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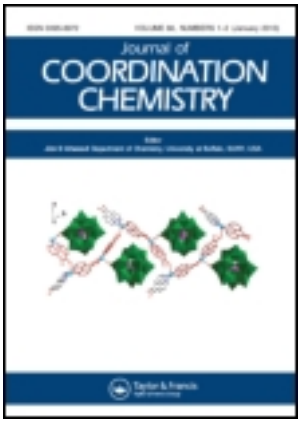

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X-ray structure and theoretical studies on a palladium(II) Schiff base complex

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X-ray structure and theoretical studies on a palladium(II) Schiff base complex

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Treatment of *N,N′*-bis(salicylidene)-1,2-cyclohexanediamine (H_2L) with $PdCl_2$ in the presence of triethylamine afforded [Pd(N_2O_2)]. Recrystallization in chloroform and acetonitrile (1 : 1) gave suitable crystals for X-ray crystallography. The solid-state structure shows that the environment around palladium is square planar. The structural parameters of the molecule obtained by density functional theory (DFT) calculation in the gas phase and by X-ray diffraction are compared. The Pd(II) Schiff base complex adopts planar geometry by DFT calculation. The coordination site structural parameters, which are obtained from geometry optimization calculation, are close to those from X-ray crystallographic data. The spectral properties such as vibrational frequencies, chemical shifts, electronic excitation and the natural bond orbital analyses of Pd(Salen) are calculated, analyzed and compared with experimental data.

Keywords: Palladium(II) complex; Crystal structure; Schiff base; DFT calculation

1. Introduction

Schiff bases and their complexes are important compounds with useful properties such as fluorescence [1], nonlinear optical [2], luminescence [3], magnetic [4], mesomorphic [5] and biological activity [6]. Many efforts have been devoted to syntheses and applications in catalysis [7], polymerization [8] and stereoselective organic transformations [9]. Palladium(II) Schiff base complexes are suitable for Suzuki cross-coupling reactions [10], oligomerization of ethylene [11] and the Heck reaction [12]. The chemistry of square planar palladium(II) complexes of nitrogen and oxygen donors have enormous biological importance [13–16].

Herein, we report synthesis of a palladium(II) Schiff base complex. X-ray diffraction is used to identify the molecular structure. Geometry and natural bond behaviors can be predicted by density functional theory (DFT) calculations. The UV–vis, ^{1}H NMR and

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frequency analyses, which were obtained from experimental and DFT calculations, are also compared with each other. With experimental techniques in hand, the DFT method would be suitable for providing assignment of experimental spectra [17–20]. The synthesis of very similar palladium complexes in which the tetradentate N_2O_2 donor coordinated to the metal center was reported by Shimazaki *et al.* They used the DFT method to study structures in solution and solid states [21].

2. Experimental

2.1. *Materials and instruments*

All solvents, starting reagents and metal salt were obtained from Aldrich and used without purification. FT-IR, UV–vis and ^{1}H NMR spectra were measured on FT-IR 8400-SHIMADZU, SHIMADZU model 2550 and Bruker BRX 100 AVANCE spectrometers, respectively. Elemental analyses were carried out with a Thermo Finnigan Flash Elemental Analyzer 1112EA. Conductivity measurement was determined at room temperature on a Metrohm 712 Conductometer using 1×10^{-3} M solution in DMSO. X-ray single crystal structure was determined on a Bruker-Nonius Kappa CCD diffractometer.

2.2. *Computational procedure*

Becke's three-parameter hybrid (B3LYP) level [22–24] was selected for DFT [25] calculations by the basis set of 6-311G++(d,p) for the H, C, N and O atoms and Lanl2dz [26] basis set for the metal center using Gaussian 98 [27]. The geometry optimization was carried out without symmetry constraints. The ^{1}H NMR, TD-DFT, natural bond orbital (NBO) and frequency calculations were performed at the same level. For ^{1}H NMR and UV–vis calculations, we applied the polarized continuum model [28–30]. The optimized geometry in the gas phase was used as the initial geometry for the calculation in solution. Thus, the optimized geometry that was calculated in solution was used for ^{1}H NMR and UV–vis calculations.

2.3. *Crystal structure determination*

Data were collected at room temperature with a Bruker-Nonius Kappa CCD using MoK_α radiation ($\lambda = 0.71073$ Å). Absorption correction was applied using SADABS. The structure was solved using direct methods with the SHELXTL NT 6.12 software package [31]. Scattering factors were taken from the literature [32]. All non-hydrogen atoms were refined anisotropically by full matrix least squares on F^2 using SHELXL [33]. All hydrogens were placed at calculated positions and constrained to ride on their parent. The experimental details of the X-ray data collection, the structure solution, and refinement of the title compound are gathered in table 1.

2.4. *Synthesis of N,N'-bis(salicylidene)-1,2-cyclohexanediamine, H_2L*

Salen (H_2L) was prepared according to the literature method [34]. Salicylaldehyde (2.44 g, 20 mmol) was added to an ethanolic solution (10 mL) of 1,2-cyclohexanediamine (1.14 g,

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Table 1. Crystal data and structure refinement for Pd(II) complex.

Empirical formula	$C_{20}H_{20}N_2O_2Pd$
Formula weight	426.78
Temperature (K)	150(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	*P-1*
Unit cell dimensions	$a = 7.5218(3)$ Å, $b = 9.4195(3)$ Å, $c = 12.5131(3)$ Å $\alpha = 106.890(2)°$, $\beta = 93.981(3)°$, $\gamma = 93.014(3)°$
V (Å^3)	843.82(5)
Z	2
D_{calcd} (mm^{-1})	1.680
Absorption coefficient	1.115
$F(000)$ (mm^{-1})	432
Crystal size (mm)	$0.24 \times 0.09 \times 0.04$
θ Range for data collection (°)	3.22–28.70
Limiting indices	$-10<=h<=10$, $-12<=k<=12$, $-16<=l<=16$
Reflections collected/unique	25,347/4344 [R(int) = 0.0500]
Completeness to θ	99.9%
Absorption correction	Semi-empirical from equivalents
Max/min transmission	1.0 and 0.845
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4343/0/226
Goodness-of-fit on F^2	1.046
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0243$, $wR2 = 0.0515$
R indices (all data)	$R1 = 0.0317$, $wR2 = 0.0538$
Largest difference peak and hole (e Å^{-3})	0.605 and -0.544 e A^{-3}

10 mmol). The yellow solution was refluxed at 100 °C for one hour. A yellow precipitate was separated after cooling, which was washed several times with cold ethanol and dried in vacuum. Yield: 5.2 g (82%). m.p. 98 °C. Elemental analysis for $C_{20}H_{22}N_2O_2$: Calcd C, 74.51; H, 6.88; N, 8.69. Found: C, 74.20; H, 6.78; N, 8.63.

2.5. *Synthesis of (N,N'-bis(salicylidene)cyclohexane-1,2diamine)-palladium(II)*

A methanolic solution of H_2L (0.645 g, 2 mmol) and triethylamine (0.404 g, 4 mmol) was added dropwise to a suspension of $PdCl_2$ (0.354 g, 2 mmol) in methanol at room temperature and then stirred for 12 h. The yellowish precipitate was separated and washed several times with cold methanol and dried in vacuum. Yield: 0.537 g (63%), m.p. 238 °C. Elemental analysis for $C_{20}H_{20}N_2O_2Pd$: Calcd C, 56.28; H, 4.72; N, 6.56. Found: C, 55.20; H, 4.81; N, 6.43. Molar conductivity (1.0×10^{-3} M; DMSO): 11 Ω^{-1} cm^2 mol^{-1}.

3. Results and discussion

A yellowish precipitate is separated by reaction of $PdCl_2$ and H_2L in a 1 : 1 mol ratio in the presence of triethylamine. The complex is purified by crystallization, on slow evaporation of a solution in acetonitrile-chloroform (1 : 1, v/v). The complex is soluble in DMF and DMSO but less soluble in common organic solvents, such as alcohols, chloroform and acetonitrile, and is insoluble in hexane, benzene, and toluene. The molar conductivity of the complex in DMSO (11 Ω^{-1} cm^2 mol^{-1}) shows nonelectrolytic behavior.

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3.1. *Crystal description*

The molecular structure of the palladium(II) Schiff base complex is shown in figure 1 and selected bond lengths and angles are given in table 2. The Pd(II) complex crystallizes in the triclinic *P-1* space group with unit cell parameters $a = 7.5218(3)$ Å, $b = 9.4195(3)$ Å, $c = 12.5131(3)$ Å, $\alpha = 106.890(2)°$, $\beta = 93.981(3)°$ and $\gamma = 93.014(3)°$ with two molecules in the unit cell (see figure 2). Coordination around palladium is square planar with L^{2-} coordinated tetradentate to palladium. Pd–N/O distances are in accord with reported values [35, 36]. The Pd-O distance, as in other palladium(II) complexes with Schiff bases, is slightly longer than the Pd–N distance [37, 38]. The Pd–N bond distance, 1.96 Å, is close to the sum of the covalent radii of palladium and nitrogen, suggesting strong coordination through the azomethine nitrogens. Four bond angles around the central ion are O(1)–Pd(1)–O(2) 87.89°, O(1)–Pd(1)–N(1) 94.25°, O(2)–Pd(1)–N(2) 93.92° and N(1)–Pd(1)–N(2) 84°. Because of forming a five-member chelating ring, N(1)–Pd(1)–N(2)–C(13)–C(8), the N(1)–Pd(1)–N(2) angle is smaller and this affects the other angles [39]. The bite angles O(1)–Pd(1)–N(2) and O(2)–Pd(1)–N(1) of 177° and 176° are slightly less than expected, 180°, which can be attributed to strain imposed by forming the chelating ring. The angles between the [O(1)–N(1)–N(2)–O(2)] plane and the planes containing [C(7)–C(6)–C(1)–O(1)–Pd(1)–N(1)] and [O(2)–C(20)–C(15)–C(14)–N(2)–Pd(1)] are 4.76° and 7.89°, respectively. The cyclohexane ring exists in chair configuration, similar to earlier report on this class of compounds [40]. The partial double bond character of C(6)–C(7) and C(14)–C(15) may be due to co-planarity of the two chelating rings with the adjacent benzene rings (ca. 8.2° between [C(19)–C(20)–C(15)–C(16)–C(17)–C(18)], [O(2)–Pd(1)–N(2)–C(14)–C(15)–C(20)] and ca. 6.79° between [C(20)–C(19)–C(18)–C(17)–C(16)–C(15)], [Pd(1)–N(2)–C(14)–C(15)–C(20)–O(2)]), supporting a large π-electron delocalization.

3.2. *Geometry optimization and NBO analyses*

The geometry of the palladium complex is optimized at lanl2dz for palladium and B3LYP level using 6-311++G(d,p) basis set for the other atoms to better reproduce structural parameters. Many articles suggest these basis sets to reproduce physico-chemical data [41, 42]. The basis set 6-311++G(d,p) is used on heavy atoms to better interpret compounds involving polar bonds [43, 44].

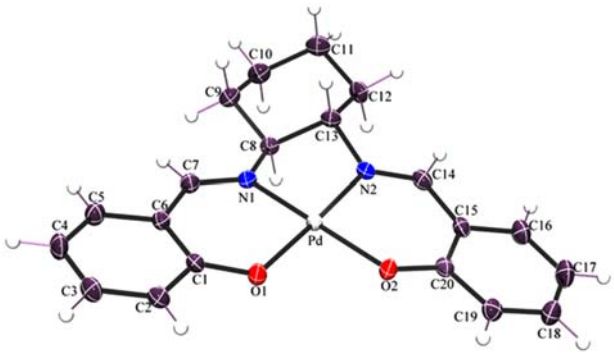

Figure 1. ORTEP drawing of $[Pd(N_2O_2)]$.

Table 2. Selected bond lengths (Å) and angles (°) in the experimental and at the B3LYP/6-311++G calculation level in the gas and solvation phases.

Type	Exp. (Å)	Calcd (Å)[a]	Calcd (Å)[b]	Type	Exp. (°)	Calcd (°)[a]	Calcd (°)[b]
Pd(1)–O(1)	1.9964	2.0368	2.0495	O(1)–Pd(1)–O(2)	87.89	90.00	89.79
Pd(1)–O(2)	2.0096	2.0368	2.0495	O(1)–Pd(1)–N(1)	94.25	93.08	93.15
Pd(1)–N(1)	1.9646	2.0025	1.9994	O(1)–Pd(1)–N(2)	177.86	176.28	176.35
Pd(1)–N(2)	1.9656	2.0025	1.9994	O(2)–Pd(1)–N(1)	176.79	176.28	176.35
O(1)–C(1)	1.3143	1.2920	1.3035	O(2)–Pd(1)–N(2)	93.92	93.08	93.15
O(2)–C(20)	1.3121	1.2920	1.3035	N(1)–Pd(1)–N(2)	84.00	83.90	83.98
N(1)–C(7)	1.2870	1.2955	1.2902	Pd(1)–O(1)–C(1)	123.86	124.45	123.98
N(1)–C(8)	1.4877	1.4797	1.4850	Pd(1)–O(2)–C(20)	123.28	124.45	123.98
N(2)–C(13)	1.4910	1.4797	1.4850	Pd(1)–N(1)–C(7)	125.19	124.45	124.69
N(2)–C(14)	1.2845	1.2955	1.2902	Pd(1)–N(1)–C(8)	111.95	111.30	111.28
C(1)–C(6)	1.4367	1.4425	1.4380	C(7)–N(1)–C(8)	122.70	123.93	123.85
C(6)–C(7)	1.4399	1.4308	1.4407	Pd(1)–N(2)–C(13)	111.55	111.30	111.28
C(8)–C(13)	1.5287	1.5437	1.5412	Pd(1)–N(2)–C(14)	125.08	124.45	124.69
C(14)–C(15)	1.4454	1.4308	1.4407	O(1)–C(1)–C(2)	118.02	117.31	117.47
C(15)–C(20)	1.4274	1.4425	1.4380	O(1)–C(1)–C(6)	125.06	125.90	125.56
				N(1)–C(7)–C(6)	126.15	127.24	127.07
				N(1)–C(8)–C(9)	116.51	116.25	116.12
				N(1)–C(8)–C(13)	106.88	107.47	107.32
				N(2)–C(13)–C(8)	105.75	107.47	107.32
				N(2)–C(13)–C(12)	115.21	116.25	116.12
				N(2)–C(14)–C(15)	125.98	127.24	127.07
				O(2)–C(20)–C(15)	125.68	125.90	125.56
				O(2)–C(20)–C(19)	117.16	117.31	117.47

[a]Calculated in gas phase.
[b]Calculated in solvation phase.

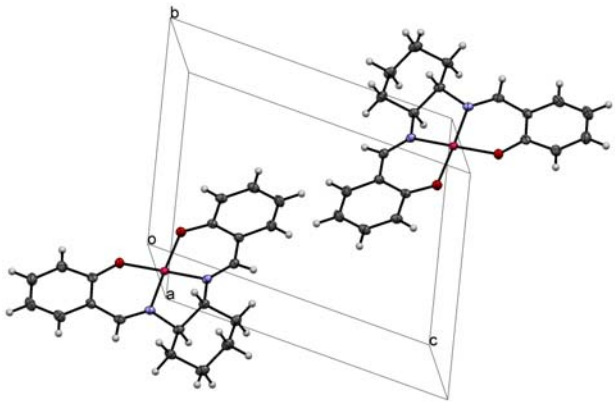

Figure 2. Unit cell of [Pd(N_2O_2)].

The optimized geometry was used in the vibrational frequency. The lack of any imaginary frequency in the calculation showed that the structure of the Pd(II) complex is fully optimized. Agreement between structural parameters from DFT calculation and X-ray crystallography is good. A little difference in the bond distances and angles may be due to the X-ray crystal diffraction in the solid state while the theoretical calculations were performed without considering chemical environment [45]. The calculated bond lengths and angles are given in table 2. The Pd(1)–O(1) bond distance and O(1)–Pd(1)–O(2) bond angle obtained by DFT differ by 0.04 Å and 2.11° from the crystallographic results. The dipole

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Table 3. Natural charges and natural electron configuration calculated in the gas phase.

Atom	NPA charges	Natural electron configuration
Pd	0.876	[core] 5S(0.34) 4d(8.77)
O	−0.674	[core] 2S(1.66) 2p(4.94)
O	−0.674	[core] 2S(1.66) 2p(4.94)
N	−0.501	[core] 2S(1.29) 2p(4.15)
N	−0.501	[core] 2S(1.29) 2p(4.15)

moment of the Pd(II) complex was evaluated as 7.6 Debye in the *XY* plane, showing all electronegative atoms located within the plane in a square plane.

The natural charges from natural population analyses for the donor and metal were calculated in the gas phase and presented in table 3. The formal charges on oxygen and nitrogen are calculated to be −0.674 a.u. and −0.501 a.u., respectively, showing that electron distribution is not limited just to coordination bonds. The 0.874 a.u. computed formal charge of central ion is smaller than defined +2, indicating charge donation of donors to palladium [46]. The electron population in the s and p orbitals of donors are less than defined values for related valence orbitals ($2s^2$ $2p^6$ and $2s^2$ $2p^5$, respectively), while the calculated electron configuration for palladium is more than the defined value for Pd(II) with d^8 electron configuration.

3.3. *^{1}H NMR study*

The ^{1}H NMR spectrum was recorded in DMSO and the atomic numbering view of the complex is depicted in scheme 1. Experimental and calculated chemical shifts are presented in table 4. The theoretical results are consistent with the experimental values, confirming selection of B3LYP/6-311++G(d,p) level for the calculation. The absence of the OH peak shows coordination takes place by deprotonated phenolic oxygen. Also, the upfield shift of the azomethine proton (HC=N) reveals complexation through the azomethinic nitrogen. Theoretically signals at 1.28–2.53 ppm are related to (H_{10}, H_{11}) and (H_9, H_{12}) protons of cyclohexane. The signals of these protons appear experimentally at 1.28–2.37 ppm as a multiplet. H_8 and H_{13} are at 3.35–3.7 ppm in the experimental and theoretical spectra, respectively. The experimental signals of aromatic ring protons are 6.52–7.38 ppm, relatively close to those obtained, 6.57–7.75 ppm, by calculation.

3.4. *Electronic structure and UV–vis study*

Some occupied and unoccupied molecular orbitals of mentioned Pd(II) complex are shown in Supplemantary material.doc. HOMO, HOMO-4 and HOMO-6 are localized on both ligand and palladium, whereas LUMO is completely on the ligand. LUMO + 2 is localized on palladium and coordination environment. Table 5 presents the assignment of the spin-allowed singlet–singlet electronic transitions calculated with the TD-DFT method and the experimental bands for [Pd(N_2O_2)]. The electronic absorption spectrum was measured at room temperature in DMSO. The experimental band at 310 nm is attributed to LLCT and MLCT bands, which can be correlated to the band at 346 nm by theoretical calculation. The observed experimental band at 410 nm is due to HOMO-6, HOMO-4 and HOMO to LUMO+2 transitions and can be assigned as mixtures of LMCT and d–d bands.

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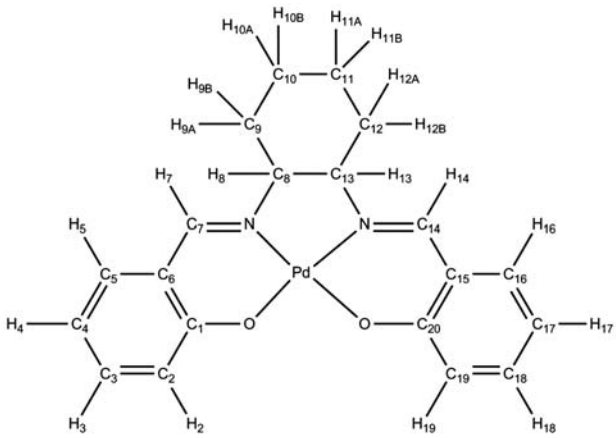

Scheme 1. The view of the palladium complex for ^{1}H NMR assignment.

Table 4. The hydrogen chemical shifts (δ, ppm) in DMSO-d_6 and calculated at B3LYP/6-311++G(d,p) level in solution.

Atoms	Calculation	Experimental
H_7, H_{14}	7.75	8
H_3, H_{18}	7.4	7.38
H_2, H_{19}	7.2	7.14
H_5, H_{16}	7	6.97
H_4, H_{17}	6.57	6.52
H_8, H_{13}	3.7	3.35
H_{10}, H_{11}	1.28	1.28–2.37
H_9, H_{12}	2.53	

3.5. *Vibrational assignments*

Experimentally and theoretically IR spectra of the Pd(II) complex are shown in Supplementary Material. The Pd(II) complex belongs to C1 point group and shows many peaks in the infrared spectrum. Important harmonic vibrational wavenumbers computed at the B3LYP/6-311G++(d,p) level and the corresponding experimental values are tabulated in table 6. The calculated frequencies were scaled by scale factor 0.968 [47]. The absence of ν(OH) in the IR spectrum of the complex confirms that L is coordinated in its deprotonated form [48, 49]. Pd(N_2O_2) exhibits a band at 3080 cm^{-1} due to CH stretch of aromatic rings and the calculated values are 3017–3093 cm^{-1} [50]. Two bands at 2931 and

Table 5. The experimental absorption bands and the predicated electronic transitions calculated with the TD-DFT method.

Orbital excitation	λ (nm)	Oscillator strength	Character	Experimental λ (nm), log ε
HOMO → LUMO	346	f = 0.0536	LLCT, MLCT	310 (4.02)
HOMO-6 → LUMO+2			d–d, LMCT	
HOMO-4 → LUMO+2	464	f = 0.0011	d–d, LMCT	410 (3.98)
HOMO → LUMO+2			d–d, LMCT	

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Table 6. Selected vibrational wavenumbers calculated for Pd(II) at B3LYP/6-311++G(d,p) level in the gas phase.

Exp. (cm^{-1})	Calcd (cm^{-1}) (unscaled)	Calcd (cm^{-1}) (scaled)	Vibrational assignments
563w	565	546	Cyclohexane ring flipping
690w	693	670	aromatic ring flipping
748m	764	739	$\delta_{o.p.b}$(CH)
1001w	1035	1001	ν(C–N) + $\delta_{o.p.b}$(CH)
1026m	1054	1020	ν(C–N)
1130m	1166	1128	ν(C–C)
1149mw	1176	1138	$\delta_{i.p.b}$(CH)
1191m	1218	1179	$\delta(CH_2)$
1249m	1266	1225	$\delta(CH_2)$ + $\delta_{i.p.b}$(CH)
1319m	1361	1317	$\delta(CH_2)$
1345s	1397	1352	ν(C–O)
1430m	1475	1427	$\delta_{i.p.b}$(CH) + ν(C=C)
1445s	1550	1500	ν(C=N) + ν(C=C)
1585s	1648	1595	ν(C=C)
1601vs.	1659	1605	ν(C=N)
2854w	2982–3023	2886–2926	$\nu_{sy}(CH_2)$
2931mw	3062–3117	2964–3017	$\nu_{asy}(CH_2)$
3080w	3117–3196	3017–3093	ν(CH)

Abbreviations: vs.: very strong; s: strong; ms: medium strong; m: medium; w: weak; vw: very weak; o.p.b: out of plane bending; i.p.b: in plane bending; sy: symmetric; asy: asymmetric.

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2854 cm^{-1} correspond to asymmetric and symmetric vibrations of CH_2 of cyclohexane [51]. Frequency calculation suggests that these bands are 2964–3017 and 2886–2926 cm^{-1}, respectively. The very strong C=N stretch at 1601 cm^{-1} in the experimental is calculated at 1605 cm^{-1}, shifted to lower frequency upon coordination of the azomethine, in agreement with data reported for the related complex [52–54]. Also, two strong bands at 1585 and 1445 cm^{-1} compared to theoretical bands of 1595 and 1500 cm^{-1}, are due to ν(C=C) and a mixture of ν(C=C) and ν(C=N), respectively [55, 56].

In-plane bending of CH of azomethine and benzene rings is at 1149 cm^{-1}. This vibration is mixed with ν(C=C) and $\delta(CH_2)$ to two bands at 1430 and 1243 cm^{-1}, respectively [57]. The related values by calculation are 1427 and 1225 cm^{-1}. The ν(C–O) with strong intensity at 1345 cm^{-1}, computed at 1352 cm^{-1}, red shifts to lower frequency in the complex [58]. This displacement confirms coordination by deprotonated OH. There are bands at 1319 and 1191 cm^{-1} which correspond to wagging and twisting of CH_2 of cyclohexane [59]. The computed wavenumbers are assigned at 1317 and 1179 cm^{-1}, respectively. The ν(C–C) and ν(C–N) of cyclohexane are at 1130 and 1026 cm^{-1} [60, 61] (1128 and 1020 cm^{-1} by calculation). The out-of-plane bending of CH-aromatic is at 748 cm^{-1} with medium intensity. This band mixes with ν(C–N) at 1001 cm^{-1} [62]. The theoretical values are computed at 739 and 1001 cm^{-1}, respectively. The cyclohexane and aromatic ring flipping modes are at 563 and 690 cm^{-1}, respectively [63, 64], calculated to be at 546 and 670 cm^{-1} by DFT.

4. Conclusions

A palladium(II) complex, Pd(ONNO)], is synthesized by reaction of Pd(II) chloride with *N,N′*-bis(salicylidene)-1,2-cyclohexanediamine (H_2L) and characterized by elemental analysis, molar conductance, FT IR, UV–vis and ^{1}H NMR spectroscopies, and by X-ray

diffraction analysis. Coordination around palladium was square planar and L^{2-} was tetradentate. To gain further insight into the spectral properties, results based on DFT calculations and experimental data were compared. The structure of the Pd(II) Schiff base complex was optimized and its vibrational frequencies, ^{1}H NMR, UV–vis and NBO analyses investigated.

Supplementary data

CCDC 888715 contains the supplementary crystallographic data for palladium complex. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk.

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