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A palladium(II) complex containing both carbonyl and imine oxime ligands: Crystal structure, experimental and theoretical UV–vis, IR and NMR studies

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HIGHLIGHTS

- A palladium(II) complex containing imine and carbonyl oximes has been synthesized.
- The compound has been characterized by UV–Vis, IR, NMR and X-ray crystallography.
- Theoretical UV–Vis, IR and NMR spectra have been calculated using DFT.
- Theoretical calculations have been compared with observed spectra.

G R A P H I C A L A B S T R A C T

A new palladium(II) complex with an imine oxime and carbonyl oxime has been synthesized and characterized. This paper reports structural and spectroscopic characterization of the complex by using both experimental methods such as X-ray, UV–vis, IR and NMR, and quantum chemical calculations.



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ABSTRACT

A new palladium(II) complex, [Pd(ppeieo)(inap)]-DMSO (ppeieo = (1*E*,2*E*)-phenyl-[(1-phenyl-ethyl)imino]-ethanal oxime and inap = isonitrosoacetophenone) has been synthesized and characterized by elemental analysis, UV–vis, IR, NMR. X-ray diffraction analysis of the DMSO solvate of the complex shows that the palladium(II) ion is coordinated in a distorted square-planar geometry by ppeieo and inap, which is formed during the hydrolysis of ppeieo. DFT (B3LYP/LANL2DZ) calculations on the complex have been carried out to correlate geometry and spectroscopic properties such as electronic, vibrational and NMR chemical shifts. The complete vibrational frequency assignments were made and the calculation results were applied to simulate infrared spectra of the title compound which shows good agreement with observed spectra. The calculated HOMO and LUMO energies show that several transitions including the $\pi \rightarrow \pi^*$ and charge transfer occur within the molecule. The chemical shifts reasonably correspond to the calculated spectra.

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Introduction

Oximes have often been used as chelating ligands in the field of coordination chemistry and their metal complexes have been of great interest for many years [1–7]. The oxime and oximate species display different coordination modes such as monodentate (N or O), bidentate chelating (N, O) and bridging (N, O) [7–12]. Owing to their coordination ability, they have been extensively used in analytical chemistry for detection and separation of metal ions [13–17]. Moreover, some oximes and their complexes have been reported to have significant biochemical activity [18–24].

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In recent years, much attention has been given to theoretical studies on oximes and their complexes. Experimental studies of oximes and metal-oximes have been matched by theoretical calculations. Density functional theory (DFT) and other theoretical methods provided geometry optimization of isomers [25-38], and allowed to study reaction mechanisms [39-42] and spectroscopic properties (UV-vis, IR, Raman and NMR) [43-51] of some oximes. On the other hand, synthesis of imine-oximes and their complexes is one of the challenging areas in the field of the oxime-coordination chemistry. Imineoximes containing schiff base and oxime groups have been extensively studied because of their biological and structural importance which lies mainly in their specific and selective reactions with metal ions [52–57]. However, theoretical studies of imine oximes and their metal complexes have received less interest. Recently, we reported a combined experimental and theoretical study of an imine oxime, namely (1E,2E)-phenyl-[(1-phenylethyl)imino]-ethanal oxime (ppeieo) [58]. The cisoid and transoid conformations of E- and Z-isomers of this compound have been identified. In addition, electronic and vibrational absorption bands have been characterized using DFT.

The first palladium(II) complex of oximes was $[Pd(dmgH)_2]$ (dmgH = dimethylglyoximate) [59], while 3-hydroxyiminopentane-2,4-dionato(pentane-2,4-dionato)palladium(II) and bis-(3hydroxyiminopentane-2,4-dionato)palladium(II) complexes were the first examples of the palladium(II) complexes of imine oximes [60]. In the present work, we report synthesis and crystal structure of a palladium(II) complex, [Pd(ppeieo)(inap)].DMSO, containing an imine oxime (ppeieo) together with a carbonyl oxime namely isonitrosoacetophenone (inap). The results of the theoretical and spectroscopic studies are presented. Theoretical data were calculated at the DFT/B3LYP level of theory. A complete vibrational analysis including corresponding assignments together with the PED was performed by combining the measured and calculated data. The UV-vis spectroscopic studies along with HOMO, LUMO analysis have been used to elucidate electronic transitions within the complex. Both calculated and experimental NMR chemical shifts have been compared.

Experimental

Measurements

The elemental analyses (C, H and N) were performed using a EuroEA 3000 CHNS elemental analyzer. UV–vis spectra were measured on a Perkin–Elmer Lambda 35 UV/vis spectrophotometer using quartz cuvettes and 1×10^{-4} M DMSO solution in the 200–800 nm range. IR spectra were recorded on a Thermo Nicolet 6700 FT-IR spectrophotometer as KBr (in the frequency range 4000–400 cm⁻¹) and CsI (in the frequency range 400–250 cm⁻¹) pellets. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on a Varian Mercury plus spectrometer in DMSO- d_6 and TMS was used as an internal standard.

Synthesis of the palladium(II) complex

The imineoxime ligand was synthesized according to the procedure described in the literature [58]. A solution of a ligand (0.126 g, 0.5 mmol) in ethanol (30 mL) was added drop wise with stirring to a solution of Na₂[PdCl₄] (0.147 g, 0.5 mmol) in water (10 mL). The mixture was stirred for 4 h at room temperature. The volume of the solutions was reduced to 10–15 mL under vacuum and then the resulting precipitate was filtered, and dried in air. Yield 83%. M.p. 141–143 °C (decomp.); *Anal.* Calc. for C₂₄H₂₁N₃O₃Pd (505.9 g mol⁻¹): C, 56.98; H, 4.18; N, 8.31. Found: C, 56.18; H, 4.42; N, 7.98%. X-ray quality orange crystals of the palladium(II) complex were obtained by the slow evaporation of the DMSO solution at room temperature within two days.

X-ray crystallography

The intensity data of the palladium(II) complex were collected using a STOE IPDS 2 diffractometer with graphite-monochromated Mo K α radiation (λ = 0.71069 Å). The structures were solved by direct methods and refined on F^2 with the SHELX-97 program [61]. All non-hydrogen atoms were found from the difference Fourier map and refined anisotropically. All hydrogen atoms were positioned geometrically and refined by a riding model. The details of data collection, refinement and crystallographic data are summarized in Table 1.

Theoretical methods

All calculations were conducted using density functional theory (DFT) as implemented in the GAUSSIAN 03 program package [62]. The geometry of the palladium(II) complex was fully optimized at restricted B3LYP [63] and LANL2DZ level in the gas phase. The atomic coordinates of the complex excluding the DMSO solvate in the crystal structure were used for ab initio calculations. The vibrational frequencies of the complex were calculated using the same method. The frequency values computed at this level contain known systematic errors and therefore, we have used a scaling factor: A modified wavenumber-linear-scaling (WLS) approach [64,65] was employed after completing the vibrational mode assignment for complex. This method was derived by determining the best-fit linear function between the experimental and theoretical data. The resulting functions are shown in the following equations:

y = 0.7328x + 682.47	$(R^2 = 0.98)$	for $4000-1700 \text{ cm}^{-1}$	(1)
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$$y = 1.0222x - 63.907$$
 ($R^2 = 0.99$) for 1700–250 cm⁻¹ (2)

Table 1

Crystallographic data and structure refinement for [Pd(ppeieo)(inap)]·DMSO.

Formula	$C_{24}H_{21}N_3O_3PdC_2H_6OS$
Molecular weight	583.97
Temperature	298(2)
Wavelength	0.71069 Å
Crystal system	Triclinic
Space group	PĪ
Unit cell dimensions	
a (Å)	9.936(5)
b (Å)	11.701(5)
<i>c</i> (Å)	12.030(5)
α (°)	103.729(5)
β (°)	100.791(5)
γ (°)	103.179(5)
Volume (Å ³)	1279.1(10)
Ζ	2
Calculated density (g/cm ³)	1.516
$\mu (\mathrm{mm}^{-1})$	0.844
F(000)	596
θ range (°)	1.80-26.00
Index ranges	$-12\leqslant h\leqslant 12$, $-14\leqslant k\leqslant 14$,
	$-14 \leqslant l \leqslant 14$
Reflections collected	17204
Independent reflections	$5027 [R_{int} = 0.0664]$
Reflections observed (> 2σ)	3469
Absorption correction	Integration
Max. and min. transmissions	0.9158 and 0.7757
Data/parameters	5027/316
Goodness-of-fit on F^2	0.818
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0327 \ wR_1 = 0.0545$
Largest diff. peak and hole (e $Å^{-3}$)	0.334 and -0.384
CCDC No	912128



Fig. 1. Molecular views of [Pd(ppeieo)(inap)]-DMSO. (a) X-ray structure and (b) optimized structure (DMSO not included).

The assignment of the calculated frequencies is aided by the animation option of GaussView 3.0 graphical interface for Gaussian programs, which gives a visual presentation of the shape of the vibrational modes [66]. Furthermore, theoretical vibrational spectra of the title compound were interpreted by means of PEDs using VEDA 4 program [67].

¹H and ¹³C NMR chemical shifts (δ_H and δ_C) of complex were calculated using the GIAO method [68] in DMSO at the B3LYP/LANL2DZ level and using the TMS shielding calculated as a reference.

Transition energies and oscillator strengths for electronic excitation to the first 48 singlet excited states of the complex were calculated using TD-DFT with the B3LYP/LANL2DZ level. In addition, the electronic absorption spectra were calculated in DMSO solution using the IEFPCM method. Orbital contribution was analyzed using GaussSum software [69].

Results and discussion

Molecular structure of [Pd(ppeieo)(inap)].DMSO

The X-ray and optimized structures of [Pd(ppeieo)(inap)].DMSO are shown in Fig. 1. The title complex crystallizes in a triclinic space group $P\bar{1}$ as a DMSO solvate. The palladium(II) ion is coordinated by two different oxime ligands, ppeieo and inap. As explained in Experimental, in the synthesis of the complex, the ppeieo ligand was aimed to coordinate palladium(II). However, in the presence of water, some of the imine oxime ligands were hydrolyzed during the reaction, resulting in the products of a carbonyl oxime (inap) and the corresponding amine (Scheme 1). Such imine bond (C=N) hydrolysis is common in the reactions of imines and imine oximes [70-75]. Consequently, the ppeieo ligand together with the hydrolysis product (inap) coordinates to palladium(II) forming a square-planar coordination geometry. The ppeieo and inap ligands deprotonate to form the corresponding monoanions. Ppeieo acts as a bidentate chelating ligand via two N atoms, while inap behaves as a bidentate N, O donor. The complex is also the first crystallographically studied palladium(II) complex of the inap ligand. A palladium(II) complex with inap was reported earlier, but its characterization was carried out from a polycrystalline powder [76]. In addition, it was reported that the ppeieo compound is chiral and its crystal structure contains both enantiomers [58]. The crystal structure analysis of the title complex shows the presence of the coordination of each enatiomers of ppeieo to palladium(II). The individual molecules of the complex were connected by two types of weak C-H. O hydrogen bonds $(C \cdots O = 3.26 - 3.39 \text{ Å})$ involving (i) the methyl hydrogen atoms of DMSO molecules and oximate O atoms of imine- and carbonyl oximes in [Pd(ppeieo)(inap)] and (ii) phenyl hydrogens of carbonyl oxime and O atoms of the DMSO molecules to form a two-dimensional network (Fig. 2). It is interesting to note that no obvious $\pi - \pi$ stacking interactions between the phenyl rings of the ligands in the adjacent molecules are present, but some phenyl hydrogens of imine oxime participate to C–H··· π interactions (C···Cg = 3.73 Å, where Cg is the centroid of the phenyl ring) with the phenyl ring of the carbonyl oxime in the neighboring molecules.

The experimental and calculated bond distances and angles for the coordination geometry around palladium(II) are listed in Table 2. 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. The optimized bond values deviate by 0.059 Å than those of the found values. This is consistent with the results obtained by the LANL2DZ/ B3LYP functional used in the calculation of metal complexes [77–



Scheme 1. Synthesis reaction of [Pd(ppeieo)(inap)].



Fig. 2. Packing of molecules of [Pd(ppeieo)(inap)].

Table 2 Selected geometric parameters of [Pd(ppeieo)(inap)].

	Experimental	LANL2DZ
Bond lengths (Å)		
C1–C2	1.422(4)	1.436
C2–C3	1.491(4)	1.497
C9–C10	1.505(4)	1.546
C17–C18	1.402(4)	1.420
C18–C19	1.478(4)	1.482
C19–C20	1.392(4)	1.416
C20–C21	1.386(4)	1.404
C21–C22	1.365(5)	1.409
C22–C23	1.375(5)	1.410
C23–C24	1.376(4)	1.403
C19–C24	1.379(4)	1.416
C9—N2	1.477(4)	1.484
C2—N2	1.293(4)	1.332
C1—N1	1.314(4)	1.351
C18-03	1.267(3)	1.313
C17—N3	1.336(4)	1.366
NI-01	1.259(3)	1.284
N3-02	1.243(3)	1.280
Pd1—N2	2.034(3)	2.081
Pd1—N1	1.989(3)	2.034
Pd1—N3	2.014(3)	2.065
Pd1-03	2.051(2)	2.110
Bond angles (°)		
C1–C2–C3	118.7(3)	117.4
C2–C3–C4	121.4(3)	121.4
C3–C4–C5	120.5(4)	120.4
C4—C5—C6	120.1(3)	120.2
C5–C6–C7	119.9(3)	119.7
C6–C7–C8	120.7(4)	120.2
C3–C8–C7	119.9(3)	120.4
C4–C3–C8	119.0(3)	119.1
$C_2 - C_3 - C_8$	119.6(3)	119.5
	122.3(3)	122.9
$C_2 = N_2 = C_9$	122.1(3)	124.2
CI-C2-N2	116.3(3)	117.1
C3-C2-N2	125.1(3)	125.5
CI = NI = OI	122.3(3)	122.5
$C_2 = C_1 = N_1$	117.1(3)	110.8
C11 - C9 - N2	108.7(3)	110.7
C10-C9-N2	109.8(3)	109.4
C10-C19-C10	110.0(3)	1 14.2 110 1
C19-C17-N2	115.1(3)	116.1
C10 - C17 - 103 C17 - C18 - O2	110.6(2)	110.0
C17 - 03 C17 - 03 - 03	119.0(3)	119.0
N1-Pd1-N2	80 3(11)	120.J QD D
N1—Pd1—N3	101 1(12)	100.2
N3-Pd1-O3	79 9(10)	79.1
N2—Pd1—O3	98.8(10)	100.0
N2—Pd1—N3	177 2(11)	179.0
N1-Pd1-03	178 7(11)	178.1
iii iui 05	1,0.,(11)	170.1



Fig. 3. Experimental and calculated IR spectra of [Pd(ppeieo)(inap)].

82], On the other hand, both calculated and experimental bond angles correlate well with each other within a difference of ca. 2°. The Pd—N(oxime) distances are 1.989(3) and 2.014(3) Å, being typical of those found in palladium(II) complexes of oximes [9,11,59,83–91].

Vibrational spectra

Vibrational assignments were carried out with support of DFT calculations using the B3LYP method with a LANL2DZ basis set having the structural geometry obtained by the same method. The calculated values were scaled as explained in the theoretical methods. The observed and calculated vibrational spectra are given in Fig. 3, while the corresponding frequencies along with the assignments and intensities are given in Table 3. In general, the absorption frequencies obtained from experiment and theory are in good agreement.

Six CH stretching bands were observed in the spectrum of the complex and four of which belongs to the phenyl rings. They appeared as weak bands in the frequency range 2929–3067 cm⁻¹. Significant vibration bands of the ligands and their metal complexes may be used for determining the ligands' mode of coordination by the comparative analysis of the spectra of the ligand and the complex, in particular in relation to the changes observed after complexation. As reported earlier, the imine group (C=N) of ppeieo appeared at 1612 cm⁻¹ and as shown in Table 3, after coordination,

 Table 3

 Experimental FT-IR and DFT-B3LYP/LANL2DZ calculated spectra for [Pd(ppeieo)(inap)] together with their assignment^a (wavenumber in cm⁻¹).

Experimental	Unscaled	Scaled	Intensity	Assignment (PED > 10)
3067w	3244	3060	120,205	vCH _{phen.} (87)
3058w	3236	3054	232,840	vCH _{phen.} (90)
	3233	3052	206,844	vCH _{phen.} (97)
	3223	3044	328,291	vCH _{phen.} (98)
	3222	3044	366,235	vCH _{phen.} (86)
	3221	3043	187,327	vCH _{phen.} (89)
3028w	3214	3038	302,836	vCH _{phen.} (91)
	3213	3037	207,925	vCH _{phen.} (97)
2974w	3137	2981	403,348	vCH _{meth.} asym. (100)
2929w	3058	2923	318,787	vCH _{meth} sym. (95)
1022	3049	2917	138,/54	vCH_{CHNO} (94)
1032111	1652	1625	200,285	$VCO(22), VCC_{phen.}(37)$
1622m	1001	1624	150,370	VCC_{phen} (28)
1025III 1598m	1542	1528	1 243 660	vCC_{1} (28) δCH_{1} (21)
155011	1534	1504	99 591	δCH_{math} (81)
	1523	1493	333.205	δCH_{meth} (25)
1493s	1520	1490	175,256	δCH_{phen} (24), vCN (11), δCH_{meth} (13)
1455s	1503	1472	3,277,110	vCC_{phen} (20), δCH_{phen} (26)
	1495	1464	3,120,560	vCN (18), vCC _{phen} (19), δCH _{CHNO} (19)
1419w	1482	1451	2,516,170	δCH _{phen.} (29), δCH _{CHNO} (13)
1396w	1476	1445	111,177	νCC _{phen.} (21), δCH _{CHNO} (50)
	1469	1438	985,217	$\delta CH_{phen.}$ (34)
	1442	1410	912,799	νCO (31), δCH _{meth.} (10)
	1439	1407	368,462	$\delta CH_{meth.}$ (40)
	1433	1401	1,085,240	vCO (44)
	1407	1374	497,930	vNO(45)
	1384	1351	128,332	$vCC_{phen.}$ (62), $\delta CH_{phen.}$ (10)
1071	1383	1350	182,300	$\partial CH_{CHNC} (46)$
1271W	1256	1320	140 572	$VCC_{\text{phen.}}$ (10), $\delta CH_{\text{phen.}}$ (35)
1244w	1284	122	874.062	$vCN (35) \delta CH_{envise} (24) \delta NCC (16)$
12285	1279	1243	2 175 080	$vNO(10)$ $vC-C(19)$ $\delta CH_{CUNO}(32)$
12200	1266	1230	222,886	$vNO(22), vC-C(21), \delta CH_{CHNO}(14)$
	1261	1225	542,050	vCN (60)
1179w	1239	1203	126,014	vCC (33)
	1226	1189	54,629	δCH _{phen.} (74)
	1224	1187	120,899	$\delta CH_{phen.}$ (72)
	1173	1135	145,115	vC–C (15), vC–N (24), δCH _{phen.} (10)
	1149	1111	185,274	$\gamma CH_{meth.}$ (31), $\gamma CNCC$ (10)
	1115	1076	205,823	$\delta CH_{phen.}$ (42), $\nu CC_{phen.}$ (15)
	1000	1069	63,406	$\partial CH_{\text{phen.}}(23), \nu CC_{\text{phen.}}(35)$
	1090	1050	80,715	$OCH_{meth.}(23)$
	1007	1027	52 811	v = c (17)
1019m	1031	1010	107 854	$v(C_{1}, (34)) \delta(C_{1}, (14))$
997m	1041	1000	92.821	δCH_{phen} (12)
962m	1039	998	78.515	δCH_{phen} (47)
921w	977	935	78,102	$vC-C$ (10), δCH_{phen} (44)
	966	924	87,684	$\delta CH_{phen.}$ (77)
	902	858	301,434	δNCC (27), δCC _{phen.} (10)
768m	852	807	176,424	δCH_{CHNO} (66)
	838	793	316,565	δCH_{CHNO} (61), $\delta OPdCN$ (11), $\delta CNCC$ (13)
	831	786	109,838	$\delta CC_{phen.}$ (22)
744	823	777	189,056	$\delta CC_{phen.}$ (22), $\tau HCCN$ (10)
744W	814	768	/22,984	$\partial CH_{\text{phen.}}(47), \partial CH_{CHNO}(15)$
	801 767	755	610,124	$OCH_{\text{phen.}}(42), OCH_{\text{CHNO}}(19)$
600c	707	681	528 170	$\delta CH_{\text{phen.}}(30)$
0555	725	679	334 086	$\delta CH_{\text{phen.}}$ (34) $\delta CC_{\text{phen.}}$ (60)
	718	670	518 365	δCH_{phen} (43) δCC_{phen} (49)
670m	699	651	244,743	v PdO (21), δ OCC (10), δ CC _{phen} (21)
	696	648	186,478	vPdN (17), δ OCC (30), δ CC _{phen} (21)
651w	690	641	85,159	$\delta CC_{phen.}$ (12)
617vw	611	561	80,144	vPdN (22), δONC (40)
	538	486	184,806	vPdO (16), δNCC (14)
536vw	531	479	73,903	δ CNCC (28)
463w	511	458	112,114	vPdN (12), $\delta CC_{phen.}$ (27)
	479	426	82,828	δ OPdCN (48)
222	452	398	54,153	$\partial P dCN (14), \delta NCC (17)$
332W	438	384	100,612	VPAN (14), $\partial CC_{\text{phen.}}$ (14), $\partial CNCC$ (18)
	267	209	323,570	vrun (20), drach (14)

^a w = weak, vw = very weak, s = strong, m = medium; v = streching, δ = in-plane bending, γ = out-of- plane bending.

Table 4		
Experimental and calculated electronic transitions, oscillator strengths and their assignments for [Pd(ppeieo)(ina	ap)] ^a .

Major contribution(CI coeff)	Character	Calculated	Calculated		Experimental		
		λ (nm)	ΔE (eV)	$f_{ m os}$	λ (nm)	ΔE (eV)	3
$H-1 \rightarrow L + 2$ (%35)	$d(Pd)/\pi(oxime) \rightarrow d(Pd)/\pi^*(oxime)$	416	2.99	0.07			
H-2 → L (44%)	π (carbonyloxime) $\rightarrow \pi^*$ (carbonyloxime)	388	3.20	0.09	414	3.00	4740
$H \to L + 1$ (23%)	π (imineoxime) $\rightarrow \pi^*$ (imineoxime)						
$H-6 \rightarrow L(22\%)$	π (pheyl) $\rightarrow \pi^*$ (carbonyloxime)	358	3.47	0.27	346	3.59	9240
$H \to L + 1$ (23%)	π (imineoxime) $\rightarrow \pi^*$ (imineoxime)						
$H-5 \rightarrow L + 1(40\%)$	$\pi(\text{oxime}) \rightarrow \pi^*(\text{imineoxime})$	354	3.51	0.11			
$H-11 \rightarrow L(12\%)$	$d(Pd)/\pi(oxime) \rightarrow \pi^*(carbonyloxime)$	307	4.05	0.14			
H-13 → L (23%)	$d(Pd)/\pi(carbonyl) \rightarrow \pi^*(carbonyloxime)$	301	4.13	0.08			
$H-6 \rightarrow L + 1 (55\%)$	π (phenyl) $\rightarrow \pi^*$ (imineoxime)	297	4.18	0.12			
$H-6 \rightarrow L + 2 (19\%)$	$\pi(\text{phenyl}) \rightarrow d(\text{Pd})/\pi^*(\text{oxime})$	269	4.62	0.06			
$H-11 \rightarrow L + 1 (20\%)$	$d(Pd)/\pi(oxime) \rightarrow \pi^*(imineoxime)$	261	4.76	0.16	289	4.30	22950
$H-9 \rightarrow L + 2 (14\%)$	$d(Pd)/\pi(carbonyl) \rightarrow d(Pd)/\pi^*(oxime)$						

^a ε = Molar absorption coefficient (dm³ mol⁻¹ cm⁻¹), f_{os} = Oscillator strength, H = Highest occupied molecular orbital, L = Lowest unoccupied molecular orbital.



Fig. 4. Experimental and calculated electronic spectra of [Pd(ppeieo)(inap)].

a 11 cm⁻¹ shift in the wave number of the imine v(C=N) band (at 1623 cm⁻¹) is observed and indicates a stronger double bond character of the imine bond. On the other hand, the stretching mode of the oxime v(C=N) group occurs at ca. 1598 cm⁻¹ in the free ppeieo and inap ligands and is shifted by 100 cm^{-1} in the palladium(II) complex. Experimental value of this absorption band (1493 cm⁻¹) well agrees with the calculated value of 1490 cm⁻¹. Such a large shift was reported for the oxime C=N stretching band of the palladium(II) complex of the inap ligand [76]. Moreover, compared to that of the free inap ligand, a significant shift (ca. 36 cm^{-1}) to the lower frequency of the v(C=0) band was observed in the present complex as a consequence of coordination through the carbonyl group. A number of C=C and C-C stretching bands with different intensities appeared between 1600 and 1100 cm⁻¹. However, the calculated vibrational frequencies significantly deviate from the experimental values, probably as coupling with other vibrational modes (Table 3). A substantial change is also observed in the N–O stretchings which appears at 985 and 1022 cm^{-1} in free inap and ppeieo ligands, respectively. In the palladium(II) complex, these bands occurred at 1228 cm⁻¹ (calcd. 1243 cm⁻¹), indicating an increase in the double bond character of the NO bond due to the loss of the hydroxyl hydrogen. This unexpected shift in the N-O frequency is consistent with those of the reported palladium(II) complexes of oximes [9,76]. Vibrational modes in the low wavenumber region of the spectrum contain v(Pd-N) and v(Pd-O) stretchings together with contributions of several modes. The title complex shows a band at 670 cm⁻¹, which can be attributed to v(Pd-O) (calcd. 651 cm⁻¹), while the three bands at 617, 463 and 332 cm⁻¹ are assigned to v(Pd-N). The calculated v(Pd-N) modes were found between 561 and 384 cm⁻¹.

UV-vis spectra

The calculated absorptions of the palladium(II) complex associated with their oscillator strengths, the main configurations, and



Fig. 5. The transitions responsible for the electronic absorptions in [Pd(ppeieo)(inap)].

their assignments as well as the experimental results are given in Table 4. The absorption bands of the title complex appear at around 289, 346, and 414 nm (Fig. 4). To understand the transition processes, the calculated absorption transition diagram is shown in Fig. 5. The high energy absorption at 289 nm is contributed by the electron excitation from HOMO–11 to LUMO+1 (29%) and HOMO–9 to LUMO+2 (14%) at 261 nm with oscillator strength of



Fig. 6. Experimental and calculated NMR spectra of [Pd(ppeieo)(inap)].

0.16. The HOMO-11 orbital is composed of 72% d(Pd) and 7% p(oxime), whereas the LUMO+1 is localized on the imine oxime ligand (57%) and thus the absorption at 289 nm can be attributed to a d(Pd) $\rightarrow \pi^*$ (imine oxime) transition (Fig. 4). The absorption at 346 nm is contributed by electron excitation from HOMO to LUMO+1 and HOMO-6 to LUMO. Table 4 and Fig. 5 show that HOMO and HOMO-6 are composed mainly of p(imine oxime) and π (phenyl) respectively. LUMO and LUMO+1 orbitals have a π character, so the absorption at 346 nm can be ascribed to a $\pi \rightarrow \pi^*$ transition at 358 nm with an oscillator strength of 0.27. The low energy transition at 414 nm (calcd. 388 nm) originates from the electron transition between HOMO $-2 \rightarrow$ LUMO (44%) and HOMO \rightarrow LUMO+1 (23%). The HOMO-2 and LUMO are dominantly localized on the carbonyl oxime group with 61% and 53%, respectively. Therefore, the absorption may be assigned mainly to a π (carbonyloxime) $\rightarrow \pi^*$ (carbonyloxime) transitions.

NMR spectra

Experimental and calculated ¹H and ¹³C NMR spectra in DMSO- d_6 with TMS as a reference are illustrated in Fig. 6 and the chemical shifts are given in Table S1. The numbering of the atoms is the

same as in Fig. 1. In some cases, the NMR spectrum is not well correlated with the calculated spectrum, since calculations are referred to the static molecule [92,93]. The CH moiety adjacent to the oximate groups resonances over 8 ppm, but it appears at 7.88 ppm in the spectrum of the ppeieo ligand [58], indicating the deshielding of this proton after coordination. The signals between 7.18 and 7.73 ppm are assigned to aromatic protons, while the doublet at 1.84 ppm is attributed to the methyl protons. In the ¹³C NMR spectrum, the signal at 175.9 ppm belongs to the carbonyl C carbon atom and was calculated at 190.9 ppm, while the signals at 139.6 and 142.0 ppm are assigned to the C=N-O groups of the ppeieo and inap ligands, respectively. The signals between 126.2 and 135.1 ppm are assigned to the phenyl carbon atoms of ppeieo and inap. The chemical shifts of the C9 and C10 (methyl C) atoms are observed at 60.1 and 19.9 ppm, respectively and were calculated at 14.5 and 60.1 ppm, respectively.

Conclusions

In this study, a palladium(II) complex, namely [Pd(ppeieo)(inap)], has been synthesized and characterized by various techniques including elemental analysis, UV–vis, IR and NMR. X-ray crystallographic analysis of the complex shows that the palladium(II) ion is coordinated by both imine and carbonyl oxime ligands which behave as bidentate ligands. In order to study electronic, vibrational and NMR properties of the palladium(II) complex, the theoretical calculations were successfully performed by using DFT with the B3LYP/LANL2DZ level. The calculated data were in agreement with the observed data. This systematic study may be useful for the analysis of the spectroscopic behavior of coordination compounds of other imine and carbonyl oximes.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2013.01.054.

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