Synthesis, Experimental and Theoretical Characterization of Bidentate 5-Nitro-2-(Pyridin-2-Yl)-1H-Benzo[D] Imidazole Ligand and its Pd (II) Complex

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Abstract In this work, we report a combined experimental and theoretical study on the molecular structure and electronic and vibrational spectra of 5-nitro-2-(pyridin-2-yl)-1H-benzo[d] imidazole ligand, npbi, and its Pd(II) complex, which coordinating atoms of npbi is the imine and pyridine nitrogens. The nature of npbi and its complex were determined by IR and UV-Vis spectroscopy. The theoretical results obtained by performing DFT calculations, using the ADF 2009 package, compared with experimental results. The optimized geometric bond lengths and bond angles of npbi and its complex confirmed the complexation. The CHN data analysis confirmed the suggested structure of complex too.

Keywords Palladium, Benzimidazole, Pyridine, ADF

containing palladium has reported with promising chemotherapeutic potential and different mechanisms in comparison platinum drugs [5]. Synthesis and structures of palladium (II) complexes containing pyrazole and thiocyanate ligands [6], and their thermal decomposition reported in the literature [7]. Synthesis, application or DFT studies of some other complexes of palladium (II) containing various Schiff bases ligand show the importance of this kind of compounds in chemistry world [8-12].

In the present work, cis-dichloro (5-nitro-2-(pyridin-2-yl)-1H-benzimidazole palladium(II) complex was synthesized and the IR or UV spectroscopy techniques were used to validate its structure.

In addition, the molecular geometry and vibration spectra of npbi and its complex were calculated by applying density functional theory (DFT) computations and then compared with obtained experimental results.

1. Introduction

Palladium coordination compounds are very important materials. They are reviewed as anti-viral, anti-fungal, anti-microbial and anti-tumor agents on not too many years ago [1]. The acyclic tridentate quinoline-2-carboxaldehyde-2-pyridylhydrazon ligand has used for synthesizing of a luminescent palladium(II) complex, which exhibits DNA binding activities and induces apoptosis in human prostate cancer cells [2]. Synthesis, spectral, electrochemical, DFT studies and evaluation of biological activity of Pd(II) and Pt(II) complexes of N,N-donor benzimidazole ligand is reported, which showed poor activity against the investigated bacteria in comparison with the free ligand [3] or no specific antimicrobial activity [4]. The worthy advantage of this report is about introducing of the synthesized ligand as a determining reagent for Pd(II) in the presence of other noble metal ions. The antimicrobial and antitumor activity of some Pd(II) complexes containing quinolinylaminophosphonates is reported reportedis reported Novel metal complexes

2. Experimental and calculations

2.1. Synthesis of Npbi Ligand

The ligand was synthesized similar to reported procedures [13, 14]. Picolinic acid (1.2g) and 1,2-diamino 4-nitro benzene (1.07g) were added to 14g polyphosphoric acid, and stirred under N₂ at 160°C for 8h. The resulting viscous solution was poured into 250 ml H₂O, producing a tan solid which was collected by suction filtration. The residue was then suspended in 250 ml of aqueous 0.5 M Na₂CO₃, and filtered giving a pale yellow powder. Recrystallization from methanol /water caused as a fine yellow solid. (mp: 213°C, conductivity: 1.800 Ω⁻¹cm²mol⁻¹)

2.2. Synthesis of Pd(Npbi)Cl₂ Complex

One 1:1 ratio of PdCl₂ and npbi ligand calculated stoichiometry relation and then weighted. PdCl₂(0.1mmol) was dissolved in 10 ml of ethanol after stirring for 1h. The

resulting brown solution was added drop wise to npbi solution (0.1 mmol in 5 ml of ethanol). Then the mixture was stirred for 72h. The green solid filtered, washed with ethanol (3*5ml) and dried at vacuum. (mp: 145°C (decomposed), conductivity: $12.5 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$), CHN analysis data: Cal : C, 34.52 ; H, 1.93 ; N, 13.42; Found : C, 34.41 ; H, 1.86 ; N, 12.32

2.3. Physical Methods

IR spectra of the ligand and platinum complex were obtained as KBr pellets and were recorded with using a Shimadzu 8400 FT-IR spectrometer in the 4000-400 cm^{-1} region. The electronic spectra was recorded in DMF using a Shimadzu 2500 UV-Vis spectrometer. Conductivity measurements were done using Herisau Metrohm CH6101 conductometer.

2.4. Computational methods

The molecular structure of the 5-nitro-2-(pyridin-2-yl)-1H-benzo[d] imidazole ligand (npbi) was optimized by a DFT method at LDA, BLYP, OLYP levels and DZ, DZP, TZ2P basis sets, all with using the ADF package. This optimization was done for $[\text{Pd}(\text{npbi})\text{Cl}_2]$ complex at OLYP as a selected level and DZ, DZP, TZ2P basis sets. The vibrational frequencies of ligand and its Pd(II) complex were calculated at preferred OLYP level.

3. Results and Discussion

3.1. Geometry Optimization

Optimized structures of npbi ligand and its Pd(II) complex with labeling of the atoms are shown in Figs.1.

Figure 1. Structure of npbi ligand and OLYP optimized geometry of related Pd complex with their labeling.

There is a very well agreement between the theoretically calculated geometric parameters of npbi ligand and the x-ray diffraction data of related or similar structures such as 2-methylbenzimidazole and 2-picoline, available in the literature [15,16].

The experimental and optimized structural parameters of npbi ligand calculated at OLYP level with DZ, DZP, TZ2P basis sets are listed in Table 1.

According to our calculations, all the bond lengths and angles of npbi ligand are in good agreement with the experimental values of similar structures. For example, the $\text{N}_1\text{--C}_8$ and $\text{C}_{12}\text{--N}_{11}$ bond lengths, also the $\text{N}_1\text{--C}_2\text{--N}_3$ angle is 1.383, 1.332 and 112.7 respectively, both in calculation or X-ray data. These data are underlined in Table 1.

The geometric parameters of $[\text{Pd}(\text{npbi})\text{Cl}_2]$ complex are compared with x-ray diffraction data available for cis-dichloro-(2-pyridin-benzimidazole) palladium (II) complex [17]. As one can see, there is a very well agreement between these data. The optimized geometric parameters of Pd(II) complex calculated by OLYP with DZ, DZP, TZ2P basis sets are listed in Table 2.

Theoretical angle values of pd(II) complex have some deviation from square-planer geometry. For example the calculated angles $\text{N}_3\text{--Pd--Cl}_2$ and $\text{N}_{11}\text{--Pd--Cl}_1$ obtained 171.5° and 175.3° respectively instead of 180°.

3.2. Chemistry

The new npbi ligand and its Pd(II) complex were characterized by spectrochemical data (UV-Vis, FTIR), conductivity and microanalysis measurements.

3.2.1. Uv. Vis Spectroscopy / Electronic Spectra

A strong absorption band is observed at 280 nm for free npbi ligand spectrum could be assigned to the $n \rightarrow \pi^*$ intra ligand transitions [18,19]. After the formation of Pd(II) complex, this absorption is undergone a red shift, which leads to appearance of a more intense band than ligand for $n \rightarrow \pi^*$ transitions at 284.8 nm. The low energy of this transition could be due to coordination of nitrogen atoms of npbi ligand to the palladium center. As we will see later; the calculated shapes and orbital distribution confirm this kind of charge transferring.

Furthermore, in the electronic spectrum of Pd (II) complex, the observed absorption at 369.2 nm in the UV region could be assigned to metal to ligand charge transfer [20].

3.2.2. HOMO and LUMO Energy Levels

During the optimization at the mentioned level and basis sets, the energy levels for the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of $[\text{Pd}(\text{npbi})\text{Cl}_2]$ complex are calculated. The HOMO energy calculated in DZ, DZP and TZ2P basis set are -5.763, -5.591 and -5.117 respectively. The LUMO energy for the same trend is calculated as -4.840, -4.323 and -4.323.

Although these results are similar but choosing the DZ basis set is shown a little more negative level of the energy

both for the HOMO and LUMO. Furthermore, the differences between these two important levels, gap, which could be considered in electronic transitions, are 0.923, 1.268 and 1.371 respectively. It means that the gap is more when calculated using TZ2P basis set.

The energy of other orbitals in all cases are calculated too. For example, the MO diagram of energy for [Pd(npbi)Cl₂] complex, calculated at OLYP level and DZ basis set is shown in Figs.2.

Table 1. Selected geometry parameters of ^anpbi, ^bmb, ^cpic, ^dPd(n) and ^ePd(p)

	a mb	b pic	npbi (calculated)			dPd(p)	cPd(n)(calculated)		
fB.L.(A°)	X-ray	X-ray	DZ	DZP	TZ2P	X-ray	DZ	DZP	TZ2P
N1-C2	1.335		1.407	1.383	1.389	-	1.386	1.366	1.386
C2-N3	1.339		1.333	1.310	1.314	-	1.345	1.322	1.344
N3-C9	1.389		1.406	1.375	1.378	-	1.400	1.378	1.400
C9-C8	1.395		1.422	1.412	1.418	-	1.420	1.409	1.420
N1-C8	1.383		1.383	1.367	1.370	-	1.388	1.369	1.388
C9-C4	1.379	-	1.392	1.388	1.396	-	1.395	1.389	1.396
C4-C5	1.382	-	1.394	1.383	1.391	-	1.391	1.381	1.391
C5-C6	1.395	-	1.414	1.402	1.409	-	1.413	1.402	1.413
C6-C7	1.360	-	1.390	1.381	1.385	-	1.389	1.379	1.389
C7-C8	1.389	-	1.400	1.390	1.396	-	1.398	1.389	1.398
C10-C15	-	-	1.405	1.397	1.403	-	1.401	1.393	1.401
C15-C14	-	-	1.399	1.387	1.391	-	1.397	1.386	1.397
C14-C13	-	-	1.399	1.387	1.391	-	1.399	1.388	1.399
C13-C12	-	-	1.400	1.392	1.396	-	1.398	1.389	1.398
C12-N11	-	-	1.355	1.331	1.332	-	1.352	1.335	1.353
N11-C10	-	1.390	1.362	1.341	1.343	-	1.374	1.354	1.373
Pd-N3	-	1.376	-	-	-	2.025	2.186	2.198	2.187
Pd-N11	-	1.367	-	-	-	2.054	2.194	2.200	2.195
Pd-C11	-	1.379	-	-	-	2.2845	2.426	2.334	2.426
Pd-C12	-	1.332	-	-	-	2.2937	2.432	2.388	2.432
		1.337							
gB.A(°)		-							
N3-Pd-N11	-	-	-	-	-	80.22	76.7	75.9	76.6
N3-Pd-C11	-	-	-	-	-	96.58	98.6	99	98.6
N11-Pd-C12	-	-	-	-	-	93.75	94.9	94.9	94.9
N3-Pd-C12	-	-	-	-	-	173.50	171.5	170.9	171.5
N11-Pd-C11	-	-	-	-	-	176.36	175.3	174.9	175.3
C11-Pd-C12	-	-	-	-	-	89.52	89.9	90.2	89.9
N1-C2-N3	112.7	-	112.1	112.7	112.2	-	110.6	111.4	110.6
C2-N3-C9	106.3	-	104.7	104.8	105.2	-	106.8	106.3	106.8
N3-C9-C8	107.6	-	110.9	110.9	110.7	-	108.8	109.1	108.8
N1-C8-C9	107.2	-	104.6	104.4	104.3	-	105.6	105.3	105.6
C9-C4-C5	118.2	-	116.5	116.6	117.1	-	115.8	115.9	115.8
C4-C5-C6	121.9	121.7	123.2	123.4	122.9	-	123.7	123.9	123.7
C5-C6-C7	120.7	119.9	120.3	120.3	120.4	-	120.3	120.3	120.3
C6-C7-C8	117.6	118.9	117	116.8	117	-	116.8	116.5	116.8
C8-C9-C4	122.1	118.5	120.6	120	119.8	-	121	120.5	121
N11-C12-C13	-	-	123.3	118.2	124.2	-	121.5	122.3	121.6
C12-C13-C14	-	-	118.6	118.2	117.9	-	119.4	119.1	119.4
C13-C14-C15	-	-	119	118.8	118.8	-	119.2	118.9	119.2
C14-C15-C10	-	-	118.8	118.7	119	-	119	119	119
C15-C10-N11	123.0	-	122.7	123.0	122.3	-	121.3	121.8	121.3

^a npbi: 5-nitro-2-(pyridin-2-yl)-1H-benzo[d]imidazole; ^b mb: 2-methylbenzimidazole; ^c pic: 2-picoline; ^d Pd(n): cis-[Pd(npbi)Cl₂]; ^e Pd(p): cis-[Pd(npbi)Cl₂]; fB.L.: bond Length; gB.A.: Bond angles.

Figure 2. MO diagram of energy for [Pd(npbi)Cl₂] complex, calculated at OLYP level and DZ basis set.

Considering the initial orbital contributions in final molecular orbitales are interesting. Some selected orbitales with related

Table 2. Selective orbitales with QCC,E(e.v), and elements percent for [Pd(npbi)Cl₂] complex, calculated at OLYP level and DZ basis set contributions and occupations, QCC, are shown in Table 2.

orbital	QCC	E(e.v)	C%	N%	O%	Cl%	Pd%
54A	2	-6.010	-	-	-	72.51Pz	19.92dyz +1.87 Pz
55A	2	-5.914	-	-	-	58.65Py +26.22Px	9.87dx ² -y ²
56A	2	-5.763	-	-	-	77.66 Pz	20.13dxy
57A	0	-4.840	37.44 Pz	27.82 Pz	24.53 Pz	-	1.65dyz
58A	0	-4.517	-	5.76 Py +4.19S +1.89 Px	-	25.31 Px +16.2 Py	39.51 dxy +2.50 dx ² -y ²
59A	0	-4.512	52.57 Pz	30.12 Pz	6.4 Pz	-	1.38 dyz +1.15 dxy

As one can see, the HOMO and LUMO are 56A and 57A orbital respectively. The P_z orbital of chloride atoms has the most contribution, 77.66%, for HOMO while the next atomic orbital is P_z of palladium, 20.13%. This fact is shown in Fig. 3., obtained from the calculation. Basis to our calculations, none of the chloride atoms orbital have a contribution in LUMO or 57A. Instead, P_z of carbon, nitrogen, oxygen has the most contribution, 37.44%, 27.82%, and 24.53% respectively in LUMO or 57A. The d_{xz} of palladium has just 1.65% contribution here.

Figure 3. HOMO and LUMO orbitales of $[Pd(npbi)Cl_2]$ complex, calculated at OLYP level and DZ basis set.

3.2.3. Vibrational Spectroscopy

The npbi ligand and its Pd(II) complex are characterized with FTIR spectroscopy. Furthermore, their harmonic vibrational frequencies computed at the OLYP method and various mentioned basis sets. The selected calculated frequencies and experimental values are listed in Table 3.

When the IR spectra of the free npbi ligand and its Pd(II)

complex are compared, some interesting facts could be obtained. There is a broad band in the region 3070.5 cm^{-1} in the IR spectrum of ligand that is shifted to 3093.6 cm^{-1} when coordination occurred. This fact could be due to the intermolecular tautomerism of ligand in imidazole N-H bond. The related N-H stretching in the Pd(II) complex at 3093.6 cm^{-1} , is sharper than the ligand due to the breaking of tautomerism, indicating the imidazole N-H is not involved in the coordination [21,22].

The band in the region 1610 cm^{-1} of the free ligand assigned to C=N stretching of imidazole. This stretching is shifted to just a little more frequency, 1612.4 cm^{-1} , after complexation [23,24]. This fact is confirmed the breaking of tautomerism again.

The difference between the C=N stretching of pyridine in free ligand, 1596.9 cm^{-1} , and complex, 1490 cm^{-1} , is suggested the interaction between the related nitrogen and palladium center. Our calculation is confirmed this advantage and the 1588 cm^{-1} band is shifted to 1546 cm^{-1} . There are two bands in the far-IR region of the calculated spectrum of Pd(II) complex, 229 cm^{-1} and 238 cm^{-1} , which we assigned theoretically to symmetrical an asymmetrical stretching of Pd-Cl bond respectively. The Pd-N_{py} stretching is obtained at 418 cm^{-1} based on our calculation. This frequency is reported at 495 cm^{-1} [25]. The other experimental and calculated frequencies for both free ligand and its palladium complex are collected in Table 3.

Table 3. Selected experimental and calculated IR vibrational frequencies (cm^{-1}) of the npbi ligand and $[Pd(npbi)Cl_2]$ complex

Experimental frequencies		Calculated frequencies		Vibrational assignment
Ligand	Pd(II) Complex	Ligand	Pd(II) Complex	
3070.5	3093.6	3567	3585	$\nu(\text{N-H})_{\text{Imi}}$
2951.6	2923.9	3210	3209	$\nu_{\text{S}}(\text{C-H})_{\text{BZ}}$
2854.5	2854.5	3204	3203	$\nu_{\text{as}}(\text{C-H})_{\text{BZ}}$
-	-	1605	1609	$\nu(\text{C=C})_{\text{BZ}}$
1610	1612.4	1514	1602	$\nu(\text{C=N})_{\text{Imi}}$
1596.9	1490	1588	1546	$\nu(\text{C=N})_{\text{PY}}$
-	-	1578	1572	$\nu(\text{C-C})_{\text{PY}}$
1512.1	1519.8	1577	1609	$\nu_{\text{as}}(\text{NO}_2)$
1442.7	1450.4	1479	1425	$\nu(\text{C=C})_{\text{BZ}}$
-	-	1464	-	$\nu(\text{C-C, C-H})_{\text{PY}}$
-	-	1418	1458	$\delta_{\text{twi}}(\text{C-H})_{\text{PY}}$
-	-	1416	1410	$\delta_{\text{twi}}(\text{N-H})$
1334.6	1334.6	1332	1327	$\nu(\text{C-NO}_2)$
-	-	1321	1425	$\nu(\text{C-C})_{\text{BZ}}$
-	-	-	1060	$\nu(\text{Pd-N}_{\text{Imi}})$
1056.9	1072.3	1056	-	$\delta_{\text{roc}}(\text{C-C})_{\text{BZ}}$
-	-	1049	1052	$\delta_{\text{roc}}(\text{C-C})_{\text{PY}}$
-	987.5	876	791	$\delta_{\text{ip}}(\text{C-H})_{\text{BZ}}$
-	894.9	871	779	$\delta_{\text{ip}}(\text{C-H})_{\text{PY}}$
-	825.5	844	829	δ_{BZ}
740.6	786.9	793	764	$\delta_{\text{OP}}(\text{C-H})_{\text{BZ}}$
-	740.5	727	718	$\delta_{\text{OP}}(\text{C-H})_{\text{PY}}$
624.9	524.6	-	-	δ_{PY}
-	-	557	510	$\delta_{\text{roc}}(\text{rig})_{\text{BZ}}$
-	432	476	492	$\delta_{\text{ip}}(\text{N-H})$
-	-	-	418	$\nu(\text{Pd-N}_{\text{PY}})$
-	-	-	229	$\nu_{\text{S}}(\text{Pd-Cl})$
-	-	-	238	$\nu_{\text{as}}(\text{Pd-Cl})$

Vibrational modes: ν , stretching; δ , bending; op, out-of-plane; ip, in-plane; roc, rocking; twi, twisting; s, symmetric; as, anti-symmetric.

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