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# FT-IR and Raman spectroscopic and quantum chemical investigations of some metal halide complexes of 1-phenylpiperazine

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#### ABSTRACT

New metal halide complexes in the form of  $M(pp)_2Cl_2$  (where pp=1-phenylpiperazine and M=Pd or Hg) have been prepared for the first time and their FT-IR and FT-Raman spectra are reported in the region of 4000–10 cm<sup>-1</sup> and 4000–50 cm<sup>-1</sup>, respectively. The optimized geometric parameters, normal mode frequencies and corresponding vibrational assignments of the present compounds are theoretically examined by means of B3LYP hybrid density functional theory (DFT) method together with Lanl2dz basis set. Furthermore, reliable vibrational assignments made on the basis of potential energy distribution (PED) were calculated and the thermodynamics functions, the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO) of these compounds have been predicted. According to the results, theoretical values have been successfully compared against experimental data.

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# 1. Introduction

Metal halides are compounds between metals and halogens, and probably the most widespread class of complexes involving ligands is that of the complexes of the halide ions, i.e. the fluoride, chloride, bromide, and iodide ions. The synthesis and study of metal halide complexes for organometallic chemistry are currently active and important areas [1–4].

The free pp ligand molecule consists of a bulky phenyl group  $(-C_6H_5)$ , with high basic strength, attached to one of the nitrogens of piperazine  $(C_4H_{10}N_2)$ . This molecule has been used as a ligand in various complexes [5–11]. The free pp exists in a chair conformation because of the steric crowding present in the boat form [9,12]. This molecule, however, can coordinate in the boat and chair forms as a bidentate ligand [10,11] or as a unidentate ligand coordinating only through the NH nitrogen [5–9].

The DFT/B3LYP method exhibits good performance on electron affinities, excellent performance on bond energies and reasonably good performance on vibrational frequencies and geometries of inorganic or ionic compounds [13,14] as well as organic and neutral compounds [12,15–21]. The Lanl (Los Alamos National Laboratory) basis sets, also known as Lanl2dz (Lanl-2-double zeta) and developed by Hay and Wadt [22–24], have been widely used in quantum

chemistry, particularly in the study of compounds containing heavy elements.

In our previous studies, we reported the vibrational spectroscopic study of pp [12], M(pp)<sub>2</sub>Ni(CN)<sub>4</sub> (M=Ni, Co, Cd, Pd or Mn) Hofmann type complexes [5], Ni(pp)<sub>2</sub>Ni(CN)<sub>4</sub> (M=Cd or Hg) Hofmann T<sub>d</sub>-type complexes [6],  $M(pp)_2Ni(CN)_4 \cdot 2C_6H_5NH_2$ (M=Ni, Co and Cd) Hofmann type aniline clathrates [7] and  $M(pp)_2Ni(CN)_4 \cdot 2C_4H_8O_2$  (M = Ni, Co and Cd) Hofmann type dioxane clathrates [8]. Studies of various complexes of pp exhibit its coordination properties. As continuation of our studies on coordinated pp, we wish to extend investigations using the theoretical model. The essence of this study is briefly to report the experimental and theoretical vibrational features of pp and some of its metal halide complexes. For the above goals, two new  $M(pp)_2Cl_2$  (M = Pd or Hg) complexes have been synthesized for the first time and their vibrational spectra are reported in the region of  $4000-10 \text{ cm}^{-1}$  together with FT-Raman and FT-FIR spectra of pp. The structural parameters, vibrational frequencies and corresponding assignments together with the PED, thermodynamics, HOMO and LUMO data of the present complexes are also calculated at DFT/B3LYP level of theory using the Lanl2dz basis set. The results of the theoretical and spectroscopic studies are reported here.

## 2. Experimental

All the chemicals used were reagent grade (Aldrich) and they were used without further purification.  $M(pp)_2Cl_2$  (M = Pd or Hg) compounds were prepared by adding slightly more than 2 mmol

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of the liquid pp to 1 mmol of  $MCl_2$  dissolved in the distilled water. The obtained products were filtered and washed successively with distilled water, ethanol, ether and dried in a desiccator using  $P_2O_5$  as desiccant.

FT-MIR and FT-FIR spectra of the present compounds or pp were recorded in the region of 4000–400 cm<sup>-1</sup> and 400–10 cm<sup>-1</sup> with Perkin-Elmer FT-IR 2000 and Bruker IFS 66v/S vacuum FT-IR spectrometers at a resolution of 4 cm<sup>-1</sup> and 2 cm<sup>-1</sup>, respectively. In order to provide better identifications for the vibrational bands of the complexes prepared in this study two different mulls (nujol and hexachloro-1,3-butadiene) were used. In the MIR region of spectra, bands of nujol were reported at 1377 cm<sup>-1</sup>, 1461 cm<sup>-1</sup>, 2858 cm<sup>-1</sup>, 2925 cm<sup>-1</sup> and of hexachloro-1,3-butadiene at 655 cm<sup>-1</sup>, 793 cm<sup>-1</sup>, 852 cm<sup>-1</sup>, 941 cm<sup>-1</sup>, 981 cm<sup>-1</sup>, 1170 cm<sup>-1</sup>, 1564 cm<sup>-1</sup>, 1610 cm<sup>-1</sup>, respectively. FT-Raman spectra of the compounds and pp molecule were recorded in the region of 4000–50 cm<sup>-1</sup> with Bruker Senterra Dispersive Raman Microscope using the 532 nm excitation from a 3B diode laser having 3 cm<sup>-1</sup> resolution.

The compounds were analyzed for Pd and Hg metals with a Perkin Elmer 4300 ICP-OES and for C, H and N via a Fisons EA-1108 elemental analyser. Pd and Hg metals were investigated at 340.458 nm and 253.652 nm, respectively. The results are as following; (found %/calculated %) Pd( $C_{10}H_{14}N_2$ )<sub>2</sub>Cl<sub>2</sub> ( $M_r$  = 501.79): C(47.52/47.87), H(5.55/5.62), N(11.02/11.17), Pd(21.00/21.21) and Hg( $C_{10}H_{14}N_2$ )<sub>2</sub>Cl<sub>2</sub> ( $M_r$  = 595.96): C(40.13/40.31), H(4.68/4.74), N(9.26/9.40), Hg(33.49/33.66).

#### 3. Calculations

All the calculations were performed by using Gaussian 09.A.01 program [25] on a personal computer and GaussView 5.0.8 [26] and Chemcraft 1.6 [27] programs were used for visualization of the structure and simulated vibrational spectra. For the calculations, the structures in Fig. 1 were first optimized in the gas phase at B3LYP level of theory using Lanl2dz basis set. The optimized geometric structures concerning to minimum on the potential energy surface were provided by solving self-consistent field equation iteratively and optimizations were performed without any molecular restrictions.

After the optimization, in order to confirm the convergence to minima on the potential surface and to evaluate the zero-point vibrational energies, harmonic vibrational frequencies and corresponding vibrational intensities of the title complexes were determined using analytic second derivatives with the B3LYP/Lanl2dz method under the keyword freq = Raman and pop = full and then scaled to generate the corrected frequencies. Scaling factors are calculated using the  $\lambda = \sum_{i}^{N} w_{i}^{\text{th}} w_{i}^{\exp} / \sum_{i}^{N} (w_{i}^{\text{th}})^{2}$  [13,14,16] where  $\lambda$  is scaling factor, *N* is the total number of vibrational modes,  $w^{\text{th}}$  and  $w^{\exp}$  are the theoretical and experimental frequencies (cm<sup>-1</sup>), respectively.

PED calculations, which show the relative contributions of the redundant internal coordinates to each normal vibrational mode of the molecule and thus make it possible to describe the character of each mode numerically, were carried out by the VEDA 4



Fig. 1. The optimized structures and atom numbering of palladium (a) and mercury (b) chloro complexes.

(Vibrational Energy Distribution Analysis) [28]. The VEDA does not scale the elements of force constant matrix as proposed by Pulay et al. [29]. For details of the PED analysis for VEDA program, more information was published in Ref. [30].

Calculated Raman activities are converted to relative Raman intensities using the following relationship derived from the intensity theory of Raman scattering:

$$I_{i} = \frac{f(v_{0} - v_{i})^{4}S_{i}}{v_{i}[1 - \exp(-hcv_{i}/kT)]}$$

where  $v_0$  is the laser exciting wavenumbers in cm<sup>-1</sup>,  $v_i$  is the vibrational wavenumbers of the *i*th normal mode,  $S_i$  is the Raman scattering activity of the normal mode  $v_i$  and f is a suitably chosen common normalization factor for all peak intensities,  $10^{-14}$ . *h*,

*k*, *c* and *T* are Planck and Boltzmann constants, speed of light and temperature in Kelvin, respectively [20,31].

# 4. Results and discussion

The results of the calculations on the geometrical parameters for the present compounds are discussed first. A brief discussion of the experimental and theoretical vibrational frequencies and intensities together with PED, HOMO and LUMO data is then presented.

#### 4.1. Geometrical structures

To clarify the vibrational frequencies, it is essential to examine the geometry of any compound as small changes in geometry can potentially cause substantial changes in frequencies. The optimized structures for square planar palladium and tetrahedral mercury



Fig. 2. MIR spectra of M(pp)<sub>2</sub>Cl<sub>2</sub> (M = Pd (a and b) and Hg (c and d)) in nujol (a and c) and hexachloro-1,3-butadiene (b and d). N and H: bands of nujol and hexachloro-1,3-butadiene.



Fig. 3. FIR spectra of pp(a) and  $M(pp)_2Cl_2$  (M = Pd (b) or Hg (c)).

halide complexes are shown in Fig. 1. The optimized geometric parameters such as bond lengths, bond and dihedral angles calculated by B3LYP/Lanl2dz are also listed in Table 1. Generally, it is expected that the bond distances calculated by electron correlated methods are longer than the experimental distance. This situation is clearly observed as expected. According to the experimental geometric parameters, Pd—Cl and Hg—Cl bond distances are ranging from 2.294 Å to 2.316 Å [4,32] and from 2.475 Å to 2.514 Å [2], respectively, whereas the calculated distances of these bonds for Lanl2dz basis set are about 2.421 Å and 2.555 Å. Experimental

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Some optimized geometric parameters of  $M(pp)_2Cl_2$  (M = Pd and Hg) complexes.

Parameters	B3LYP/Lanl2dz	$M(pp)_2Cl_2$
	Pd	Hg
Bond lenghts (Å)		
M—N <sup>a</sup>	2.088	2.515
M—Cl <sup>a</sup>	2.421	2.555
C—C <sup>a</sup>	1.540	1.540
C—N <sup>a</sup>	1.489	1.488
C—H <sup>a</sup>	1.089	1.099
Bond angles (°)		
C—C—N <sup>a</sup>	111.3	111.4
C—N—C <sup>a</sup>	111.7	112.1
H—C—H <sup>a</sup>	108.1	107.8
Cl—M—N		
2-55-28	87.7	98.5
1-55-28	92.3	95.7
1-55-3	92.3	95.7
2-55-3	87.7	98.5
М—Л—С		
29-28-55	113.5	113.1
30-28-55	113.0	114.0
5–3–55	113.5	113.1
4-3-55	113.0	114.0
Dihedral angles (° )		
C—N—M—Cl		
5-3-55-1	62.9	-45.4
5-3-55-2	-116.9	159.1
4-3-55-2	116.6	31.2
4-3-55-1	-63.6	-173.3
30-28-55-1	63.5	173.2
30-28-55-2	-116.6	-31.2
29-28-55-1	-63.0	45.3
29-28-55-2	116.9	-159.2

<sup>a</sup> Average value of the related bond lenghts or angles.

Pd—N and Hg—N bond distances are ranging from 1.998 Å to 2.033 Å [4] and from 2.190 Å to 2.565 Å [33,34], respectively, while the calculated distances of these bonds are about 2.088 Å and 2.515 Å. Overall, the calculated bond lengths are in good agreement with experimental results.

The calculated bond lengths for piperazine of pp ligand in the present complexes are also similar to previously reported experimental data. The average C–C, C–N and C–H bond distances of piperazine are experimentally 1.540 Å, 1.467 Å and 1.110 Å [35], respectively, whereas the calculated distances of these bonds are 1.540 Å, 1.489 Å and 1.089 Å for Pd and 1.540 Å, 1.488 Å and 1.099 Å for Hg. Similarly, the average C–C–N, C–N–C and H–C–H bond angles of piperazine are experimentally 110.4°, 109.0° and 109.1° [35], respectively, while the calculated angles are 111.3°, 111.7° and 108.1° for Pd and 111.4°, 112.1° and 107.8° for Hg (Table 1).

Table 2
Some thermodynamic parameters of $M(pp)_2Cl_2$ (M = Pd and Hg) complexes.

Parameters	B3LYP/Lanl2dz					
	Pd(pp) <sub>2</sub> Cl <sub>2</sub>	$Hg(pp)_2Cl_2$				
Thermal total energy (kcal/mol)	310.495	309.197				
Heat capacity (kcal/(mol K))	0.101	0.010				
Entropy (kcal/(mol K))	0.187	0.021				
Vibrational energy (kcal/mol)	308.718	307.419				
Zero point vibrational energy (kcal/mol)	293.767	291.425				
Rotational constants (GHz)						
Α	0.4676	0.11368				
В	0.0435	0.06396				
С	0.0420	0.04687				
Dipole moment (Debye)	1.3905	5.1402				

The vibrational energies are at room temperature.



Fig. 4. Raman spectra of pp(a) and  $M(pp)_2Cl_2$  (M = Pd (b) or Hg (c)).

The optimized and important Cl—M—N, M—N—C and C—N—M—Cl bond or dihedral angles for the present metal halide complexes calculated by B3LYP/Lanl2dz are shown in Table 1.

Several thermodynamics parameters, capacity, zero point energy, entropy, etc. calculated by B3LYP/Lanl2dz level are presented in Table 2. The variation in the zero point vibrational energy of the both compounds seems to be insignificant. The dipole moment for Hg halide complex is considerably larger than Pd due to the electronegativity.

## 4.2. Vibrational studies

The measured and calculated vibrational frequencies for the present compounds along with corresponding vibrational

#### Table 3

Experimental and calculated vibrational frequencies  $(cm^{-1})$  of  $M(pp)_2Cl_2$  (M = Pd and Hg) complexes.

Mode	Experimental						B3LYP/Lanl2dz						PED (≥10%)	
	рр			$Pd(pp)_2Cl_2$ $Hg(pp)_2Cl_2$			Pd(pp) <sub>2</sub> C	l <sub>2</sub>		Hg(pp) <sub>2</sub> C	l <sub>2</sub>			
	Ass. <sup>a</sup>	IR <sup>a</sup>	R	IR	R	IR	R	Scaled freq <sup>b</sup> .	I <sub>IR</sub>	I <sub>R</sub>	Scaled freq <sup>b</sup> .	I <sub>IR</sub>	I <sub>R</sub>	
$   \nu_1 $ $   \nu_2 $	ν(NH)	3278 sb	3325 vw	3215 m	3228 m	3212 vs	3210 vw	3330 3328	25.26 5.46	11.21 0.91	3372 3372	1.82 1.89	7.05 5.10	ν(NH) 100/97 ν(NH) 99/97
ν <sub>9</sub> ν <sub>10</sub>	ν(CH)	3091 m	-	-	3080 m	3089 vw	-	3099 3099	9.99 7.99	8.80 8.11	3080 3080	14.64 0.74	10.03 8.17	ν(CH) 77/81 ν(CH) 78/81
ν <sub>15</sub> ν <sub>16</sub>	ν(CH)	3059 m	3067 m	-	-	3060 sh	3067 m	3096 3096	4.28 0.01	2.01 3.51	3077 3077	19.61 13.52	6.77 5.12	ν(CH) 66/83 ν(CH) 67/84
ν <sub>17</sub> ν <sub>18</sub>	ν(CH)	3036 m	-	3038 <sup>c</sup> vw	3037 vw	-	-	3082 3081	18.57 7.69	2.45 2.02	3072 3071	18.57 8.84	2.17 1.33	ν(CH) 89/97 ν(CH) 89/98
ν <sub>19</sub> ν <sub>20</sub>	ν(CH)	3023 m	-	3006 <sup>c</sup> vw	-	3021 <sup>c</sup> vw	-	3049 3049	37.85 0.96	4.10 0.09	3047 3046	41.13 2.89	2.11 0.01	ν(CH) 93/94 ν(CH) 93/95
$   \nu_{21} \\   \nu_{22} $	CH <sub>2</sub> str.	2944 s	2950 w	2982 <sup>c</sup> w	2991 m	2975 <sup>c</sup> w	2976 m	3025 3025	4.38 2.96	6.20 0.04	3010 3010	17.29 21.12	8.27 2.17	ν(CH) 76/96 ν(CH) 76/97
ν <sub>23</sub> ν <sub>24</sub>	CH <sub>2</sub> str.	2910 m	-	2931 <sup>c</sup> w	-	2953 <sup>c</sup> vw 2930 <sup>c</sup> vw	2954 w 2927 w	3023 3023	37.24 0.39	3.09 0.10	3002 3002	14.67 20.62	5.90 3.08	ν(CH) 86/94 ν(CH) 86/95
$ u_{25} $ $ u_{26} $	CH <sub>2</sub> str.	2881 w	-	2978 <sup>c</sup> vw	2961 w	2900 <sup>c</sup> vw	2900 w	2874 2874	225.07 7.97	16.71 1.05	2878 2878	195.89 41.31	15.80 3.19	ν(CH) 85/84 ν(CH) 85/84
$ u_{27} \\ u_{28} $	CH <sub>2</sub> str.	2824 vs	2825 w	2829 <sup>c</sup> w	-	2869 <sup>c</sup> vw 2805 <sup>c</sup> vw	2870 w 2836 w	2865 2865	87.14 1.60	7.02 1.01	2869 2869	81.52 4.67	5.00 1.06	ν(CH) 93/84 ν(CH) 94/83
ν <sub>29</sub> ν <sub>30</sub>	(NH) <sub>def.</sub>	1670 w	-	1632 <sup>c</sup> vw	1627 w	1654 <sup>c</sup> vw	-	1583 1583	15.65 6.99	2.03 3.01	1583 1583	15.63 6.85	2.14 2.03	v(CC) 55/45 v(CC) 47/34
ν <sub>33</sub> ν <sub>34</sub>	C=C str.	1600 vs	1600 s	1595 s	1609 vs	1600 vs	1600 s	1615 1615	27.53 271.62	12.63 4.41	1615 1614	146.85 113.39	7.70 7.13	v(CC) 42/42 v(CC) 42/42
ν <sub>37</sub> ν <sub>38</sub>	Ring str.	1579 m	-	-	-	1576 w	1577 vw	1498 1497	26.86 169.68	0.01 0.00	1497 1496	120.01 71.49	0.00 0.02	δ(HCC) 44/47 δ(HCC) 44/47
ν <sub>41</sub> ν <sub>42</sub>	Ring str.	1498 vs	-	1496 w	-	1493 s	-	1489 1488	2.14 80.67	1.11 3.15	1487 1487	21.67 57.01	1.54 2.42	δ(HNC) 38/23 δ(HNC) 30/22
ν <sub>43</sub> ν <sub>44</sub>	CH <sub>2</sub> sci.	1452 s	1452 w	1452 m	1457 w	1453 s	1453 vw 1443 m	1450 1450	7.42 0.00	1.64 4.04	1448 1448	1.66 0.26	1.12 0.01	δ(HCH) 76/76 δ(HCH) 74/75
v <sub>45</sub> v <sub>46</sub>	Ring str. + CH <sub>2</sub> sci.	_	_	1427 <sup>c</sup> w	-	1431 <sup>c</sup> vw	-	1448 1448	10.39 0.67	0.01 4.42	1441 1441	23.04 0.03	0.10 1.67	ν(CC) 20/-+δ(HNC) 18/50 δ(HNC) 30/50
ν <sub>47</sub> ν <sub>48</sub>	CH <sub>2</sub> wag.	1407	-	-	-	1401 sb	-	1391 1391	15.89 121.73	0.09 0.03	1389 1389	45.43 21.62	0.10 0.02	δ(HCH) 26/35 δ(HCH) 29/34
v <sub>51</sub> v <sub>52</sub>	NC <sub>6</sub> H <sub>5</sub> str.	1380 s	1378 w	1380 <sup>c</sup> s	1378 m	1380 <sup>c</sup> m	1377 m	1376 1375	7.54 8.10	8.03 3.86	1378 1376	2.24 1.88	4.75 1.01	ν(NC) 22/11 + δ(HCH) 10/- ν(NC) 22/10 + δ(HCH) 12/-
ν <sub>57</sub> ν <sub>58</sub>	Ring str.+CH <sub>2</sub> twi.	1325 s	1324 w	1341 w	-	1317 s	-	1345 1345	0.80 0.07	1.08 3.04	1344 1344	9.93 3.52	5.77 2.69	$\delta$ (HCC) 28/11 $\delta$ (HCC) 28/10

Mode	Experimental	l						B3LYP/La	nl2dz					PED (≥10%)
	рр			$Pd(pp)_2Cl_2$		$Hg(pp)_2Cl_2$		Pd(pp) <sub>2</sub> C	l <sub>2</sub>		Hg(pp) <sub>2</sub> C	Cl <sub>2</sub>		
	Ass. <sup>a</sup>	IR <sup>a</sup>	R	IR	R	IR	R	Scaled freq <sup>b</sup> .	I <sub>IR</sub>	I <sub>R</sub>	Scaled freq <sup>b</sup> .	I <sub>IR</sub>	I <sub>R</sub>	
$v_{59}$ $v_{60}$	$v_{\rm ring}$ + $\delta(\rm CH)$	1285 m	1285 w	1248 vs	1260 s	1241 vs	1240 m	1245 1244	36.04 440.89	15.59 0.13	1238 1237	198.97 194.92	8.76 2.02	ν(CC) 33/33 ν(CC) 35/35
ν <sub>65</sub> ν <sub>66</sub>	$\delta(CH)$	1190 m	-	1175 w	1173 m	1188 m 1168 vw	1168 m	1179 1178	17.55 3.54	1.17 3.84	1177 1177	2.32 0.81	3.05 0.44	$\delta$ (HCC) 28/60 $\delta$ (HCC) 31/60
ν <sub>71</sub> ν <sub>72</sub>	$\delta(CH)$	1146	1156 m	1158 vw	-	1158 vw 1144 w	-	1164 1160	3.09 4.24	7.03 0.71	1144 1144	1.74 20.74	2.79 0.07	δ(HCC) 13/22 δ(HCC) 15/22
ν <sub>75</sub> ν <sub>76</sub>	$\delta(CH) + CH_2$ rock.	1081 m	1104 m	1099 w	_	1086 w	-	1095 1093	26.76 0.03	2.43 0.08	1102 1102	36.95 0.32	0.10 0.01	τ(HNCC) 29/11 τ(HNCC) 10/11
ν <sub>77</sub> ν <sub>78</sub>	Ring str.	1059 s	1058 m	1067 m	1067 s	1076 vw 1045 vw	1058 m	1076 1066	0.12 152.31	11.95 4.10	1049 1047	2.56 0.47	7.38 4.71	ν(CC) 32/20 ν(CC) 31/20
$ u_{81} $ $ u_{82}$	$v_{\rm ring}$	1032 s	1032 s	1019 s	1004 m	1016 vw	1031 m	1020 1016	23.92 177.60	5.90 6.48	1002 1002	0.55 0.50	1.39 1.15	ν(CC) 42/42 ν(CC) 48/47
ν <sub>85</sub> ν <sub>86</sub>	Ring breath.	992 s	991 vs	998 w	-	993 w	993 vs	985 985	1.57 19.31	8.28 2.90	980 980	3.47 3.67	6.08 2.21	δ(CCC) 47/53 δ(CCC) 47/54
ν <sub>91</sub> ν <sub>92</sub>	CH <sub>2</sub> wag.	937 s	937 m	920 s	936 w	921 m	930 w	932 927	1.47 13.07	2.01 0.01	926 926	3.16 5.90	1.85 0.01	δ(HCC) 22/22 δ(HCC) 21/21
$v_{101} \\ v_{102}$	$\gamma$ (CH)+Ring str.	881 s	-	880 vw	888 vw	883 m 860 w	886 vw 856 w	899 898	3.20 11.66	0.12 0.02	897 898	27.21 5.95	0.09 0.01	τ(HCCC) 67/53 τ(HCCC) 45/43
ν <sub>109</sub> ν <sub>110</sub>	(CH) <sub>def.</sub>	758 vs	-	760 s	-	761 vs	761 w	770 770	138.23 19.14	1.03 0.01	770 770	63.77 92.28	0.03 0.01	τ(HCCC) 42/31 τ(HCCC) 31/31
ν <sub>111</sub> ν <sub>112</sub>	γ(CH)	735 sh	732 m	732 vw	-	735 w 723 vw	735 m	715 715	1.33 23.30	4.07 0.11	710 710	0.26 9.88	5.01 1.07	$\nu$ (NC) 23/33 + $\delta$ (CCC) 18/21 $\nu$ (NC) 23/34 + $\delta$ (CCC) 20/22
V115 V116	$\gamma_{ m ring}$	693 vs	-	693 s	686 m	693 s	-	701 701	73.35 3.35	0.47 0.01	701 701	42.47 33.23	0.09 0.01	$ u(MN) $ 15/22 + $\tau(MCCN)$ 18/49 $ u(MN) $ 15/21 + $\tau(MCCN)$ 14/48
ν <sub>117</sub> ν <sub>118</sub>	$\delta_{ m ring}$ + Ring band	625 s	617 m	630 sh	-	666 vw 650 vw	653 m	620 620	0.71 0.07	0.88 3.90	619 619	0.37 1.06	2.17 1.55	$\delta(\text{CCC}) 71/71$ $\delta(\text{CCC}) 71/71$
$v_{121} \\ v_{122}$	$\delta_{ m ring}$	517 vs	564 m	520 w	527 vw	525 w 498 vw	-	524 524	28.85 0.08	2.30 0.02	523 523	22.01 3.95	1.98 0.76	τ(NCCC) 34/30 τ(NCCC) 34/30
ν <sub>125</sub> ν <sub>126</sub>	(NH) <sub>rock.</sub>	485 w	-	481 vw	456 vw	480 vw 455 vw	482 vw 457 m	471 471	2.18 1.43	0.01 0.14	467 465	3.98 0.67	0.03 1.02	$\delta$ (CNC) 41/-+ $\tau$ (CCCC) -/60 $\delta$ (CNC) 41/-+ $\tau$ (CCCC) -/51
ν <sub>129</sub> ν <sub>130</sub>	$\delta_{ m ring}$	437 m	435 m	430 vw	421 vw	417 vw	430 vw	426 424	0.49 3.65	1.24 0.97	414 414	1.71 1.10	0.45 0.05	$\delta$ (CNC) 29/23 δ(CNC) 17/24

Table 3 (Continued)

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ν <sub>131</sub> ν <sub>132</sub>	378 w	-	-	-	362 356	13.83 0.41	0.04 0.81	317 317	4.47 0.33	1.05 1.37	ν(MN) 27/10 ν(MN) 20/20
ν <sub>133</sub> ν <sub>134</sub>	348 s 322 m	344 m 293 vs	331 vs 324 sh	315 m	316 336	35.34 27.32	0.56 3.97	302 304	5.31 0.77	1.02 0.06	ν(MCl) 54/58 ν(MCl) 59/53
ν <sub>136</sub> ν <sub>137</sub>	276 sh	-	285 vw	_	274 261	3.04 0.06	0.19 4.01	247 245	0.15 10.67	0.14 0.03	δ(MNC) 10/11 ν(MCl) 97/-+δ(MNC) -/11
$\nu_{138}$	-	_	269 s	267 s	259	6.09	0.01	243	15.68	5.61	ν(MCl) -/96 + δ(CNC) 20/-
ν <sub>141</sub> ν <sub>142</sub>	211 s	-	229 s	210 m	224 205	5.92 16.95	0.99 0.02	162 158	0.00 1.61	0.56 0.12	ν(MN) 24/-+δ(MNC) 13/13 ν(MN) 24/10+δ(MNC) 10/-
V143 V144	182 s	185 m	_	_	178 176	0.06 21.06	0.45 0.02	117 112	1.48 1.35	0.01 1.90	ν(MN) -/31+δ(CNM) 17/- δ(NMN) 27/-+τ(CCCN) 10/-+τ(MCCN) -/17
ν <sub>145</sub> ν <sub>146</sub>	144 m	-	132 w	-	146 122	4.19 1.24	3.76 0.32	85 83	0.73 0.79	1.03 0.02	δ(CIMCI) 12/32+δ(CIMN) 23/24 δ(CNC) 11/11
ν147 ν148	114 s	127 s	93 vs	118 vs	116 112	6.91 0.50	0.14 2.25	82 77	3.77 0.06	0.24 0.04	δ(CIMCI) 44/52 + τ(CINCIM) 15/12 ν(MN) 41/67
ν <sub>149</sub> ν <sub>150</sub>	-	-	68 m	73 m	96 93	1.33 4.04	0.02 0.26	61 60	25.60 10.19	0.07 1.03	δ(MNC) 28/34 τ(CINCIM) 44/81
ν <sub>154</sub> ν <sub>155</sub>	42 w	-	-	-	58 37	2.48 0.61	0.94 3.39	31 30	1.24 0.05	1.16 0.67	τ(CNCC) 19/57 τ(CNCC) 11/10+τ(NMNC) 29/33+τ(CINNM) 32/35

<sup>a</sup> Taken from Ref. [5].

<sup>b</sup> Scaled with 0.9923.

<sup>c</sup> In hexacholoro-1,3-butadiene.

Ass., assignments; str., stretching; sci., scissoring; twi., twist; wag., wagging; breath., breathing; def., deformation; rock., rocking; IR and R, experimental infrared and Raman frequencies;  $I_{IR}$  and  $I_R$ , calculated infrared and Raman intensities; Freq, frequency; vs, very strong; s, strong; m, medium; w, weak; vw, very weak; b, broad; sh, shoulder. PED  $\geq 10\%$ , M = Pd or Hg. In PED list, the former represents Pd while the latter stands for Hg chloro complexes.





assignments and intensities are given in Table 3 and their theoretical and experimental vibrational spectra are shown in Figs. 2-5. All calculated frequency values presented in this paper are obtained within the harmonic approximation which allows us to describe vibrational motion in terms of independent vibrational modes each of which is governed by a simple one dimensional harmonic potential. These compounds consist of 55 atoms, so they have 159 normal vibrational modes and they belong to the point group  $C_1$  with only identity (E) symmetry element or operation. It is difficult to determine vibrational assignments of these complexes in the observed spectrum due to its low symmetry. Therefore, the assignments of vibrational modes for the present complexes of pp have been tabled according to the vibrational assignments of the free pp [12] and PED data provided by VEDA 4 [28] in Table 3. According to the calculations, about 130 modes are in the mid-IR range and the rest are in the far-IR region of spectrum.

The spectral data for pp in the complexes exhibit characteristics of a coordinated ligand. On coordination, the NH and CH<sub>2</sub> stretching frequencies attributed to piperazine molecule within the pp ligand should decrease and increase due to the consecutive inductive effects, respectively [36]. It is clearly observed in Table 3 that these requirements are fulfilled for pp in the present compounds. These shifts in frequencies are explained in terms of coupling of the internal vibration of pp ligand with M—N vibrations [5–8]. The coupling is not the only factor for the frequency shifts with respect to those of the ligand. Due to the change of the geometrical parameters, diagonal force constants have small changes as well. Another strong CN stretching band attributed to phenyl attached to one of the nitrogens of piperazine has no shift in the compounds. Regarding the phenyl molecule within the pp, the vibrational bands possess small shifts due to the environmental changes on the complexion.

From the comparison of the spectral data presented in Table 3, it can be concluded that the pp molecules in the present compounds are coordinated in the chair form as a unidentate ligand coordinating only through the NH nitrogen. Unidentate coordination of the pp has been supported by the shifts in the position of the NH deformation mode from the free ligand value of 1670 cm<sup>-1</sup> to 1600 cm<sup>-1</sup> and no shift in the position of the CN stretching [5–9].

Vibrational modes in the low wavenumber region of the spectrum contain contributions of several internal coordinates and their assignment is a reduction approximation to one of two of the internal coordinates. As it can be seen from Table 3 and Figs. 3 and 4, vibrational spectra of Pd chloro complex show two IR and two Raman bands at  $348 \text{ cm}^{-1}$  (IR),  $344 \text{ cm}^{-1}$  (R),  $322 \text{ cm}^{-1}$ (IR), 293 cm<sup>-1</sup> (R) and two IR and one Raman bands at 211 cm<sup>-1</sup> (IR),  $127 \text{ cm}^{-1}$  (R),  $114 \text{ cm}^{-1}$  (IR) which can be attributed to  $\nu$ (Pd–Cl) and  $\nu$ (Pd–N) stretches, respectively. However, vibrational spectra of Hg chloro complex show three IR and two Raman bands at 331 cm<sup>-1</sup> (IR), 324 cm<sup>-1</sup> (IR), 315 cm<sup>-1</sup> (R), 269 cm<sup>-1</sup> (IR), 267 cm<sup>-1</sup> (R) and two IR and two Raman bands at  $229 \, \text{cm}^{-1}$  (IR),  $210 \, \text{cm}^{-1}$ (R), 118 cm<sup>-1</sup> (R), 93 cm<sup>-1</sup> (IR) which can be attributed to  $\nu$ (Hg–Cl) and  $\nu$ (Hg–N), respectively. The observed values for  $\nu$ (M–N) and  $\nu$ (M–Cl) stretches are in compliance with the previously reported data for palladium and mercury chloro complexes of various ligands



Fig. 6. Plot of the calculated vs. experimental frequencies of  $M(pp)_2Cl_2$  (M = Pd (a and b) or Hg (c and d)).



Fig. 7. The atomic orbital compositions of the frontier molecular orbital for M(pp)<sub>2</sub>Cl<sub>2</sub> (M = Pd (a) or Hg (b)).

[37,38]. This suggests that the palladium and mercury chloro complexes have structure in which the palladium and mercury atoms are in square planar and tetrahedral environments, respectively.

The differences between the calculated and experimental values for the some vibrational modes are often attributed to the neglect of anharmonicity and incomplete inclusion of electronic correlation effects. Additional reasons of these differences are the truncated basis sets and approximations used in the B3LYP computational model. As it can be seen from Table 3 and Figs. 2–5, there is a good agreement between the experimental and theoretical vibrational frequencies. In order to compare the experimental frequencies, we have found the correlation graphics based on the average theoretical and experimental data. The correlation values between the experimental and calculated vibrational frequencies are found to be 0.9990 (IR and R) for Pd and 0.9990 (IR) and 0.9989 (R) for Hg halide complexes. It can be seen that the B3LYP/Lanl2dz calculation is reliable for vibrational spectra and the results for Hg and Pd metals are consistent with together (Fig. 6).

As it can be seen from Table 3, if the vibrational assignments are investigated one-by-one for both metals, the assignments are generally consistent with together. When it is paid a special attention on PED data for these compounds, however, some values are somewhat different. Regarding the calculated fundamentals, in general, the computed vibrational intensities in the gas phase are in reasonable agreement with the experimental results in both high and low frequency regions. It is also important to note that calculations have been performed for a single structure in the gaseous state contrary to the experimental values recorded in the presence of intra- and intermolecular interactions.

The HOMO describes the ability to donate an electron and LUMO as an electron acceptor. The absorption of electronic transition is defined from the ground to the first excited state. In other words, the transitions can be described from HOMO to LUMO. The HOMO is located over all carbon atoms of pp whereas the LUMO dominate for Pd or Hg metal atoms and N atoms of pp which are bounded to metals. The atomic compositions of frontier molecular orbital and their orbital energies for palladium and mercury halide complexes are shown in Fig. 7.

# 5. Conclusion

The experimental and theoretical vibrational investigations of palladium and mercury chloro complexes of pp are successfully

performed by using FT-IR, FT-Raman and quantum chemical calculations. In conclusion, following results can be summarized:

- (1) The pp molecules in the compounds presented which are further examples of metal halide complexes are coordinated in the chair form as a unidentate ligand coordinating only through the NH nitrogen.
- (2) Comparing the computed vibrational frequencies with the infrared experimental data, a scaling factor such as 0.9923 is derived for B3LYP/Lanl2dz level in the  $M(pp)_2Cl_2$  (M = Pd or Hg) complexes.
- (3) The energy of the Pd complex is lower than that of the Hg complex is not characteristic on the chemical system. However, it is the result of the Lanl2dz effective core potentials used for Pd and Hg.
- (4) Theoretical applications of B3LYP/Lanl2dz for  $M(pp)_2Cl_2$ (M = Pd or Hg) complexes are in agreement with the experimental values. Theoretical results for vibrational data of Hg and Pd metals have similar trends with correlation coefficients values of 0.9990.
- (5) Results indicate that B3LYP method with Lanl2dz effective core basis set also makes easier the understanding of vibrational spectrum and structural parameters of the metal halide complexes.

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