

Scientific paper

Experimental and DFT Study on the Compounds [PdCl₂L₂] (L = 4-methylpyrazole, 4-iodopyrazole)

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Abstract

Theoretical molecular structures of the complexes [PdCl₂(HmPz)₂] (**1**) and [PdCl₂(HIPz)₂] (**2**) (HmPz = 4-methylpyrazole; HIPz = 4-iodopyrazole) were studied using B3LYP/DFT method. The new complex **2** and the complex **1** were synthesized and characterized by elemental analysis and IR spectroscopy. The calculated bond distances and angles showed that both compounds exhibited a slightly distorted square planar coordination environment around the palladium center. The theoretical IR spectra of C_s symmetry (electronic state 1A') of the complexes agree well with the experimental data.

Keywords: DFT calculation · Infrared Spectroscopy · Palladium(II) complexes · Pyrazoles

1. Introduction

N-unsubstituted pyrazolyl-type ligands have been widely employed in coordination and metallosupramolecular chemistry since they possess two chemically distinct nitrogen atoms, one pyrrolic and one pyridinic N atoms, which are very useful for coordination and hydrogen bonding interactions, respectively.^{1,2} Under the crystal engineering point of view, ligands of this type are of interest because their mononuclear metal-based derivatives can be used as molecular building blocks for the rational design of new hydrogen bonded metallosupramolecular species.³

Furthermore, palladium complexes attract attention due to the biological proprieties.^{4–7} A great variety of palladium complexes already exhibit significant cytotoxicity, in most cases surpasses the activity of platinum analogs.⁸ The palladium(II) compounds containing pyrazole as ligands have been studied by Keter and it has been confirmed *in vitro* that these compounds cause apoptosis of cancer cells of human and ovarian fibroma of hamster.⁹ In addition, our previous studies have been showed the capacity of palladium complexes to bind to DNA. These

compounds affect the DNA structure and cause a low electrophoretic mobility.¹⁰

Previous investigations in our laboratory have been devoted to the study of the molecular self-assembly *via* hydrogen bonds of pyrazolyl metal complexes of general formulae [MX₂(HPz)₄] (M = Co(II), Ni(II); X = N₃, SCN; HPz = pyrazole),¹¹ [PdX₂(HdmPz)₂] (X = N₃, SCN; HdmPz = 3,5-dimethylpyrazole),¹² and [Cd(μ-X)₂(HPz)₂]_n (X = Cl, SCN).¹³ Particularly, we are interested in acquiring more information about the building blocks [PdCl₂L₂] (L = 4-substituted pyrazoles) since the reaction of these compounds with azide ion gives rise to unusual coordination polymers instead of hydrogen-bonded supramolecular arrays.^{14,15}

As a part of our ongoing studies involving DFT calculations for metal-based compounds,¹⁶ we describe herein the synthesis and spectroscopic characterization of the two molecular building blocks dichlorobis(4-methylpyrazole)palladium(II) (**1**) and dichlorobis(4-iodopyrazole)palladium(II) (**2**) together with the results of DFT calculations *via* B3LYP method. The geometry of the complexes **1** and **2** were optimized and their theoretical IR spectra were discussed based on the experimental data.

2. Experimental

2. 1. Materials and Methods

The reagents were employed without further purification and the solvents were dried by usual procedures. Elemental analysis was performed on an analyzer CE Instrument model EA 1110-CHNS-O. The IR data were recorded on a Nicolet FT-400 spectrophotometer in the range from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} in KBr pellets.

The synthesis of dichloro(4-methylpyrazole)palladium(II) (**1**) was realized as described in the literature.¹⁷ Synthesis of dichloro(4-iodopyrazole)palladium(II) (**2**): to a deep orange solution of $[\text{PdCl}_2(\text{MeCN})_2]$ (50 mg, 0.19 mmol) in 10 mL of a MeOH, 4-iodopyrazole (75 mg, 0.38 mmol) in 1 mL of MeOH was added dropwise. The mixture was stirred at room temperature for 1 h. The light yellow suspension was filtered off and the yellow solid obtained was washed with methanol and dried under vacuum. (Yield 82%) Anal. Calcd. for $\text{C}_6\text{N}_4\text{H}_6\text{Cl}_2\text{I}_2\text{Pd}$ (%): C, 12.75; N, 9.91; H, 1.07. Found: C, 12.39; N, 9.43; H, 1.50.

2. 2. Computational Strategy

In this work, the employed quantum chemical approach to determining the molecular structures was Becke three-parameter hybrid method¹⁸ using the Lee-Yang-Par (LYP) correlation functional¹⁹ and the basis sets used for

calculations were: [4s] for H (^2S),¹⁹ [5s4p] for C (^3P) and N (^4S),²⁰ [11s7p] for Cl (^2P),²¹ [16s9p5d] for I (^2P),²² and [12s8p5d] for Pd (^1S).²⁰ In order to better describe the properties of **1** and **2** in the implementation of the calculations, it was necessary to include polarization functions for all atoms of the compounds. The strategy to choice of the polarization functions was previously described.²⁰ The polarization functions are: $\alpha_p = 0.33353749$ for H (^2S), $\alpha_d = 0.72760279$ and $\alpha_d = 0.35416230$ for C (^3P) and N (^4S), respectively, and $\alpha_f = 0.14057699$ for Pd (^1S) atoms.²⁰ For Cl atom (^2P), the polarization function to the basis set previously reported¹⁹ is $\alpha_d = 0.47236655$. The polarization function for I atom (^2P) reported in this work is $\alpha_f = 0.51068618$.²² For the complexes **1** and **2** a constraint of C_s symmetry (electronic state $^1\text{A}'$) was added to the geometry optimization as condition.

The performed molecular calculations in this work were done using the Gaussian 03 routine.²³ The computational strategy used in this work has already been used successfully in previous studies on coordination compound and organic molecules.^{16,20,21}

3. Results and Discussion

Compounds of general formulae $[\text{PdX}_2\text{L}_2]$ (X = halides and pseudohalides; L = pyrazolyl type ligands) have

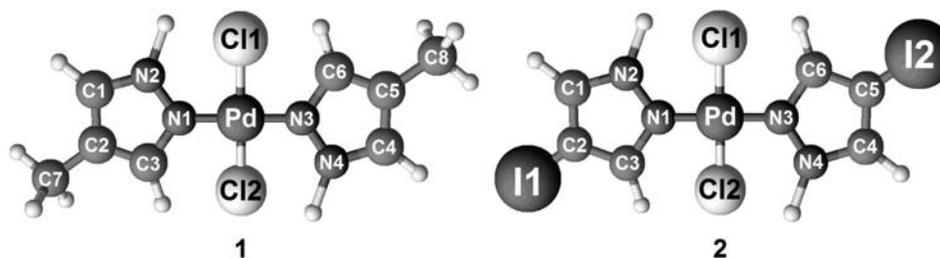


Figure 1. Computed structure of $[\text{PdCl}_2(\text{HmPz})_2]$ (**1**) and $[\text{PdCl}_2(\text{HIPz})_2]$ (**2**).

Table 1. Selected calculated bond lengths (Å), bond and torsion angles ($^\circ$) for $[\text{PdCl}_2(\text{HmPz})_2]$ (**1**), $[\text{PdCl}_2(\text{HIPz})_2]$ (**2**) and they analogue $\text{trans-}[\text{PdCl}_2(\text{Hpz})_2]$.²⁵

1		Bond lengths (Å)		2		<i>trans-}[\text{PdCl}_2(\text{Hpz})_2]²⁵</i>	
Pd-N1	2.08	Pd-N1	2.07	Pd-N	2.028(6)		
Pd-N3	2.08	Pd-N3	2.07	-	-		
Pd-Cl1	2.31	Pd-Cl1	2.30	Pd-Cl	2.3079(6)		
Pd-Cl2	2.31	Pd-Cl2	2.30	-	-		
1		Bond angles ($^\circ$)		2		<i>trans-}[\text{PdCl}_2(\text{Hpz})_2]²⁵</i>	
Cl1-Pd-Cl2	179.97	Cl1-Pd-Cl2	180.00	Cl1-Pd-Cl2	180		
Cl1-Pd-N1	90.51	Cl1-Pd-N1	90.51	Cl1-Pd-N1	90.08		
Cl1-Pd-N3	89.48	Cl1-Pd-N3	89.49	Cl1-Pd-N3	89.92		
Cl2-Pd-N3	90.49	Cl2-Pd-N3	90.51	Cl2-Pd-N3	90.08		
Cl2-Pd-N1	89.52	Cl2-Pd-N1	89.49	Cl2-Pd-N1	89.92		
N1-Pd-N3	179.99	N1-Pd-N3	180.00	N1-Pd-N3	180		

attracted considerable interest since they are able to self-assembly in interesting hydrogen-bonded supramolecular species during the crystallization. Since single crystals suitable for crystallographic studies of **1** and **2** could not be grown, we undertook a computed geometry optimization using the optimized algorithm of Berny.²⁴ The calculated molecular structures of **1** and **2** are illustrated in Figure 1.

According to our calculations, in the calculated molecular structures of **1** and **2**, the palladium atom lies in a square planar coordination environment made by two chloro ligand and two nitrogen atoms from the pyrazolyl ligand (N1 and N3), in a trans relationship. The four donor atoms in **1** and **2** are coplanar. A selection of calculated bond lengths and angles is shown in Table 1.

The calculated structures for **1** and **2** show a satisfactory agreement with the available crystal structure data of similar compounds of the type $[\text{PdCl}_2\text{L}_2]$ (L = pyrazolyl ligands), mainly in terms of bond angles. The calcu-

lated Pd-N bond lengths in **1** and **2** are ca. 0.05 Å longer than those found for analogous compounds.^{12,26}

To achieve a more accurate assignment of the vibrational spectra obtained for the palladium(II) compounds **1** and **2**, we have initially undertaken the study of the experimental and computed vibrational spectra FT-IR of the ligands 4-methylpyrazole (HmPz) and 4-iodopyrazole (HIPz) (Figures 2–3). Despite the fact that experimental IR and Raman spectra of HmPz and HIPz have been tentatively assigned by Vos and Groeneveld,^{27,28} there are no reports for these ligands dealing with the IR spectra calculated from DFT study. Theoretical infrared spectra of HmPz and HIPz were calculated using a harmonic field²⁹ based on C_1 symmetry (electronic state 1A). Table 2 and 3 list some selected experimental FT-IR and computed IR frequencies for 4-methylpyrazole and 4-iodopyrazole, respectively, together with relative intensities, assignments and description of vibrational modes. The theoretical frequencies values are not scaled.

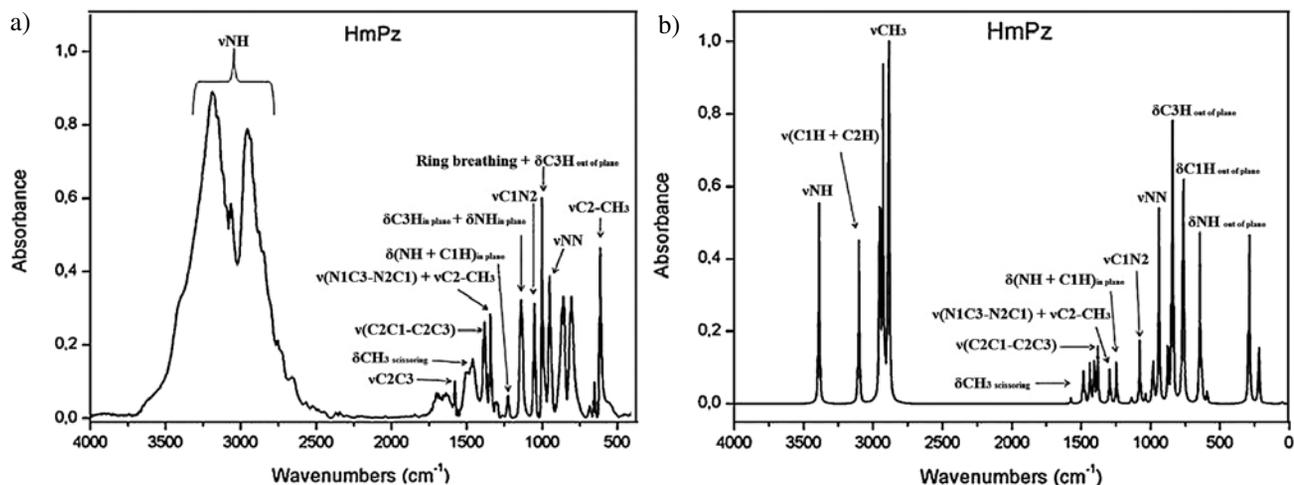


Figure 2. Experimental (a) and theoretical (b) IR spectra of the HmPz.

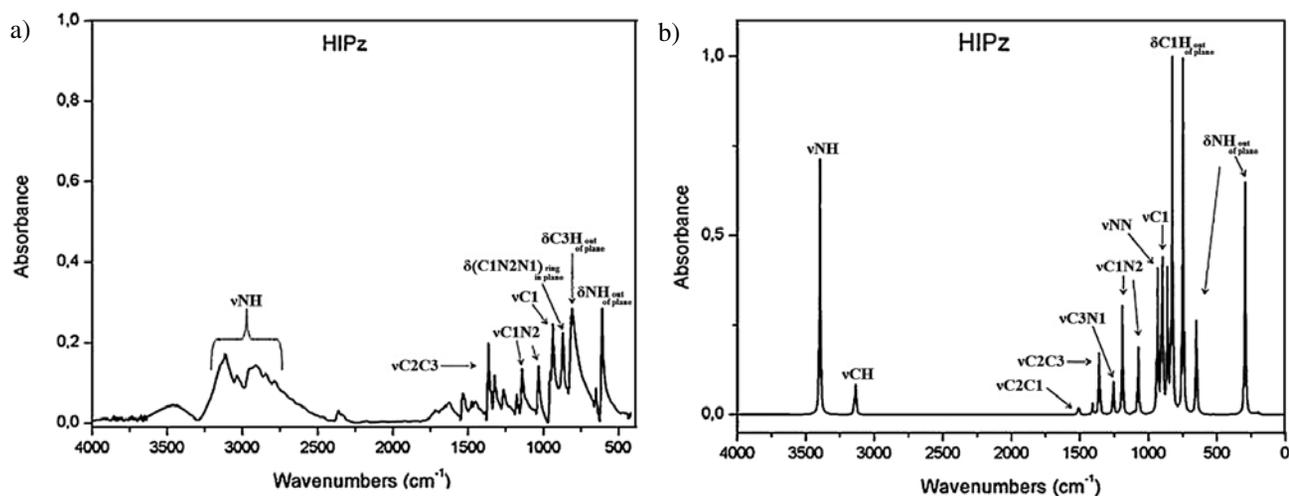
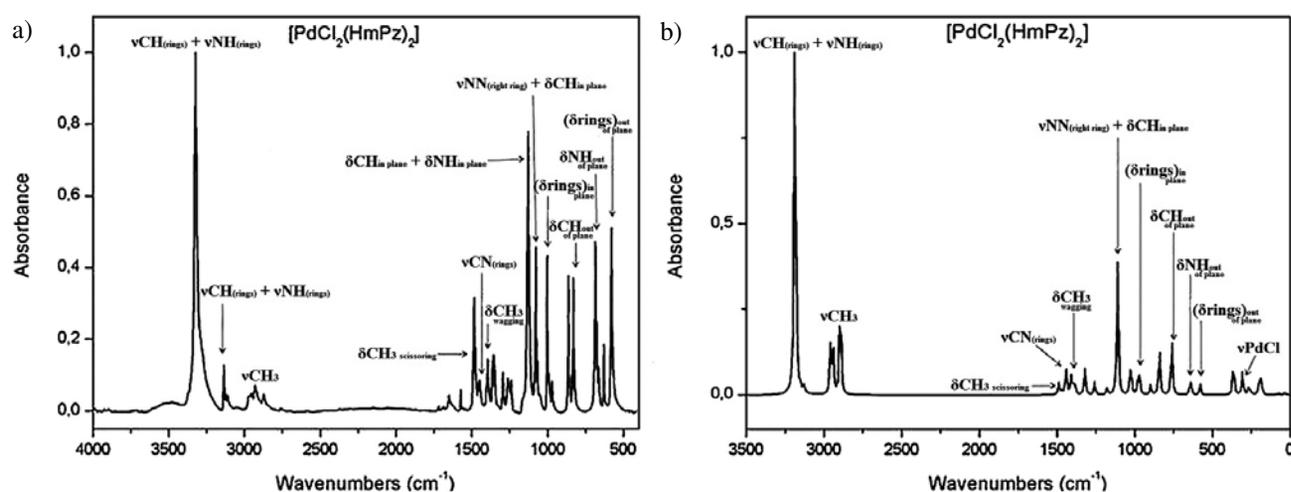


Figure 3. Experimental (a) and theoretical (b) IR spectra of the HIPz.

Table 2. Experimental and theoretical frequencies of 4-methylpyrazole (HmPz).

Vibrational Mode	Frequencies (cm ⁻¹)			Relative Intensities	Percentual Error (%)	Assignment
	Experimental	Theoretical				
1	3400	3389		0.36	-0.32	vNH
2	3184	3114		0.01	-2.20	v(C1H + C2H)
3	3067	3101		0.29	+1.11	v(C1H+C2H)
4	2953	2951		0.57	-0.07	vCH ₃
5	–	2927		0.60	–	vCH ₃
6	–	2887		1.00	–	vCH ₃
7	1578	1575		0.01	-0.19	v(C2-C3)
8	1497	1486		0.07	-0.93	δCH ₃ scissoring
9	1460	1474		0.03	+0.96	δCH ₃ scissoring
10	–	1436		0.07	–	δNH _{in plane}
11	1387	1404		0.10	+1.22	δCH ₃ umbrella + v(C3-N1)
12	1381	1379		0.10	-0.15	v(C2C1-C2C3)
13	1342	1293		0.08	-3.65	v(N1C3-N2C1) + v C2-CH ₃
14	1225	1245		0.08	+1.63	δ(NH + C1H) _{in plane}
15	1138	1137		0.01	-0.09	δC3H _{in plane} + δNH _{in plane}
16	1051	1075		0.12	+2.28	v(C1-N2)
17	–	1038		0.02	–	δCH ₃ out of plane
18	1001	984		0.07	-1.70	Ring breathing + δCH ₃ out of plane
19	–	980		0.03	–	δCH ₃ out of plane
20	949	939		0.35	-1.05	vNN
21	–	875		0.09	–	δring _{in plane}
22	858	842		0.58	-1.86	δC3H _{out of plane}
23	804	766		0.61	-4.73	δC1H _{out of plane}
24	650	644		0.30	-0.92	δNH _{out of plane}
25	613	630		0.04	+2.77	vC2-CH ₃
26	–	592		0.03	–	δC2H _{out of plane}
27	–	298		0.01	–	δCH ₃ out of plane
28	–	289		0.38	–	δNH _{out of plane} + δCH ₃ out of plane
29	–	220		0.14	–	δNH _{out of plane}
30	–	51		0.01	–	δCH ₃ rocking

* Broad and intense band

Figure 4. Experimental (a) and theoretical (b) IR spectra of the [PdCl₂(HmPz)₂].

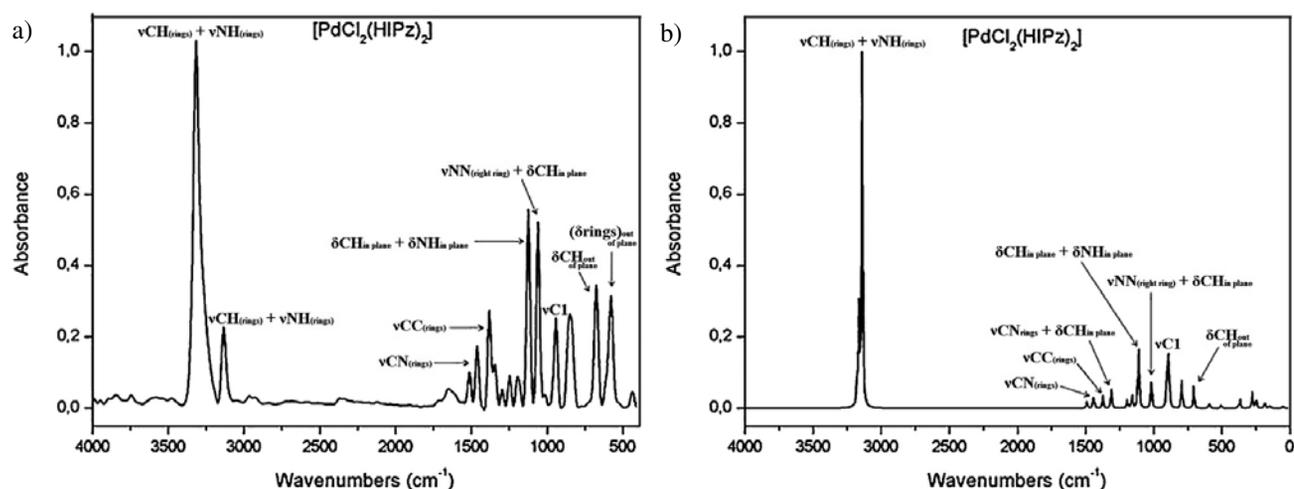
The experimental and theoretical vibrational spectra FT-IR for the compounds **1** and **2** are showed in Figures 4 and 5, and in Tables 4 and 5, respectively. The theoretical

infrared spectra were also calculated using a harmonic field²⁹ based on C_s symmetry (electronic state ¹A'). Frequency values (not scaled), intensities, assignments and

Table 3. Experimental and theoretical frequencies of 4-iodopyrazole (HIPz).

Vibrational Mode	Frequencies (cm ⁻¹)		Relative Intensities	Percentual Error (%)	Assignment
	Experimental	Theoretical			
1	–	3396	0.74	–	νNH
2	3137	3145	0.04	+0.25	νCH
3	3114	3135	0.09	+0.67	νCH
4	1533	1508	0.03	-1.63	νC2C1
5	1423	1406	0.03	-1.19	νC1N2
6	1363	1357	0.18	-0.44	νC2C3
7	1263	1256	0.13	-0.55	νC3N1
8	1140	1190	0.30	+4.39	νC1N2
9	1117	1109	0.01	-0.72	δC3H _{in plane}
10	1032	1073	0.22	+3.97	νC1N2
11	955	933	0.47	-2.30	νNN
12	935	899	0.66	-3.85	νC-I
13	870	859	0.45	-1.26	δ(C1N2N1) _{ring in plane}
14	808	827	1.00	+2.35	δC3H _{out of plane}
15	779	748	1.00	-3.98	δC1H _{out of plane}
16	607	649	0.36	+6.92	δNH _{out of plane}
17	534	527	0.01	-1.31	δC2H _{out of plane}
18	*	308	0.01	–	νC-I
19	322	294	0.64	-8.69	δNH _{out of plane}
20	–	233	0.01	–	δC2H _{out of plane} + δN2H _{out of plane}
21	–	199	0.01	–	δC2-I _{in plane}

* not detected

Figure 5. Experimental (a) and theoretical (b) IR spectra of the [PdCl₂(HIPz)₂].

description of vibrational modes are presented. The calculations of vibrational frequencies were also employed to determine whether optimized geometry constitutes minimum or saddle points. The principal infrared-active fundamental modes assignments and descriptions were done by the GaussView W 4.1.2 graphics routine.³⁰

3. 1. N–H and C–H Vibrations

The two experimental spectra of the HmPz and HIPz ligands (Figs. 2(a) and 3(a), respectively) show a very

broadened and intense NH...N association bands over the 3600–2500 cm⁻¹ range. The theoretical calculations predict that the N–H stretches should occur as single peaks at 3389 and 3396 cm⁻¹ (Figs. 2(b) and 3(b), respectively). Two C–H stretching modes are expected for HmPz (3114 and 3101 cm⁻¹) and HIPz (3145 and 3135 cm⁻¹). Nevertheless, the broad range of the NH...N bands covers the C–H stretching absorptions, preventing the comparison between the experimental and theoretical values.

In the calculated IR spectrum of HmPz, the bands at 1245 and 1137 cm⁻¹ are assigned to an in-plane N-H ben-

Table 4. Experimental and theoretical frequencies of [PdCl₂(HmPz)₂] (1).

Vibrational Mode	Frequencies (cm ⁻¹)		Relative Intensities	Percentual Error (%)	Assignment
	Experimental	Theoretical			
1	3325	3186	1.00	+4.18	vCH _(rings) + vNH _(rings)
2	3134	3128	0.01	-0.19	vCH _(rings) + vNH _(rings)
3	2956	2960	0.06	+0.10	vCH _{3(left ring)}
		2959	0.04		vCH _{3(right ring)}
4	2925	2942	0.09	+0.58	vCH ₃
5	2869	2895	0.25	+0.91	vCH ₃
6	1483	1490	0.02	+0.47	(δCH ₃) _{scissoring}
7	1450	1443	0.07	-0.48	vCN _(rings)
8	1394	1407	0.05	+0.93	(δCH ₃) _{wagging}
9	1355	1386	0.03	+2.29	vCC _(rings) + (δCH ₃) _{scissoring}
10	1292	1322	0.06	+2.32	vCN _(rings) + (δCH ₃) _{wagging}
11	1255	1259	0.03	+0.32	δCH _{in plane} + δNH _{in plane}
12	1128	1111	0.28	-1.51	δCH _{in plane} + δNH _{in plane}
13	1076	1026	0.06	-4.65	vNN _(right ring) + δCH _{in plane}
		1025	0.02		vNN _(left ring) + δCH _{in plane}
14	1001	974	0.07	-2.70	(δring) _{in plane}
15	862	843	0.10	-2.20	δCH _{out of plane} + δNH _{out of plane}
16	829	762	0.12	-8.08	δCH _{out of plane}
17	682	644	0.03	-5.57	δNH _{out of plane}
18	576	580	0.02	+0.69	(δring) _{out of plane}
19	331	365	0.06	-9.31	δNH _{out of plane}
20	302	307	0.05	+1.65	vPdCl
21	286	266	0.02	-7.52	vPdN
22	–	202	0.03	–	δPdN _{in plane}
23	–	187	0.03	–	δPdCl _{in plane}

Table 5. Experimental and theoretical frequencies of [PdCl₂(HIPz)₂] (2).

Vibrational Mode	Frequencies (cm ⁻¹)		Relative Intensities	Percentual Error (%)	Assignment
	Experimental	Theoretical			
1	3315	3176	0.10	-4.19	vCH _(rings) + vNH _(rings)
2	–	3162	0.31	–	vCH + vNH _(rings)
3	3136	3139	1.00	+0.09	vCH _(rings) vNH _(rings)
4	1512	1489	0.03	-1.52	vCN _(rings) + vCC _(rings)
5	1462	1441	0.05	-1.44	vCN _(rings)
6	1381	1373	0.04	-0.58	vCC _(rings)
7	1344	1311	0.07	-2.46	vCN _(rings) + δCH _{in plane}
8	1246	1193	0.03	-4.25	δCH _{in plane} + δNH _{in plane}
9	1194	1159	0.05	-2.93	δCH _{in plane} + δNH _{in plane}
10	1124	1111	0.24	-1.16	δCH _{in plane} + δNH _{in plane}
11	1061	1017	0.12	-4.15	vNN _(rings) + δCH _{in plane}
12	941	903	0.13	-4.04	vC-I _(rings)
13	849	890	0.08	+4.83	δCH _{in plane} + δNH _{in plane}
		889	0.11	+4.71	δCH _{out of plane} + δNH _{out of plane}
14	675	707	0.07	+4.74	δCH _{out of plane}
15	579	592	0.02	+2.24	(δring) _{out of plane}
16	368	366	0.03	-0.54	vPd-Cl
17	288	276	0.04	-4.17	δPdN _{in plane} + vPdCl
18	–	248	0.04	–	vPdN + δPdCl
19	–	184	0.02	–	δPdCl

ding with contribution from in-plane C–H bending vibrational modes. This is in disagreement with Vos and Groe-

neveld,²⁸ who assigned the experimental bands at 1225 and 1140 cm⁻¹ to C–CH₃ stretching and ring vibrations.

For HIPz molecule, the experimental band at 1117 cm^{-1} is assigned to the in-plane C–H bending mode. The $850\text{--}750\text{ cm}^{-1}$ region is where the most intense bands arising from out-of-plane C–H bending vibrational modes ($\delta_{\text{o.p.}}\text{C-H}$) are found. The two theoretical frequencies for $\delta_{\text{o.p.}}\text{C-H}$ modes for HmPz (842 and 766 cm^{-1}) and HIPz (827 and 748 cm^{-1}) are in good agreement with those experimentally found (Tables 2 and 3). The out-of-plane N–H bending mode appears at 644 cm^{-1} and 220 cm^{-1} in the calculated IR spectrum of HmPz. Vos and Groeneveld²⁸ attributed the band at 650 cm^{-1} , observed in the experimental spectrum of HmPz, to C–CH₃ stretching and ring vibrations. The $\delta_{\text{o.p.}}\text{N-H}$ vibration gives a band at 607 cm^{-1} in the measured IR spectrum of HIPz which agrees well with that observed in its calculated spectrum at 649 cm^{-1} .

The N–H and C–H vibrations of compounds **1** and **2** correlate well with the IR data of transition metal complexes bearing pyrazole derivatives literature data.³¹ In the experimental IR spectra of the complexes **1** and **2** (Figs. 4(a) and 5(a), respectively), it is observed two peaks of different intensities in the spectral range of $3325\text{--}3134\text{ cm}^{-1}$, which belong to the C–H stretching mode with considerable $\nu\text{N-H}$ content. The bands appearing in the $1246\text{--}1124\text{ cm}^{-1}$ range in both experimental spectra are due to in-plane C–H bending ($\delta_{\text{i.p.}}\text{C-H}$), with contributions from in-plane N–H bend, $\delta_{\text{i.p.}}\text{N-H}$. The major contributions to the bands 862 (**1**) and 849 cm^{-1} (**2**) are out-of-plane C–H bending, $\delta_{\text{o.p.}}\text{C-H}$, together with out-of-plane N–H bending, $\delta_{\text{o.p.}}\text{N-H}$. The intense experimental band at 682 cm^{-1} in the IR spectrum of **1** is assigned to $\delta_{\text{o.p.}}\text{N-H}$ mode only.

3. 2. CH₃ Vibrations

Three fundamental νCH_3 absorptions related to one symmetric and two asymmetric vibrations are usually observed in the region between 2950 and 2990 cm^{-1} .³² Our calculations predict these modes for HmPz at 2951 ($\nu_{\text{as}}\text{CH}_3$), 2887 ($\nu_{\text{as}}\text{CH}_3$) and 2927 cm^{-1} ($\nu_{\text{s}}\text{CH}_3$). However, the presence of a broad and intense band in the $3600\text{--}2700\text{ cm}^{-1}$ region of the experimental IR spectrum of HmPz has prevented us to make some comparisons with the experimental values. For compound **1**, the calculated modes 2960 ($\nu_{\text{as}}\text{CH}_3$), 2895 ($\nu_{\text{as}}\text{CH}_3$) and 2942 cm^{-1} ($\nu_{\text{s}}\text{CH}_3$) agree very well with the experimental values observed at 2956 , 2869 and 2925 cm^{-1} , respectively.

The bending vibrational modes of the methyl groups are expected to appear between at 1410 and 1550 cm^{-1} .³² The two bands located at 1497 and 1460 cm^{-1} in the experimental IR spectrum of HmPz involve the vibrations arising from methyl H–C–H bends, $\delta_{\text{as}}\text{CH}_3$. This is in agreement with the earlier study of Vos and Groeneveld.³³ The peak at 1387 cm^{-1} , which was previously assigned to ring vibrations,²⁸ is a mixture of the $\delta_{\text{s}}\text{CH}_3$ (umbrella) and νCN modes. In the experimental IR spectrum of complex

1, the bands associated with the bending modes of methyl groups appear at 1483 and 1394 cm^{-1} , which are in accordance with the calculated values at 1490 and 1407 cm^{-1} , respectively.

3. 3. C–I Vibrations

According to the data available in the literature,^{34,35} there appears to be no pure C–I stretching vibration band for iodo-aryl compounds due to its coupling with ring vibration. The position of C–I band is strongly dependent on many factors, such as the type of the ring, the mass and relative position of their substituents. Therefore, the assignment and comparison of C–I stretching vibrations in the IR spectra of aromatic compounds remains a difficult task since only a restricted number of iodo-aromatic compounds have been investigated. In addition, the description on the νCI frequencies remains at least contradictory in some reports. For instance, in the spectra of *p*-substituted iodobenzenes ($\text{R} = \text{OH}$, Me , COOMe),³⁶ the νCI frequencies occur within the spectral range of $1060\text{--}1055\text{ cm}^{-1}$ whereas the νCI appears at 454 cm^{-1} for *p*-iodonitrobenzene.³⁷ PM3 calculations on 5-iodo-2'-deoxyuridine performed by Bailey et al.³⁸ indicated that C–I stretching vibration found at 554 cm^{-1} agrees well with the experimental value. In the FT-IR spectrum of 2-amino-5-iodopyridine, Sundaraganesan et al.³⁹ assigned the strong absorption at 514 cm^{-1} to C–I stretching vibration. However, their theoretical calculations predicted the νCI vibration at 228 cm^{-1} . Vos and Groeneveld²⁷ assigned the C–I stretching vibration in the IR spectrum of 4-iodopyrazole to the band at 321 cm^{-1} . Our calculations predict this mode at 899 cm^{-1} which shows a good agreement with the experimental value of 935 cm^{-1} . It is also expected an absorption of low intensity at 308 cm^{-1} which could not be detected in the experimental IR spectrum of HIPz. For compound **2**, the calculated frequency of 903 cm^{-1} agrees very well with the experimental values observed at 941 cm^{-1} .

3. 4. CC, CN and ring Vibrations

According to literature, pyrazole nucleus possesses several absorptions of variable intensities in the range of $1530\text{--}1013\text{ cm}^{-1}$ due to CC, CN and ring stretching motions.⁴⁰ The identification of νCN and νCC stretching frequencies is a very difficult task, since the mixing of bands is very common in this region.

In the experimental IR spectrum of HmPz [Fig. 2(a)], the band located at 1578 cm^{-1} involves the vibrations arising from C2–C3 stretching. The absorption associated with the asymmetric stretching mode of the C2–C1 and C2–C3 bonds is predicted to occur at 1379 cm^{-1} , which agrees well with the experimental value of 1381 cm^{-1} . The major contributions to the experimental band at 1342 cm^{-1} are symmetric stretching mode of the C3–N1

and C1–N2 bonds together with C–CH₃ stretching motion. The peak at 1051 cm⁻¹ in the experimental IR spectrum of HmPz, which was previously assigned to in-plane C–H and methyl bending modes,²⁸ is due to the C1–N2 stretching vibration.

The band at 1450 cm⁻¹ observed in the FT-IR spectrum of [PdCl₂(HmPz)₂] (**1**) arises from C–N stretches and compares well with the calculated value of 1443 cm⁻¹. In addition, we find that the experimental band at 1355 cm⁻¹ is a combination of νCC and methyl bends, with its neighbor at 1292 cm⁻¹ arising from C–N stretching motion with contributions from methyl bends.

With regard to the FT-IR spectrum of HIPz (Fig. 3), the C–C stretching bands appear at 1533 and 1363 cm⁻¹ whereas the absorptions at 1423, 1263, 1140, and 1032 cm⁻¹ arise from C–N stretches only. These experimental IR bands show good agreement with those predicted by our calculations (Table 3).

In the experimental IR spectrum of [PdCl₂(HIPz)₂] (**2**) [Fig. 5(a)], a mixture of C–C and C–N stretching motions contributes to the band at 1512 cm⁻¹ whereas the absorptions at 1462 and 1381 cm⁻¹ arises from C–N and C–C stretching vibrational modes, respectively. The next band, at 1344 cm⁻¹, is a combination of νCN and δ_{i.p.}C–H.

Our calculations predict the N–N stretching vibrational mode for HmPz and HIPz at 939 and 933 cm⁻¹, respectively. These calculated frequencies compare well with those observed in their FTIR spectra (HmPz, 949 cm⁻¹; HIPz, 935 cm⁻¹). Our theoretical νNN frequencies are significantly lower than that found in the calculated IR spectrum of 3,5-dimethylpyrazole (1125 cm⁻¹).⁴¹ Regarding the FT-IR spectra of [PdCl₂(HmPz)₂] (**1**) and [PdCl₂(HIPz)₂] (**2**), a combination of νNN and δ_{i.p.}C–H motions contributes for the band at 1076 cm⁻¹ (**1**) and 1061 cm⁻¹ (**2**). Taking into account both experimental and theoretical spectra it can be concluded that positions of the peaks representing the νNN mode occurring within the pyrazolyl-type ligand differ significantly from these for a free molecule and for molecules involved in the complex. The νNN band shifts up to 127 cm⁻¹ towards greater wave numbers upon complexation. The blue-shift of the νNN frequencies found in the spectra of **1** and **2** may be attributed to the increase of the NN bond force constant and bond order in the complex relatively to the free pyrazolyl molecules.

The ring stretching motions frequencies in HmPz, HIPz, **1** and **2** are predicted to occur below 1000 cm⁻¹. The experimental IR absorption positioned at 1001 cm⁻¹ in the spectrum of HmPz involve the vibrations arising from ring breathing with a contribution from methyl H–C–H bends whereas the peak at 870 cm⁻¹, observed in the experimental IR spectrum of HIPz, is associated with in-plane ring stretching vibration. Such IR bands are localized at wavenumbers comparable to those predicted by our calculations at 984 cm⁻¹ (HmPz) and 859 cm⁻¹

(HIPz). For complex **1**, the experimental bands at 974 and 576 cm⁻¹ are due to in-plane ring stretching and out-of-plane ring bending vibrations, respectively. The peak associated with the out-of-plane ring bending vibration in the experimental IR spectrum of complex **2** appear at 579 cm⁻¹, which is in accordance with the calculated value at 592 cm⁻¹.

3. 5. Pd-N and Pd-Cl Vibrations

According to Nakamoto,⁴² terminal M–Cl stretching bands are expected to occur in the region of 300–200 cm⁻¹. Particularly, the νPd–Cl absorption observed in the experimental IR spectra of square-planar Pd(II) compounds falls between 360 and 300 cm⁻¹. Theoretical studies on K₂PdCl₄ performed by Zhang et al.⁴³ indicated that Pd–Cl stretching vibration found at 292 cm⁻¹ agrees well with the experimental value (336 cm⁻¹). Our calculations predict the Pd–Cl stretching vibrational mode for **1** and **2** at 307 and 368 cm⁻¹, respectively. These calculated frequencies compare well with those observed in their FT-IR spectra (**1**, 302 cm⁻¹; **2**, 366 cm⁻¹), which is depicted in Figure 6. These experimental values are similar to those found in *trans*-[PdCl₂L₂] where L = diethylsulphide (358 cm⁻¹),⁴¹ triethylphosphine (355 cm⁻¹),⁴² pyridine (350 cm⁻¹),⁴⁴ 2-thiophenecarboxylic hydrazide (341 cm⁻¹).³³

The Pd–N stretching and in-plane bending vibrational modes for compound **1** are predicted to occur at 266 and 202 cm⁻¹, respectively. For complex **2**, a combination of δ_{i.p.}Pd–N and νPd–Cl motions contributes for the theoretical band at 276 cm⁻¹ whereas the theoretically predicted absorption at 248 cm⁻¹ is a mixture νPd–N and δ_{i.p.}Pd–Cl vibrations.

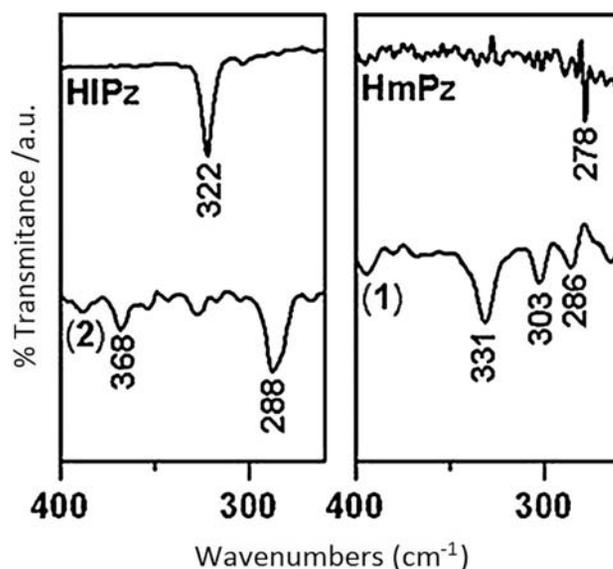


Figure 6. Far FT-IR spectra of the compounds HmPz, HIPz, **1** and **2**.

- Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazayev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.
24. H. B. Schelegel, in J. Bertran (Ed.): *New Theoretical Concepts for Understanding Organic Reactions*, Academic: The Netherlands, **1989**, pp. 33–53.
http://dx.doi.org/10.1007/978-94-009-2313-3_2
25. C. J. Adams, M. F. Haddow, R. J. I. Hughes, M. A. Kurawa, A. G. Orpen, *Dalton Trans.* **2010**, 39, 3714–3724.
<http://dx.doi.org/10.1039/b919665j>
26. A. V. G. Netto, A. E. Mauro, R. C. G. Frem, A. M. Santana, R. H. A. Santos, J. R. Zoia, *J. Coord. Chem.* **2001**, 54, 129–141. <http://dx.doi.org/10.1080/00958970108027149>
27. J. G. Vos, W. L. Groeneveld, *Inorg. Chim. Acta* **1978**, 26, 71–76. [http://dx.doi.org/10.1016/S0020-1693\(00\)87190-X](http://dx.doi.org/10.1016/S0020-1693(00)87190-X)
28. J. G. Vos, W. L. Groeneveld, *Transition Metal Chem.* **1979**, 4, 137–141. <http://dx.doi.org/10.1007/BF00619054>
29. D. Z. Goodson, S. K. Sarpal, P. Bopp, M. Wolfsberg, *J. Phys. Chem.* **1982**, 86, 659–663.
<http://dx.doi.org/10.1021/j100394a014>
30. GaussView W 4.1.2, Gaussian Inc., Semichem Inc. **2000-2006**.
31. G. W. Cushing, W. A. Howard, K. Pang, *J. Mol. Struct.* **2006**, 797, 165–173.
<http://dx.doi.org/10.1016/j.molstruc.2006.03.047>
32. E. Kucharska, W. Sasiadek, J. Janczak, H. Ban-Oganowska, J. Lorenc, Z. Weglinski, Z. Talik, K. Hermanowicz, J. Hanuza, *Vib. Spectrosc.* **2010**, 53, 189–198.
<http://dx.doi.org/10.1016/j.vibspec.2010.02.003>
33. P. Drozdowski, A. Brozyna, M. Kubiak, T. Lis, *Vib. Spectrosc.* **2006**, 40, 118–126.
<http://dx.doi.org/10.1016/j.vibspec.2005.07.007>
34. G. Socrates, in Wiley (Ed.): *Infrared Characteristic Group Frequencies. Tables and Charts*, 2nd ed., Wiley, Chichester, New York, **1997**.
35. N. B. Colthup, L. H. Daly, S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, 3rd ed., Academic Press, San Diego, **1990**.
36. A. R. Katritzky, J. M. Lagowski, *J. Chem. Soc.* **1960**, 2421–2422. <http://dx.doi.org/10.1039/jr9600002421>
37. S. Ahmad, S. Mathew, P. K. Verma, *Ind. J. Pure Appl. Phys.* **1993**, 31, 395–398.
38. L. Bailey, R. Navarro, A. Hernanz, *J. Mol. Struct.* **1999**, 480–481, 465–469.
[http://dx.doi.org/10.1016/S0022-2860\(98\)00773-X](http://dx.doi.org/10.1016/S0022-2860(98)00773-X)
39. N. Sundaraganesan, C. Meganathan, B. Anand, B. D. Joshua, C. Lapouge, *Spectrochim. Acta Part A* **2007**, 67, 830–836.
<http://dx.doi.org/10.1016/j.saa.2006.08.040>
40. N. Sundaraganesan, E. Kavitha, S. Sebastian, J. P. Cornard, M. Martel, *Spectrochim. Acta Part A* **2009**, 74, 788–797.
<http://dx.doi.org/10.1016/j.saa.2009.08.019>
41. G. E. Coates, C. Parkin, *J. Chem. Soc.* **1963**, 421–429.
<http://dx.doi.org/10.1039/jr9630000421>
42. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, 4th ed., Wiley, New York, **1986**.
43. L. Zhang, H. Wei, Y. Zhang, Z. Guo, L. Zhu, *J. Phys. Chem. A* **2002**, 106, 3819–3822.
<http://dx.doi.org/10.1021/jp011543d>
44. R. J. H. Clark, C. S. Williams, *Inorg. Chem.* **1965**, 4, 350–357. <http://dx.doi.org/10.1021/ic50025a020>

Povzetek

Izračunane molekulske strukture kompleksov [PdCl₂(HmPz)₂] (**1**) in [PdCl₂(HIPz)₂] (**2**) (HmPz = 4-metilpirazol; HIPz = 4-jodopirazol) so bile proučevane z B3LYP/DFT metodo. Sintetizirana novi kompleks **2** in kompleks **1** sta bila okarakterizirana s pomočjo elementne analize in IR spektroskopije. Izračunane vrednosti razdalj in kotov kažejo, da imata obe spojini rahlo popačeno kvadratno-planarno razporeditev ligandov okoli paladijevega centralnega atoma. Izračunani IR spektri za strukturi s C_s simetrijo (elektronsko stanje 1A') se dobro ujemajo z eksperimentalnimi podatki.