexes along with some of their physical properties are listed in Table 1.

3.1. Conductivity

The molar conductance values for 10^{-3} M solutions for the complexes (Table 1) are in good agreement with those reported for similar complexes (Girolami et al., 1999). The complexes [Pd(biq)(tyr)$_2$] and [Pd(biq)(phe)$_2$]$\cdot 2.5H_2O$ behave as non-electrolytes while [Pd(biq)(gly)]Cl, [Pd(biq)(ser)]$PF_6 \cdot 0.5H_2O$, [Pd(biq)(tyr)]$PF_6 \cdot H_2O$, [Pd(biq)(phe)]$PF_6 \cdot H_2O$ and [Pd(biq)(ala)]Cl.1$\cdot 5H_2O$ act as 1:1 electrolytes.

3.2. IR spectra

Assignments of IR peaks for all complexes (Table 2) were made on the basis of the reported data for free amino acids and their complexes (El-Sherif, 2011; Mital et al., 1991; Jin and Ranford, 2000; Nijasure et al., 1999; Krylova et al., 2006, 2008; Appleton, 1997; Nakamoto, 1997; Kumar et al., 1984; Corradi et al., 1994; Calaf et al., 1995; Akat'eva et al., 2004), particularly those of $[M(NN)(NO)]^{n+}$ (where M = Pd(II), Pt(II); NN = bpy, phen; NO = anions of the following amino acids: glycine, L-alanine, -leucine, -serine, -cysteine, -methionine, -phenylalanine, -tyrosine, -tryptophan, -valine, -proline, -histidine, -aspartic acid, -glutamic acid, -arginine, -phenylglycine, -lysine, -asparagines, -glutamine and -methylcysteine; n = 0, 1) (Kumar et al., 1982, 1984; Mital et al., 1991; Jin and Ranford, 2000; Puthraya et al., 1986; Nijasure et al., 1999; Erickson et al., 2003).

The reported IR spectra of free amino acids which exist in the zwitterionic form, $H_3N^+CH(R)COO^-$ exhibit a broad band at about 3400 cm^{-1} which is assigned to the N—H stretching vibrations, ν(NH), in addition to another strong band at about 1600 cm^{-1} that is assigned to the —COO^- asymmetric stretching vibrations, ν(COO^-). However, the reported IR spectra of coordinated amino acid anions show the ν(NH) and ν(COO^-) in the range 3100–3200 cm^{-1} and 1620–1690 cm^{-1}, respectively. These shifts in both stretching vibrations were reported to confirm the bidentate coordination of the amino acid anion to

Table 1 Analytical and physical data for the new Pd(II) complexes.

Complex	Color	Decomp. point (°C)	Yield %[a]	Analysis: found (calc) (%)			Λ_m[b]
				C	H	N	
[Pd(biq)(gly)]Cl	Dark yellow	170	77	50.494 (50.867)	3.918 (3.416)	8.329 (8.899)	15.22
[Pd(biq)(ser)]$PF_6 \cdot 0.5H_2O$	Yellow	190	48	40.000 (40.600)	2.916 (2.937)	7.332 (6.936)	23.09
[Pd(biq)(tyr)$_2$]	Dark yellow	174	43	61.090 (59.889)	4.880 (4.570)	8.899 (8.310)	1.86
[Pd(biq)(tyr)]$PF_6 \cdot H_2O$	Dark yellow	210	51	45.711 (45.939)	3.746 (3.426)	6.176 (5.952)	21.80
[Pd(biq)(phe)$_2$]$\cdot 2.5H_2O$	Yellow	162	44	58.091 (58.737)	4.759 (4.991)	8.304 (7.806)	6.93
[Pd(biq)(phe)]$PF_6 \cdot H_2O$	Yellow	178	35	49.471 (49.451)	4.104 (3.914)	6.732 (6.607)	19.70
[Pd(biq)(ala)]Cl.1$\cdot 5H_2O$	Yellow	160	55	49.168 (49.140)	4.454 (4.125)	8.194 (8.187)	21.83

[a] Calculated based on the starting complex A.
[b] The molar conductance (in $ohm^{-1}\ cm^2\ mol^{-1}$) of 1×10^{-3} M solution at 25 °C in DMSO.

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Table 2 Important IR frequencies for the complexes (cm^{-1}).

Complex	ν(C═C), (C═N) & δ(NH_2)	ν(COO^-)	ν(N—H)	ν(Pd—N), (Pd—O)	ν(O—H)	ν(P—F)
[Pd(biq)(gly)]Cl	1595 s, 1514 m, 1420 m	1684 s	3080 m, 3048 m, 3000 m	458 m, 399 m, 336 m, 315 m	–	–
[Pd(biq)(ser)]PF_6·0.5H_2O	1585 m,1515 s,1436 m	1648 s	3252 m	418 w, 397 m, 353 m, 325 m	[a]3447 m, b	847 s, 560 s
[Pd(biq)(tyr)$_2$]	1596 m, 1510 s, 1498 s, 1446 m	1644 s	[b]3384–3065 s, b	472 m, 420 w, 347 w, 326 m	–	–
[Pd(biq)(tyr)]PF_6·H_2O	1591 m, 1516 s, 1419 m	1660 s, 1640 s	3105 m, b	408 m, 360 m, 342 m, 325 m	[c]3549 m, b, 3500 sh, 3314 m	846 s, 559 s
[Pd(biq)(phe)$_2$]·2.5H_2O	1565 m, 1548 m, 1511 m, 1502 m, 1463 m	1666 vs	[d]3453 s, b	412 m, 345 m, 319 m, 310 m	–	–
[Pd(biq)(phe)]PF_6·H_2O	1589 m, 1516 m, 1440 m	1660 s	3101 m, b, 3010 sh	490 m, 409 m, 373 m, 329 m	3309 m, b	839 s, 559 s
[Pd(biq)(ala)]Cl.1·5H_2O	1516 m	1658 s	3132 sh, 3095 m, 3019 m	407 m, 381 w, 345 m, 325 m	3526 m, b, 3429 m	–

vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; b, broad.
[a] For the hydroxyl group of the serinate and water of hydration.
[b] Hydrogen bonded NH_2 and ν(O—H) of phenolic group of tyrosinate.
[c] For phenolic group and water of hydration.
[d] For ν(N—H) and ν(O—H).

the metal through —NH_2 and —COO^- groups forming a 5-membered chelate ring, Fig. 2.

Similarly, the IR spectra of our complexes were studied along with their corresponding free amino acids and the starting complex A (Zaghal and Qaseer, 1991). The main points are given below:

(i) The IR spectra of all complexes show the characteristic bands of coordinated biq: the strong-medium bands in the range 1595–1419 cm^{-1} (Table 2) are assigned to ν(C═C) and ν(C═N) of course mixed with some ν(C═C) of the aromatic amino acid anions like tyrosinate and phenylalaninate and δ(NH_2); the bands in the range 1150–1000 cm^{-1} may be assigned to in-plane while those in the range 950–730 cm^{-1} to out-of-plane bending modes of the C—H bonds.

(ii) The IR spectra of the complexes [Pd(biq)(gly)]Cl, [Pd(biq)(ser)]PF_6·0.5H_2O, [Pd(biq)(tyr)]PF_6·H_2O, [Pd(biq)(phe)]PF_6·H_2O and [Pd(biq)(ala)]Cl.1·5H_2O exhibit bands in the region 3252–3000 cm^{-1}, assigned to ν(NH), and in the region 1684–1640 cm^{-1}, assigned to ν(COO^-) which confirm the bidentate coordination of the amino acid anion to Pd(II) through the —NH_2 and —COO^- groups forming a 5-membered chelate ring as shown in Fig. 2.

(iii) The IR spectra of [Pd(biq)(tyr)$_2$] and [Pd(biq)(phe)$_2$]·2.5H_2O show strong broad bands at 3384–3065 and 3453 cm^{-1}, respectively. These bands may be assigned to H-bonded —NH_2 groups in addition to ν(O—H) of the phenolic groups of bonded tyrosinate and of water of hydration in phenylanalinate complexes. Their presence in this region suggests that the —NH_2 groups are not bonded. However, the appearance of very strong bands at 1644 and 1666 cm^{-1} confirms the coordination of the carboxylate groups of tyrosinate and phenylalaninate, respectively, in bonding to Pd(II).

(iv) The low-frequency region (Table 2) of all the isolated complexes shows four bands in the range 490–310 cm^{-1} which may be assigned to the stretching vibrations of Pd—N (biq and —NH_2) and Pd—O of the —COO^- groups of the amino acid anions.

(v) The strong absorption bands appearing in the range 839–847 and 559–560 cm^{-1}, which are assigned to ν(P—F) vibrations, indicate the presence of ionic PF_6^- groups (Nakamoto, 1997) in the complexes [Pd(biq)(ser)]PF_6·0.5H_2O, [Pd(biq)(tyr)]PF_6·H_2O and [Pd(biq)(phe)]PF_6·H_2O.

(vi) The broad medium bands in the range 3549–3309 cm^{-1} (Table 2) in the spectra of the complexes [Pd(biq)(ser)]PF_6·0.5H_2O, [Pd(biq)(tyr)]PF_6·H_2O, [Pd(biq)(phe)$_2$]·2.5H_2O, [Pd(biq)(phe)]PF_6·H_2O, [Pd(biq)(ala)]Cl.1·5H_2O and [Pd(biq)(tyr)$_2$] may be assigned to ν(OH) of water of hydration and/or the hydroxyl group of serinate and the ν(OH) of the phenolic groups of tyrosinates.

3.3. Electronic spectra

The electronic spectra of the isolated complexes were assigned (Table 3) on the basis of earlier studies made on $[M(NN)(NO)]^{n+}$ complexes, where NN = bpy, phen;

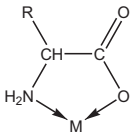


Figure 2 The coordination of NH_2 and COO^- groups forming a 5-membered chelate ring.

NO = various amino acid anions; $n^+ = 0$ or 1 (El-Sherif, 2011; Kumar et al., 1982, 1984; Mital et al., 1991; Jin and Ranford, 2000; Jain et al., 1987) in addition to the reported spectrum of the starting complex which shows 3 bands: a broad one at 371 nm, assigned to MLCT transition and two LC strong bands at 338 and 330 nm due to π–π^* transitions (Zaghal and Qaseer, 1991).

The dominant features of the spectra of our mixed biq amino acid complexes in this study, are the strong broad bands which are assigned to metal to ligand charge-transfer (MLCT) or ligand to metal charge-transfer (LMCT) transitions in addition to the ligand centered (LC) or π–π^* transitions which are characteristic of biquinoline.

The MLCT bands in the prepared complexes are in the range: 231–235, 240–243, 258–274 nm. In some complexes the latter band is mixed with the LC band of biq (Table 3) while other complexes have the LC band of biq at 273–274 nm. The two bands in the range 310–315 and 324–328 nm are assigned to MLCT and LMCT transitions from Pd(II) to the amino acid and vice versa, except for the serinate complex which has a strong broad band at 324 nm, assigned to MLCT and LMCT transitions from Pd(II) to the ligands and vice versa. The band appearing at 342 or 341 nm, in some complexes, may be assigned to LC (π–π^*) of biquinoline. The broad band in the range 369–382 nm may be assigned to MLCT transitions from Pd(II) to biq.

The bands due to d–d transitions were not observed since they are forbidden and expected to be very week. Thus they may be obscured by the LC, MLCT or LMCT bands. The latter two transitions as well as the d–d transitions are responsible for the characteristic yellowish colors of Pd(II) complexes (Cotton et al., 1999) as shown in Table 1.

3.4. ^1H and ^{13}C NMR Spectra

The ^1H and ^{13}C NMR spectral data for the isolated complexes are presented in Table 4. The peak assignments for the amino acids were made with the aid of earlier studies for amino acids such as L-valine, -isoleucine, -aspartic acid, -glutamic acid, -glutamine, -proline, -cystein, -glycine, -alanine, -tyrosine, -tryptophan, -histidine and -arginine and their mono-, bis- and mixed-ligand complexes (El-Sherif, 2011; Kumar et al., 1982, 1984; Mital et al., 1991; Jin and Ranford, 2000; Puthraya et al., 1986; Nijasure et al., 1999; Krylova et al., 2006; Yamauchi and Odani, 1981; Erickson et al., 2003).

It has been mentioned that the coordination of amino acid anions to metal ions particularly Pd(II) and Pt(II) produces shifts for amino acid protons and carbons. Moreover, the bonding of $-NH_2$ and $-COO^-$ groups of the amino acid anion mainly affects the α-protons, α-carbons and the carboxylate group carbon (COO^-), (El-Sherif, 2011; Kumar et al., 1982, 1984; Mital et al., 1991; Jin and Ranford, 2000; Puthraya et al., 1986; Nijasure et al., 1999; Krylova et al., 2006; Yamauchi and Odani, 1981; Erickson et al., 2003). The shifts found for the protons of coordinated amino acid complexes are very small, in most cases less than 0.4 ppm and in both directions either downfield or upfield (Kumar et al., 1982, 1984; Mital et al., 1991; Jin and Ranford, 2000; Casas et al., 2003; Puthraya et al., 1986; Calaf et al., 1995; Erickson et al., 2003). However, these small shifts may also be affected by concentrations, temperatures and solvents used for measurements. Furthermore, a detailed comparison between the coordinated and the free ligand cannot be made since the intermolecular forces including H-bonding are different in both cases in addition to the fact that the free amino acid is in the zwitterionic form and its NMR studies are carried out in deuterated water while the coordinated one is the anion of the amino acid and the reported spectral measurements are not all done in D_2O.

On the other hand, the reported downfield shifts for the carboxylate (COO^-) carbon and the α-carbon are 5–12 and 3–6 ppm, respectively. Such values can be clearly used to confirm the bonding mode of amino acids through the $-NH_2$ and $-COO^-$ groups (Nijasure et al., 1999; Krylova et al., 2006). Therefore, the signals due to the protons will be listed and emphasis will be on the ^{13}C NMR spectra.

The ^1H NMR spectrum of the starting complex A, shows the peaks at 8.80 (d, H8, 8′); 8.58 (d, H3, 3′); 8.18 (d, H4, 4′), 8.08 (d, H5, 5′); 7.86 (t, H7, 7′); (t, H6, 6′) ppm (Fig. 1). The ^{13}C NMR spectrum shows only 9 signals for 9 different carbon atoms at 155.26, 147.18, 137.23, 130.09, 129.33, 128.10, 128.00, 127.35, and 118.79 ppm. This result indicates that the complex is symmetrical and the two quinoline groups are equivalent.

Therefore, the ^1H and ^{13}C NMR spectra of our mixed biq-amino acid complexes of Pd(II) were assigned by comparing them with the reported data (El-Sherif, 2011; Kumar et al., 1982, 1984; Mital et al., 1991; Jin and Ranford, 2000; Puthraya et al., 1986; Nijasure et al., 1999; Krylova et al., 2006; Yamauchi and Odani, 1981; Erickson et al., 2003) as well as with the starting complex cis-[Pd(biq)Cl_2]. The main points are given below:

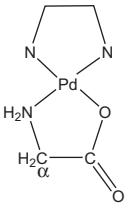
(i) The ^1H NMR spectrum of [Pd(biq)(gly)]Cl shows the presence of 10 different peaks (Table 4) corresponding to 16 protons. Some biq protons are equivalent on both sides, others are not, i.e the quinoline protons here are not symmetrical on both sides like the starting complex. However, the ^{13}C NMR spectrum shows only 9 different peaks (Table 4) due to 9 different carbon atoms of biq and thus suggesting that the two quinolines are equivalent. These peaks appear at 155.25, 147.18, 137.22, 130.09, 129.32, 128.10, 127.97, 127.34 and 118.78 ppm. They are almost the same as the starting complex. One may conclude that the σ-skeleton of biquinoline is symmetrical and is not affected by the unsymmetrical bonding of the glycinate anion like the protons. On the other hand, coordinated glycinate (**I**) shows a triplet peak at

Table 3 Electronic absorption spectra of the complexes.

Complex (1×10^{-5} M DMSO solutions)	λ (nm)	$\varepsilon \times 10^{-3}$ ($l\ mol^{-1}\ cm^{-1}$)	Assignment
[Pd(biq)(gly)]Cl	235	32.3	MLCT[a]
	243	34.4	MLCT[a]
	262 sh	92.0	MLCT[a,b] & LC[b]
	315	29.9	MLCT & LMCT[a]
	327 br	33.2	MLCT & LMCT[a]
	369	5.70	MLCT[b]
[Pd(biq)(ser)]$PF_6 \cdot 0.5H_2O$	234	22.7	MLCT[a]
	240	22.9	MLCT[a]
	258 sh	68.0	MLCT[a,b] & LC[b]
	324 br	14.6	MLCT & LMCT[a,b]
[Pd(biq)$(tyr)_2$]	231	34.7	MLCT[a]
	243	39.1	MLCT[a]
	262 sh	10.7	MLCT[a,b], LC[b]
	310	32.1	MLCT & LMCT[a]
	328	38.7	MLCT & LMCT[a]
	342	31.3	LC[b]
	382	2.90	MLCT[b]
[Pd(biq)(tyr)]$PF_6 \cdot H_2O$	272 sh	95.5	LC[b]
	374 br	34.0	MLCT[a,b]
[Pd(biq)$(phe)_2$]$\cdot 2.5H_2O$	265	124.5	MLCT[a,b]
	274 sh	122.0	LC[b]
	342	32.9	LC[b]
	381 br	41.2	MLCT[b]
[Pd(biq)(phe)]$PF_6 \cdot H_2O$	274 sh	173.9	LC[b]
	381 br	68.1	MLCT[a,b]
[Pd(biq)(ala)]Cl.$1 \cdot 5H_2O$	243	39.0	MLCT[a]
	264	72.2	MLCT[a]
	273 sh	65.1	LC[b]
	310	11.9	MLCT & LMCT[a]
	327	20.1	MLCT & LMCT[a]
	341	19.6	LC[b]
	378 br	20.8	MLCT[b]

br, broad; sh, shoulder.
[a] To amino acid.
[b] To biq.

3.65 ppm (free glycine at 3.52 ppm) for the two α-protons. The peaks at 5.1 and 4.7 ppm are assigned to the $-NH_2$ protons. The $-COO^-$ and α-carbon atoms show two signals at 181.40 and 46.67 ppm, respectively, while free glycine shows these signals at 172.38 and 41.44 ppm. The measurable downfield shifts confirm the bonding of both $-NH_2$ and $-COO^-$ groups to Pd(II).



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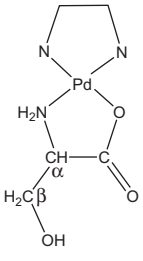

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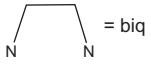

(ii) The ^{13}C NMR spectrum of [Pd(biq)(ser)]$PF_6 \cdot 0.5H_2O$ shows the following peaks for biq at 155.26, 147.77, 136.52, 129.76, 129.19, 129.09, 128.10, 128.02, and 120.60 ppm. The coordinated serinate ion (**II**) shows 3 signals at 179.08, 60.29 and 61.76 ppm due to the carboxylate-, α- and β-carbon atoms, respectively. Free serine shows the corresponding peaks at 172.31, 56.32 and 60.10 ppm. The ^1H NMR spectrum shows the following peaks for bonded serinate: a multiplet at 7.07 ppm which is assigned to the —OH proton; a doublet of a doublet at 5.69 ppm, assigned to the β-protons; a triplet and a doublet at 5.88 and 5.01 ppm which are assigned to the $-NH_2$ protons and a doublet at 4.84 ppm for the α-proton. Free serinate shows the α- and β-protons at 3.73 and 3.85 ppm. These downfield shifts indicate that the $-NH_2$ and $-COO^-$ groups are coordinated to Pd(II).

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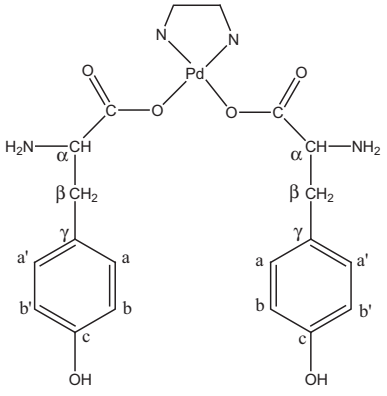
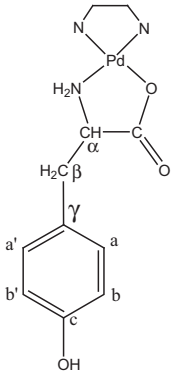
Table 4 ^{1}H and ^{13}C NMR data (in DMSO–d_6) for the complexes.

Complex	NMR band shift: δ, ppm	NMR band shift: δ, ppm
[Pd(biq)(gly)]Cl	8.86 (m, 4H), 8.57 (d, 1H), 8.24 (d, 1H), 8.18 (d, 1H), 8.07 (t, 2H), 7.86 (m, 2H), 7.68 (t, 1H), 5.1 (m, 1H), 4.7 (m, 1H), 3.65 (t, 2H)	181.40, 155.25, 147.18, 137.22, 130.09, 129.32, 128.10, 127.97, 127.34, 118.78, 46.67
[Pd(biq)(ser)]PF_6·0.5H_2O	9.16 (d, 2H), 8.97 (d, 2H), 8.68 (d, 2H), 8.34 (d, 2H), 8.11(dt,2 H), 7.97 (dt, 2H), 7.07 (m, 1H), 5.88 (t, 1H), 5.69 (dd, 2H), 5.01(d, 1H),4.84 (d, 1H)	179.08, 155.26, 147.77, 136.52, 129.76, 129.19, 129.09, 128.10, 128.02, 120.60, 61.76, 60.29
[Pd(biq)(tyr)$_2$]	9.34 (s, 2H), 8.87(d, 2H), 8.64 (d, 2H), 8.25 (d, 2H), 8.14 (d, 2H), 7.91 (dt, 2H), 7.75 (dt, 2H), 7.08 (d, 4H), 6.74 (d, 4H), 4.60 (t, 2H), 4.00 (t, 2H), 2.93 (dd, 4H), 2.73 (t, 2H)	180.14, 156.07, 155.26, 147.19, 137.24, 130.14, 130.10, 129.33, 128.10, 127.98, 127.35, 127.08, 118.79, 115.24, 59.19, 38.10
[Pd(biq)(tyr)]PF_6·H_2O	9.17 (s, 1H), 9.08 (d, 2H), 8.80 (d, 2H), 8.62 (d, 2H), 8.32 (d, 2H), 8.02 (t, 2H), 7.93 (d, 2H), 7.74 (d, 2 H), 6.36 (t, 1H), 6.15 (d, 2H), 3.60 (t, 1H), 2.98 (dd, 1H), 2.84 (dd, 1H), 2.73 (t, 1H)	180.61, 156.01,155.86,142.55,137.22, 130.65, 129.69, 129.31, 129.05, 126.02, 125.98, 120.53, 114.67, 114.58, 60.23, 36.13
[Pd(biq)(phe)$_2$]·2.5H_2O	8.84 (d, 2H), 8.61 (d, 2H), 8.23 (d, 2H), 8.11 (d, 2H), 7.89 (dt, 2H) 7.74 (dt, 2H), 7.67 (t,2H), 7.32 (d, 4H), 7.24 (d, 4H), 4.59 (d, 2H), 4.09 (d, 2H), 3.36 (d, 2H), 3.01 (dd, 2H), 2.77 (t, 2H)	181.00, 155.24, 147.17, 137.52, 137.16, 130.11, 129.71, 129.31, 128.45, 128.21, 127.98, 127.36, 126.58, 118.78, 58.24, 38.79
[Pd(biq)(phe)]PF_6·H_2O	9.02 (d,1H), 8.82 (d, 2H), 8.12 (d,2H), 7.97(t, 2H), 8.58 (d, 2H), 8.20 (t, 2H), 8.00 (dt, 1H), 7.89 (t, 2H), 7.69(t, 1H), 7.32 (d,1H), 7.23 (d,1H), 4.55 (d,1 H), 4.08 (d,1 H), 2.96(dd,1H), 2.77 (dd,1 H), 2.67 (t, 1H)	180.04, 157.42, 147.68, 137.34, 137.25, 130.11, 129.56, 129.20, 128.68, 128.46, 128.23, 127.98, 127.36, 126.52, 125.95, 118.78, 58.84, 39.25
[Pd(biq)(ala)]Cl.1·5H_2O	8.81 (d, 2H), 8.59 (d, 2H), 8.25 (d, 2H), 8.18 (d, 2H), 7.85 (dt, 2H), 7.68 (t, 2H), 5.56 (d, 1H), 5.20 (d, 1H), 3.65 (m, 1H), 1.18 (d, 3H)	181.96, 155.24, 147.17, 137.23, 130.09, 129.23, 128.09, 127.97, 127.34, 118.78, 53.63, 19. 43

d, doublet; m, multiplet; s, singlet; t, triplet; dd, doublet of doublet; dt, doublet of triplet.



III



IV

(iii) The ^{13}C NMR spectrum of [Pd(biq)(tyr)$_2$] shows 9 peaks, as expected for a symmetrical biq at 155.26, 147.19, 137.24, 130.10, 129.33, 128.10, 127.98, 127.35 and 118.79 ppm. One may notice that they are almost the same as the coordinated biq in the starting complex A. The coordinated tyrosinates (**III**) show the peaks at 156.07, 130.14, 127.08 and 115.24 ppm for the aromatic carbons (c; γ, a, a′; b, b′), indicating that the two tyrosinate groups are symmetrical. The peak at 180.14 ppm, assigned to the carboxylate carbon (COO^-), suggests that this group is involved in bonding to Pd(II). The presence of only two peaks for the two α- and two β-carbons at 59.19 and 38.10 ppm, respectively, further suggests that the complex is symmetrical. The ^{1}H NMR spectrum shows a single peak at 9.34 ppm which is assigned to the two equivalent phenolic protons. The two triplets at 4.60 and 4.00 ppm may be assigned to the protons of the two $-NH_2$ groups. The doublet of a doublet signal at 2.93 ppm is assigned to the four β-protons while the triplet at 2.73 ppm to the two α-protons.

(iv) The ^{13}C NMR spectrum of [Pd(biq)(tyr)]PF_6·H_2O exhibits 16 different peaks for the 9 different carbon atoms of the symmetrical biq and the 7 different carbons of coordinated tyrosinate (**IV**). Here, it is noteworthy that some of the biq peaks are shifted upfield or downfield, as compared to the starting complex, and cannot all be differentiated from the carbon atoms of the phenyl group of tyrosinate (Table 4). However, the peaks due to the carboxylate, α- and β-carbons of bonded tyrosinate are easy to distinguish. They appear at 180.61, 60.23 and 36.13 ppm, respectively. Its ^{1}H NMR spectrum shows the following peaks for coordinated tyrosinate: two triplets at 6.36 and 3.60 ppm, assigned to the NH_2 protons; two doublet of a doublet at 2.98 and 2.84 due to the two β-protons and a triplet at 2.73 ppm, assigned to the α-proton. The single peak at 9.17 ppm is assigned to the phenolic proton. These results confirm the chelation of the $-NH_2$ and $-COO^-$ groups to Pd(II).

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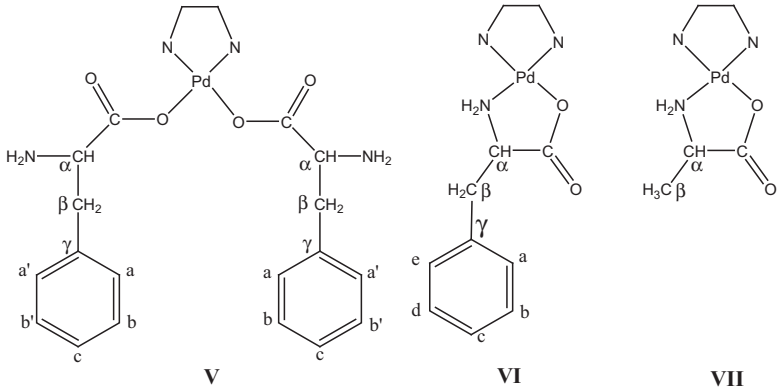

V VI VII

(v) The ^{13}C NMR spectrum of $[Pd(biq)(phe)_2]\cdot 2.5H_2O$ shows peaks for the symmetrical biq carbons at 155.24, 147.17, 137.52, 130.11, 129.31, 128.21, 127.98, 127.36 and 118.78 ppm. These bands are similar to those of the starting complex and the biq in the tyrosinate complex $[Pd(biq)(tyr)_2]$. The 4 peaks at 137.16, 129.71, 128.45 and 126.58 ppm which are assigned to the phenyl carbons (γ, a, a′, b, b′, c) of coordinated phenylalaninate (**V**) again suggest that the complex is symmetrical. The signal at 181.00 ppm, which is assigned to the two carboxylate carbons, suggests that the $-COO^-$ groups are coordinated to Pd(II) and are symmetrical. Free phenylalanine shows the corresponding signal at 173.89 ppm. Furthermore, the presence of only two peaks for the two α- and two β-carbons at 58.24 and 38.79 ppm, suggests that the complex is symmetrical. The ^1H NMR spectrum exhibits the following peaks for bonded phenylalaninate: two doublets at 4.59 and 4.09 ppm which may be assigned to the protons of the two $-NH_2$ groups; a doublet and a doublet of a doublet at 3.36 and 3.01 ppm that are assigned to the four β-protons and a triplet at 2.77 ppm which is assigned to the two α-protons. This pattern indicates that the $-NH_2$ is not involved in bonding, when compared to $[Pd(biq)(tyr)_2]$, $[Pd(biq)(tyr)]PF_6\cdot H_2O$ and the next complex $[Pd(biq)(phe)]PF_6\cdot H_2O$.

(vi) The ^{13}C NMR spectrum of $[Pd(biq)(phe)]PF_6\cdot H_2O$ shows 18 signals for 18 different carbon atoms. The symmetrical biq shows 9 peaks at 157.42, 147.68, 137.34, 130.11, 129.56, 128.23, 127.98, 127.36 and 118.78 ppm, with the carbon atoms close to the coordination site are the ones expected to undergo downfield shifts while those that are not affected are away from that site. The coordinated phenylalaninate (**VI**) shows 9 different signals, unlike the analogous tyrosinate complex $[Pd(biq)(tyr)]PF_6\cdot H_2O$. It shows peaks at 137.25, 129.20, 128.68, 128.46, 126.52 and 125.95 ppm that are assigned to the 6 different aromatic carbons (γ, a, b, c, d, and e). The peak at 180.04 ppm, which is assigned to the carboxylate carbon, confirms the involvement of the $-COO^-$ group in coordination to Pd(II). The downfield shifts of the α- and β-carbon signals (at 58.84 and 39.25, respectively), as compared to those of $[Pd(biq)(phe)_2]\cdot 2H_2O$, confirm the chelation of $-NH_2$ and $-COO^-$ groups to Pd(II). Free phenylalanine has the corresponding peaks at 55.99 and 36.31 ppm. The ^1H NMR spectrum of coordinated phenylalaninate exhibits two doublets 4.55 and 4.08 ppm due to the two $-NH_2$ protons; two doublets of a doublet at 2.96 and 2.77 ppm assigned to the two β-protons and a triplet at 2.67 ppm that is assigned to the α-proton. This part of the spectrum is different from that for $[Pd(biq)(phe)_2]$. Therefore, one may conclude that the $-NH_2$ group is bonded to Pd(II).

(vii) The ^{13}C NMR spectrum of $[Pd(biq)(ala)]Cl.1.5H_2O$ shows the following 9 peaks at 155.24, 147.17, 137.23, 130.09, 129.23, 128.09, 127.97, 127.34 and 118.78 ppm for the 9 different carbons of the symmetrical biq. The three peaks at 181.96, 53.63 and 19.43 ppm, which are assigned to the carboxylate, α- and β-carbons, respectively, confirm the chelation of the $-NH_2$ and $-COO^-$ groups to Pd (II) (**VII**). Free alanine shows the corresponding peaks at 175.73, 50.30 and 16.05 ppm, respectively. All peaks undergo downfield shifts indicating withdrawal of electrons from the amino acid anion, by coordination through $-NH_2$ and $-COO^-$ groups, to Pd(II). The ^1H NMR spectrum shows the following peaks for the coordinated alaninate: two doublets at 5.56 and 5.20 ppm that are assigned to the protons of the $-NH_2$ group; a multiplet at 3.65 ppm and a doublet at 1.18 that are assigned to α- and β-protons, respectively. Free alanine shows the peaks for the α- and β-protons at 3.75 and 4.8 ppm. These shifts suggest the bonding of alaninate through the $-NH_2$ and $-COO^-$ groups.

4. Conclusion

The reactions of amino acid anions with $[Pd(biq)Cl_2]$, using 1:1 molar ratios (with slight excess of the ligand), resulted in the formation of two types of complexes: (a) complexes having one amino acid anion, acting as a bidentate through the $-NH_2$ and $-COO^-$ groups, as in $[Pd(biq)(gly)]Cl$, $[Pd(biq)(ser)]PF_6\cdot 0.5H_2O$, $[Pd(biq)(tyr)]PF_6\cdot H_2O$, $[Pd(biq)(phe)]PF_6\cdot H_2O$ and $[Pd(biq)(ala)]Cl.1\cdot 5H_2O$; (b) complexes having two monodentate amino acid anions with the carboxylate $-O^-$ being the donor ion, as in $[Pd(biq)(tyr)_2]$ and $[Pd(biq)(phe)_2]\cdot 2.5H_2O$.

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