

# Synthesis and Characterization of Palladium (II) Complexes with Hydrazo- $\beta$ -diketone Ligands

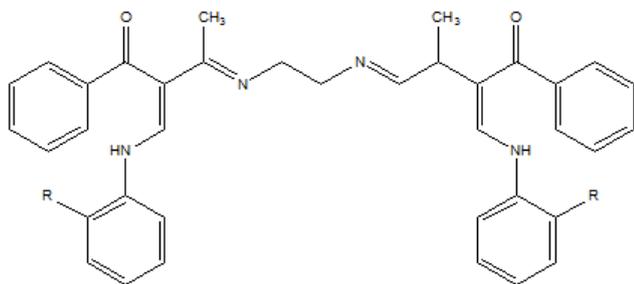
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**Abstract:** Phenyl hydrazo- $\beta$ -diketone ligands were prepared and their complexes with Pd(II) were studied. The  $\beta$ -diketone moieties included acetyl acetone (AA), benzoyl acetone (BA) and dibenzoyl methane (DBM), while the aniline part included 2-methoxy-, 2-chloro-, 3-nitro-, 3-bromo- and 4-fluoro- moieties. The stability constants and protonation constants of Pd(II) complexes and the ligand were studied in 75% (v/v) dioxane-water spectrophotometrically. Solid complexes of Pd(II) were established by elemental analysis, IR spectra, mass spectra and  $^1\text{H-NMR}$  methods. A linear relationship exists between the chemical shift of hydrazo proton and the protonation constants of the ligand, in addition to the linear relation obtained between the stability constants and the ligand basicities ( $\Sigma pK^H$ ).

**Keywords:** hydrazo- $\beta$ -diketone ligand, potentiometric and spectrophotometric studies of Pd(II)-PHBDH complexes, preparation of solid complex.

## I. INTRODUCTION

Previous studies of the chelating tendencies of some phenyl hydrazo di-benzoyl methane and its derivatives with palladium (II) ion have demonstrated quantitatively the capability of forming bis-chelates with the ligand acid [1]. In addition to the known condensation reactions between  $\beta$ -diketone and amines, the preparation and condensation of hydrazo- $\beta$ -diketone with ethylene diamine took place through one of the two ketonic groups of the hydrazo- $\beta$ -diketone compounds. The resulting Schiff base was used as chelating agent with palladium (II) ions [1,2]. This type of ligands viz: 1,10-diphenyl-2,9-bis(R-phenylhydrazo)-3,8-dimethyl-4,7-diazadeca-3,7-diene-1,10-dione structure (1), formed with palladium (II) stable square planer complexes in which the ligand behaves as diprotic tetra dentate one [2]. In the present communication the palladium (II) binding characteristics of a number of phenyl hydrazo- $\beta$ -diketones (structure 2) is described.



Structure I (R = 2-Cl or 2-OCH<sub>3</sub>)

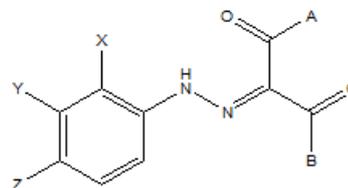
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Structure (2)

PHDBM: phenyl hydrazo dibenzoyl methane X=Y=Z= -H; A=B= -C<sub>6</sub>H<sub>5</sub>

2-Cl-PHDBM: 2-chloro phenyl hydrazo dibenzoyl methane; Y=Z= -H, X=-Cl, A=B= -C<sub>6</sub>H<sub>5</sub>

2-OCH<sub>3</sub>-PHDBM: 2-methoxy phenyl hydrazo dibenzoyl methane; Y=Z= -H, X= -OCH<sub>3</sub>, A=B= -C<sub>6</sub>H<sub>5</sub>

3-Br-PHDBM: 3-bromo phenyl hydrazo dibenzoyl methane; X=Z= -H, Y= -Br, A=B= -C<sub>6</sub>H<sub>5</sub>

3-NO<sub>2</sub>-PHDBM: 3-nitro phenyl hydrazo dibenzoyl methane; X=Z= -H, Y= -NO<sub>2</sub>, A=B= -C<sub>6</sub>H<sub>5</sub>

4-OCH<sub>3</sub>-PHDBM: 4-methoxy phenyl hydrazo dibenzoyl methane; X=Y= -H, Z= -OCH<sub>3</sub>, A=B= -C<sub>6</sub>H<sub>5</sub>

4-Br-PHDBM: 4-bromo phenyl hydrazo dibenzoyl methane; X=Y= -H, Z= -Br, A=B= -C<sub>6</sub>H<sub>5</sub>

2-Cl-PHBA: 2-chloro phenyl hydrazo benzoyl acetone; Y=Z=-H, X= -Cl, A= -CH<sub>3</sub>, B= C<sub>6</sub>H<sub>5</sub>

2-OCH<sub>3</sub>-PHBA: 2-methoxy phenyl hydrazo benzoyl acetone; Y=Z= -H, X= -OCH<sub>3</sub>, A= -CH<sub>3</sub>, B= C<sub>6</sub>H<sub>5</sub>

2-Cl-PHAA: 2-chloro phenyl hydrazo acetyl acetone; Y=Z= -H, X= -Cl, A=B= -CH<sub>3</sub>

4-F-PHAA: 4-fluoro phenyl hydrazo acetyl acetone; Y=Z= -H, X= -Cl, A=B= -CH<sub>3</sub>

## II. EXPERIMENTAL

i. Preparation of solid ligands: The ligands under investigation are prepared by coupling the diazonium salts of aniline or its derivatives with acetyl acetone or benzoyl acetone or dibenzoyl methane, in acetate buffer. The crude materials were crystallized using ethanol. The obtained ligands were characterized by elemental analysis, IR,  $^1\text{H-NMR}$ , UV-Vis and mass spectroscopy methods.

ii. Synthesis of palladium (II) complexes: The complexes were prepared by reflux 50 ml mixture of 2:1 molar ratios of ligand to palladium nitrate in 50% (v/v) dioxane-water for one hour. Solid crystals were separated gradually by cooling and addition of solid carbonate. The complexes were filtered, washed several times by aqueous dioxane and dried to constant weight under vacuum. Analytical data for the complexes were given in Table 1.

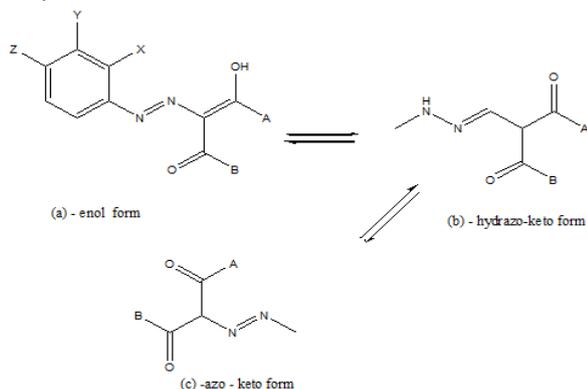
iii. Reagents and Materials: Stock solution of palladium nitrate (BDH) was prepared and standardized gravimetrically. Purification of dioxane was completed as described earlier [3].

iv. Measurements: A TOA HM-5ES pH-meter fitted with a combined glass-calomel electrode was used for pH measurements. The potentiometric titration procedures were described previously [1]. For the determination of proton-ligand stability constant, the ligand solution (0.003 M; 30 ml) was titrated against carbonate free KOH at constant ionic strength of 0.10 M KNO<sub>3</sub> using 75% (v/v) dioxane-water as solvent. Infrared, UV-Vis, <sup>1</sup>H-NMR and mass spectra all are the same as described before [1]. Magnetic susceptibilities were measured with magnetic susceptibility balance model MKI, Johanson Alfa products Cambridge U.K. The calibration and the corrections for the diamagnetism were the same as described previously [4].

### III. RESULTS

#### Spectroscopic studies

The electronic absorption spectra of the compounds under investigation exhibit mainly four-five bands. These bands are referred to A, B, C, D, E from shorter wave lengths side. Bands A and B are located at 210-220 nm and 230-248 nm, respectively due to moderated energy (corresponding to 1La-1A transitions) and low energy (corresponding to 1Lb-1A transitions)  $\pi \rightarrow \pi^*$  transition of the aromatic systems. The band C which is located at 256-270 nm range is due to  $\pi \rightarrow \pi^*$  transition within C=O group. The band D is observed in some compounds (280-340 nm range) and absent in others which indicates the presence of different azo-enol, azo-keto and hydrazo-keto tautomeric forms (scheme 1). This band could be assigned to  $\pi \rightarrow \pi^*$  transitions within C=N group (structure b). The electronic spectra of all compounds under investigation exhibit band E within 364-420 nm range due to  $\pi \rightarrow \pi^*$  transition with considerable charge transfer (CT) character. The CT character of this band is substantiated by the effect of substituent (aromatic) on its location and intensity. In general, this band exhibits a marked red shift when the substituent is an electron donating one. Also, the broadness (extended from 320 to 460 nm) of this band can be considered as an evidence for its CT nature [5]. Such charge transfer may take place from the aryl moiety as the donor to the carbonyl group on the  $\beta$ -diketone part. In addition to that the IR spectra support such CT character. The appearance of carbonyl stretching at lower frequencies is characterized for polarized C=O group Table 2. This band is splitted and this splitting indicates that the compounds under investigation are subjected to keto-enol or keto-hydrazo tautomerism scheme 1.



The proton NMR data with their respective assignments are summarized in Table 2. The spectra of PHDBM and its substituted derivatives exhibit a well-resolved singlet with shift typical of -NH proton in the range 13.26-14.00 ppm. Addition of deuterioxide (D<sub>2</sub>O) to the ligand with firm shaking leads to the disappearance of the proton signal for NH group, due to the H/D isotopic exchange. It was noticed that the time of disappearance (3.0-15.0 minutes) depend on the nature of the substituent. The proton signal of the -NH group for the ligands: PHDBM, 3-NO<sub>2</sub>-PHDBM, 3-Cl-PHDBM and 3-Br-PHDBM disappeared after short time (nearly three minutes), these observations could be attributed to the presence of electron donating groups in ortho- and para- positions strengthen the N-H bond and hence hinder and slow the H/D isotopic exchange. Also, the presence of such electron releasing substituent will cause desheilding due to electron donation which causes the proton to absorb down field. An electron-withdrawing substituent (-Cl-, -NO<sub>2</sub>-, etc) should exert an opposite effect [5]. A parallel effect is observed for the <sup>1</sup>H-NMR chemical shifts (for NH proton) and the dissociation constant K<sub>H</sub> for NH group as is cleared by the straight line (correlation coefficient 0.990) obtained in Fig. 1. In general, the presence of an electron-releasing group would then be expected to result in a down field shift of the NH proton and will tend to reduce the acid strength. In a similar way, the presence of electron-repelling group results in an field shift and increase in the acid strength.

#### Complexation Studies:

When a solution of any of the different ligands is mixed with Palladium (II), different colors (brown, green and red) are detected. On increasing the pH of the solution above two, a precipitation mainly Palladium metal is occurred. Accordingly, all the measurements are performed at pH=1.0. This pH value is considered as the optimum pH for the formation of Pd(II)-ligand complexes.

The stiochiometrics of complexes formed in 75% (v/v) dioxane-water and at optimum pH value are determined using molar ratio method. The results obtained indicated that Pd(II) form complex species with different ligands with stiochiometric ratios 1:1 and 1:2, M:L.

Under optimum pH the absorbance  $C_{Pd^{2+}}$  plot gives straight line of correlation coefficient (R) 0.999, indicating the validity of Beer's law within certain concentration range. These ranges together with  $\lambda_{max}$  values indicate that these ligands can be readily utilized for the micro determination of Pd(II) ion. Under optimum conditions, the relative standard deviation was 0.6%-1.8% (all approximately the 3.5 ppm level).

The stability constants of the formed complexes are determined using spectrophotometric method [6]. In the region of overlapping spectrograms of the free metal ion and its complexes, and assuming that only 1:1 complexes are formed ( $CL/CH < 0.3$ ), the following relation holds [6] :

$$[L^-] = \left(1 - \frac{A}{A_0}\right)^{-1} (K_{ML}^M - \alpha) - K_{ML}^M \quad (1)$$

where, A and A<sub>0</sub> are the absorbance in the presence and absence of ligand,  $\alpha = K_{ML}^M (\epsilon_o / \epsilon_m)$  and

$\epsilon_o, \epsilon_m$  are the molar extinction of the complex and metal ion respectively. Plots of  $[L^-]$  vs.  $(1 - A/A_o)^{-1}$  gives straight line whose intercept is  $K_{ML}^M$ . The free ligand concentration has been calculated at any particular pH using the equation:

$$C_L = [L^-] + K^H [H^+] \quad (2)$$

The calculated values obtained are included Table 3.

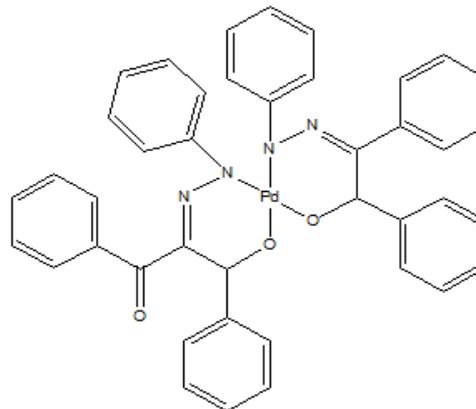
#### IV. DISCUSSION

The active segment of chelating agent under investigation responsible for palladium ion coordination is hydrazo- $\beta$ -diketone. However, all are similar in that they behave as N-, O- donors toward palladium ion forming 5-membered chelate ring. Accordingly, a plot of  $\log K_1$  as a function of the respective ligand basicity (*i.e.*  $pK_1^H$ ) is expected to be a straight line of unit slope [7]. The deviation from unit slope *i.e.* slope value equals 1.46 (Fig. 1b) is perhaps associate with significant steric effects of the substituent adjacent to the chelating centers. It could be stated that in a selected series of complexing agents two important factors were considered *i.e.*, steric and basicity effects. In addition to the substitution effects on the phenyl ring (Fig. 1b), the nature of the end group on the  $\beta$ -diketone part has an apparent effect on the values of the stability constant of the formed complexes. The ligands were arranged according to decreasing basicity in the following order: - PHAA < - PHBA < - PHDBM. The more basic ligand forms the most stable complex. In addition, the role of steric effect due to the bulky phenyl group is quite clear on the stability order of the complexes for - PHDBM (two phenyl groups). The electronic spectra of Pd(II) complexes (Figs. 2, 3 and 4) show more bands in the region 20833 - 23809, 20000 - 22727 and 17609 - 20792  $cm^{-1}$ , which may be assigned to the transitions,  $^1A_{1g} \rightarrow ^1A_{2g}$ ;  $^1A_{1g} \rightarrow ^1E_{1g}$  and  $^1A_{1g} \rightarrow ^1B_{1g}$  respectively. A strong charge transfer band formed at 24272 - 25000  $cm^{-1}$  in the studied complexes.

The crystal field stabilization energies for Pd(II) complexes obtained from the relation:  $E_{(v)} = \Delta - 35F_u$  [8], [F = 60 $cm^{-1}$  for Pd(II)] are summarized in Table (4). The diamagnetic behavior and electronic spectra of the complexes suggest square planar stereo-chemistry [9,10]. The values of the ligand field parameters  $\Delta_1$ ,  $\Delta_2$  and  $\Delta_3$  are in the range 21400 - 30000 and 10000 - 11000  $cm^{-1}$  respectively, which indicates that the difference in energy states of  $d_{xy}$  ( $b_{2g}$ ) and  $d_{xz}$ ,  $d_{yz}$  ( $e_g$ ) levels is very small which suggest simple  $\sigma$  donation from  $-C=N-NH$  group of the ligand. The higher values of  $\Delta_3$  also represent a simple  $\sigma$  bonding between metal and OH (enol) group of the ligand.

Palladium (II) may coordinate with phenyl hydrazo- $\beta$ -diketone ligands in a variety ways. The IR spectra of the ligands show strong bands between 1645 and 1555  $cm^{-1}$  which may be assigned to  $\nu C=O$  stretching modes. A band occurring between 1540 and 1490  $cm^{-1}$  is attributed to  $\nu C=C$  stretching mode coupled slightly with

$\nu C-H$  in-plane bending mode. In the complex of Pd(II) the hydrazo group is disappeared which indicates the participation of hydrazo nitrogen after deprotonation the chelate. This is substantiated by the appearance of non ligand band at 330-370  $cm^{-1}$  in the complexes due to  $\nu M-N$  bond. In addition the broad in the ligands appears at 1350-1370  $cm^{-1}$ , Table (5) summarizes the main IR frequencies ( $cm^{-1}$ ) and their assignment obtained for Pd(II) complexes. The coordination of hydrazo nitrogen and ketonic oxygen in complex formation is confirmed by the appearance of non-ligand band on the complexes at 460 - 510 and 350 - 370  $cm^{-1}$  which could be assigned to  $\nu M-O$  and  $\nu M-N$  respectively.



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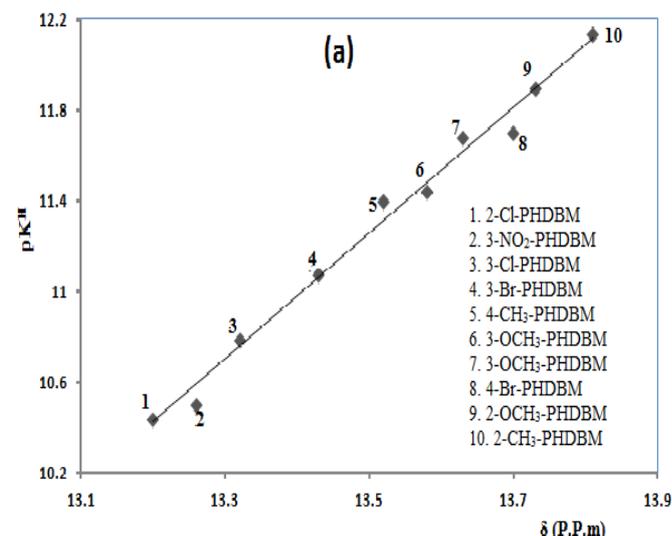


Fig. 1 (a): Relation between the values of  $pK^H$  and  $^1H$  nmr chemical shift

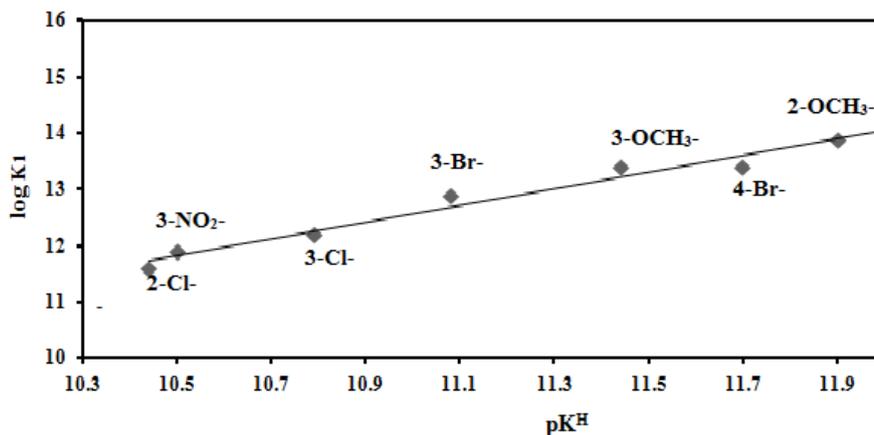


Fig. 1 (b): Relationship between the values of  $\log K_1$  and  $pK^H$

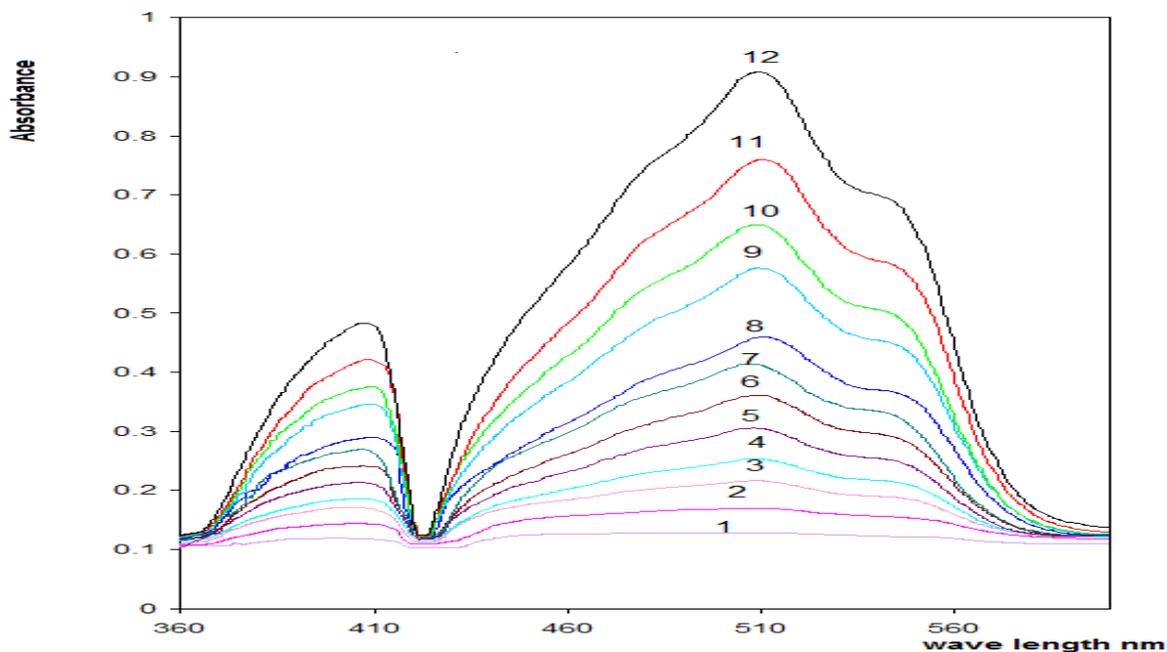


Fig. 2: Electronic Absorption Spectra of 2-Cl-PHAA-Pd(II) Complexes in 75% (v/v) dioxane-water

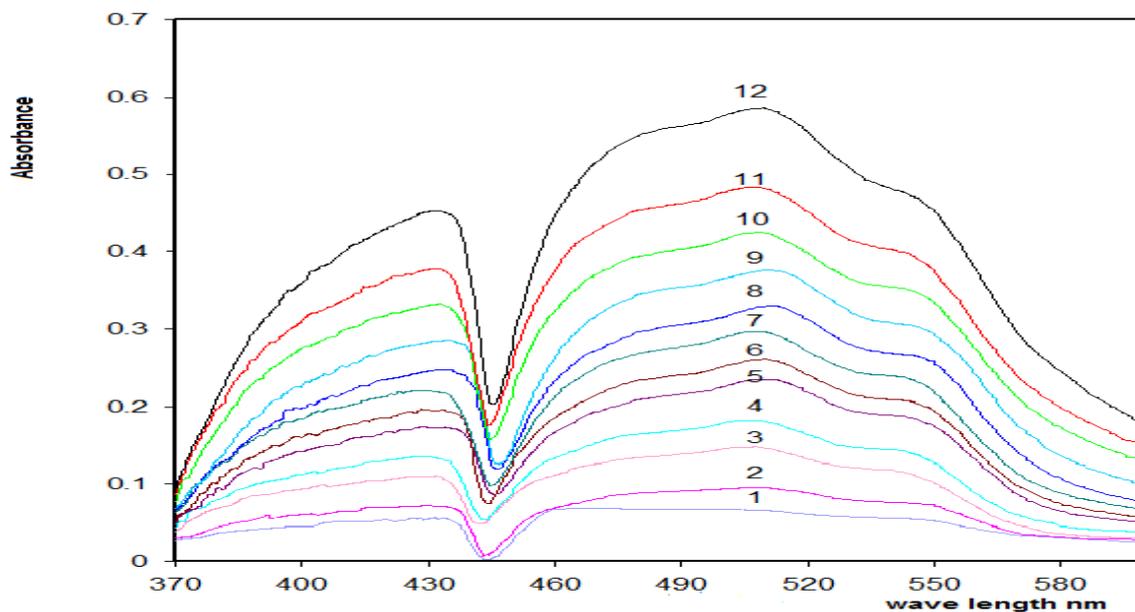


Fig. 3: Electronic Absorption Spectra of 2-OCH<sub>3</sub>-PHAA-Pd(II) Complexes in 75% (v/v) dioxane-water

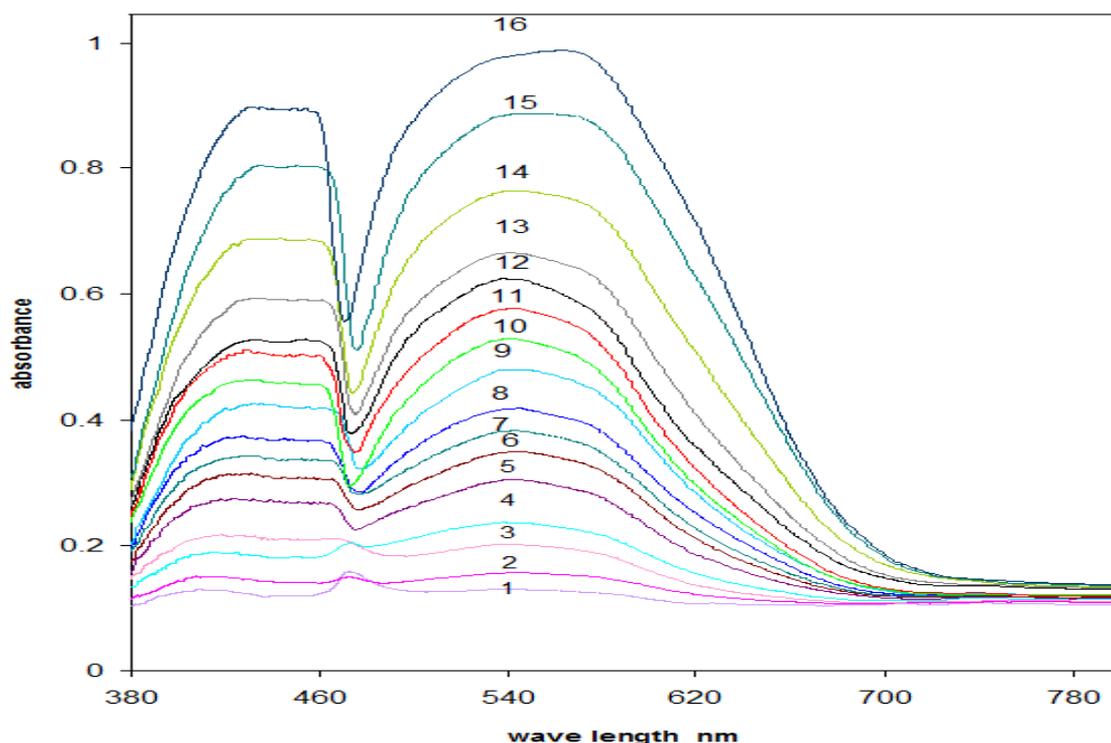


Fig. 4: Electronic Absorption Spectra of 2-OCH<sub>3</sub>-PHDBM-Pd(II) Complexes in 75% (v/v) dioxane-water

Table 1: Analytical and Spectral data of the ligands

Formula	M. P. (°C)	Found (Calc.)			<sup>1</sup> HNMR Spectra			Mol. Wt. m/e
		%C	%H	%N	CH <sub>3</sub> proton	Aromatic proton	NH δ before D <sub>2</sub> O (ppm)	
1) PHDBM C <sub>21</sub> H <sub>16</sub> O <sub>2</sub> N <sub>2</sub>	147	76.77 (76.81)	4.81 (4.88)	8.50 (8.54)	---	8.11-6.96	15.58	328
2) 2-O-CH <sub>3</sub> -PHDBM C <sub>22</sub> H <sub>18</sub> O <sub>3</sub> N <sub>2</sub>	156	73.71 (73.79)	5.00 (5.03)	7.80 (7.82)	3.92	8.14-6.96	13.73	358
3) 3-Br-PHDBM C <sub>21</sub> H <sub>15</sub> O <sub>2</sub> N <sub>2</sub> Br	191	61.83 (61.93)	3.79 (3.69)	6.80 (6.88)	---	8.13-7.12	13.32	406
4) 3-Cl-PHDBM C <sub>21</sub> H <sub>15</sub> O <sub>2</sub> N <sub>2</sub> Cl	193	69.62 (69.59)	4.10 (4.14)	7.71 (7.73)	---	8.13-6.94	13.33	362.5
5) 3-NO <sub>2</sub> -PHDBM C <sub>21</sub> H <sub>15</sub> O <sub>4</sub> N <sub>3</sub>	185	67.40 (67.56)	4.00 (4.02)	11.20 (11.26)	---	8.13-7.20	13.26	373.0
6) 4-Br-BHDBM C <sub>21</sub> H <sub>15</sub> O <sub>2</sub> N <sub>2</sub> Br	145	61.82 (61.93)	3.60 (3.69)	6.80 (6.88)	---	8.11-7.00	13.00	406
7) 4-OCH <sub>3</sub> -PHDBM C <sub>22</sub> H <sub>18</sub> O <sub>3</sub> N <sub>2</sub>	154	73.66 (73.74)	5.00 (5.03)	7.80 (7.82)	---	---	13.50	358
8) 2-Cl-PHAA C <sub>11</sub> H <sub>11</sub> O <sub>2</sub> N <sub>2</sub> Cl	119	55.30 (55.35)	4.60 (4.61)	11.70 (11.74)	---	---	---	238.5
9) 4-F-PAA C <sub>11</sub> H <sub>11</sub> O <sub>2</sub> N <sub>2</sub> F	112	59.40 (59.46)	4.92 (4.96)	12.59 (12.61)	---	---	---	222

Table 2: Electronic Spectral bands of organic ligand in 75%(v/v) dioxane-water

Ligand	$\pi \rightarrow \pi^*$ $\lambda_{(nm)} (\log \epsilon)$	$n \rightarrow \pi^*$ $\lambda_{(nm)} (\log \epsilon)$	Intermolecular CT $\lambda (\log \epsilon)$	Intramolecular CT $\lambda (\log \epsilon)$
2-Cl-PHDBM	244 (4.15)	320 (3.85)	386 (4.32)	400(431)
2-OCH <sub>3</sub> -PHDBM	220 (4.46)	245 (4.42)	300 (4.03)	420 (4.48)
2-Br-PHDBM	280 (4.33)	250 (3.36)	300 (3.08)	388 (3.39)
3-Br-PHDBM	220 (4.26)	300 (3.82)	370 (4.22)	400 (4.29)
3-Cl- PHDBM	250 (4.39)	295 (4.05)	370 (4.32)	400 (4.27)
3-OCH <sub>3</sub> -DBM	248 (4.42)	270 (4.42)	295 (4.22)	390 (4.44)
4-Br-DBM	250 (3.56)	295 (3.21)	310 (3.10)	400 (3.55)
2-Cl-PHBA	249 (4.29)	256 (4.30)	270 (4.08)	364 (4.53)
2-Br-PHBA	246 (4.04)	300 (3.96)	370 (3.96)	400 (3.80)
2-OCH <sub>3</sub> -PHBA	230 (4.18)	260 (3.99)	290 (4.88)	400 (4.33)
2-OCH <sub>3</sub> -PHAA	254 (4.33)	280 (3.44)	280 (3.94)	420 (4.57)
2-Cl-PHAA	250 (4.43)	270 (3.94)	270 (3.94)	364 (4.57)

 Table 3: Protonation, Stability constants and <sup>1</sup>NMR chemical shift for ligands

Compound	pK <sup>H</sup>	$\delta$ in ppm	log K <sub>1</sub>
2-OCH <sub>3</sub> -PHDBM	11.99	13.73	14.03
2-Cl-PHDBM	10.44	13.20	11.62
3-Br-PHDBM	11.08	13.45	13.03
3-Cl- PHDBM	10.96	13.32	12.16
4-Br-PHDBM	11.81	13.71	13.59
2-Cl-PHBA	10.20	---	9.28
2-OCH <sub>3</sub> -PHBA	10.02	---	10.28
3-NO <sub>2</sub> -PHDBM	10.53	13.26	11.85
4-CH <sub>3</sub> -PHDBM	11.38	10.53	---
2-CH <sub>3</sub> -PHDBM	12.10	13.80	---
PHDBM	11.40	13.58	---
3-OCH <sub>3</sub> -PHDBM	11.96	13.64	13.47

Table 4: Electronic Spectral data for Pd(II) Complexes

Complex	Electronic bands (cm <sup>-1</sup> )	$\Delta$ (cm <sup>-1</sup> )	Tentative assignment
Pd(II)-3-Cl-PHDBM	23810	35910	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> A <sub>2g</sub>
	22222	24322	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> E <sub>1g</sub>
	17857	20827	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> B <sub>1g</sub>
Pd(II)-2Cl-PHDBM	23148	25248	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> A <sub>2g</sub>
	22422	24522	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> E <sub>1g</sub>
	18727	20827	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> B <sub>1g</sub>
Pd(II)-3-NO <sub>2</sub> -PHDBM	21739	23839	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> E <sub>1g</sub>
	18450	20550	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> B <sub>1g</sub>
Pd(II)-2-OCH <sub>3</sub> -PHDBM	22472	24572	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> A <sub>2g</sub>
	20000	22100	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> E <sub>1g</sub>
	18116	20216	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> B <sub>1g</sub>
Pd(II)-3-OCH <sub>3</sub> -PHDBM	22989	25089	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> A <sub>2g</sub>
	21505	23605	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> E <sub>1g</sub>
	18450	20550	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> B <sub>1g</sub>
Pd(II)-2Br-PHBA	21739	23839	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> A <sub>2g</sub>
	20000	22100	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> E <sub>1g</sub>
	19048	19276	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> B <sub>1g</sub>

Pd(II)-4Br-PHDBM	23697	25797	$^1A_{1g} \rightarrow ^1A_{2g}$
	21645	23745	$^1A_{1g} \rightarrow ^1E_{1g}$
	17731	19831	$^1A_{1g} \rightarrow ^1B_{1g}$
Pd(II)-3Br-PHDBM	23529	25629	$^1A_{1g} \rightarrow ^1A_{2g}$
	22727	24827	$^1A_{1g} \rightarrow ^1E_{1g}$
	15699	19799	$^1A_{1g} \rightarrow ^1B_{1g}$

Table 5: Main IR frequencies ( $\text{cm}^{-1}$ ) and their assignment

	2-OCH <sub>3</sub> -BA (Pd)	OCH <sub>3</sub> -AA	Aniline DBM (-Pd)	2-OCH <sub>3</sub> -DBM (-Pd)
$\nu_{\text{NH}}$	---	---	3420 m	---
$\nu_{\text{OH}}$	---	3000 w	3020 w	---
$\nu_{\text{C=O}}$	1660 s (1655 w) 16455 s (16455)	1670 vs (1650 sb) 1630 vs (1640 s)	1650 m (1620 w) 1605 m (1605 w)	16655 1605 s 1630 m
$\nu_{\text{C=N}}$	1620 s (1630 w)	1600 s (1592 m)	1580 w (1580 w)	1580 w (1580 w)
$\nu_{\text{C=C}}$	1535 w (1500 w)	1540 w (1510 s)	1545 mb (1550 s)	1545 s (1550 s)
$\nu_{\text{C-N1}}$	1350 vs (1325) Structure b	1375 s (1370 m)	1355 b (1365 b)	1555 b (---)
$\nu_{\text{C-N2}}$	1270 s (1280 s) Structure a	1285 s (1270 s)	1280 m (1260 b)	1280 s (1265 w)
$\nu_{\text{C3=C4}}$	995 s (980 s) Structure a	985 s (975 s)	940 b (950 b)	990 b 995 w
$\nu_{\text{N-N}}$	875 s (850 m)	925 w (930 s)	860 w 875 w	880 sb (---)
$\nu_{\text{M-O}}$	(450 m)	(445 m)	(460 b)	(455 b)
$\nu_{\text{M-N}}$	(380 m)	(380 m)	(370 w)	(415 w)