

Crystal Structure of Palladium (II) Complexes with Tridentate Diazene Ligand Having O, N, O Donor Set

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Abstract: *The solid state structures of [Pd (L) (D)], 1a and 1b (D = 4 - picoline and PPh₃ respectively), have been determined by single crystal X - ray diffraction. The crystal structures have revealed that diazene ligands, 1 - (2' - hydroxy - 1' - naphthylazo) - 2 - hydroxynaphthalene (H₂L), bind to the metal ion as dianionic tridentate O, N, O donors and the fourth coordination position is occupied by Lewis base (D). The tetra co - ordination around palladium (II) is almost planar. Intermolecular association in the solid state is observed due to C - H... π interactions.*

Keywords: Palladium, Cyclopalladates, Crystal structure, X - ray crystallography

1. Introduction

The activation of C - H bonds in organic compounds promoted by transition metal complexes are of considerable interest in view of its diverse synthetic potential [1 - 9]. In this regard, cyclopalladation reactions have received increased attention, because they represent a facile method for the activation of a C - H bond in aromatic rings and have potential applications in organic synthesis. The C - H bond activation reactions promoted by palladium (II) salts enjoy a special status for their wide application potential in metaloxylation reactions [10 - 14]. We have already reported C (naphthyl) - H bond activation by palladium (II) and subsequent stoichiometric as well as catalytic metaloxylation of Pd - C (naphthyl) bond [15]. Synthesis via non - oxidative route and characterization of structurally similar palladium (II) compound with tridentate 1 - (2' - hydroxy - 1' - naphthylazo) - 2 - hydroxynaphthalene (H₂L) ligand has also been reported [15]. In continuation of our previous work, herein we wish to establish, based on single - crystal X - ray crystallography technique, the molecular structure of the cyclopalladates [Pd (L) (D)] and to discuss crystallographic analysis of the compound.

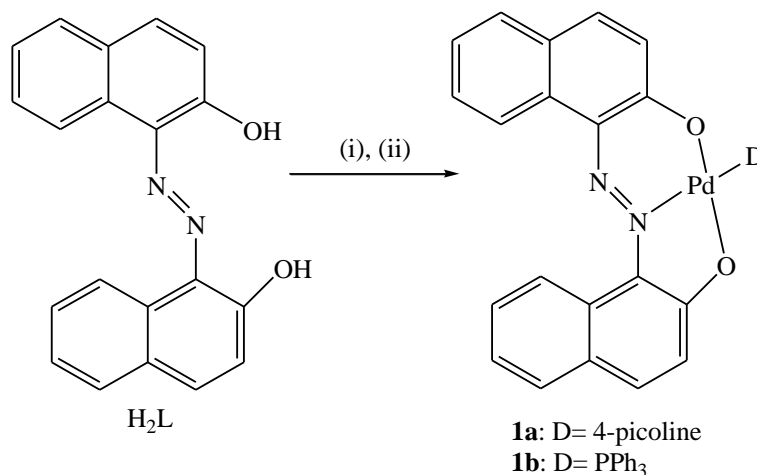
2. Methodology

Single crystals of complexes **1a** and **1b** were grown by slow diffusion of n - hexane into dichloromethane solutions of the

cyclopalladates. Selected crystal data and data collection parameters are given in Table 3. Crystallographic data collection were performed on a Bruker SMART 1000 CCD area - detector diffractometer using graphite monochromated MoK α ($\lambda = 0.71073 \text{ \AA}$) radiation by ω scan. The structure was solved by direct methods using SHELXS - 97 [16] and difference Fourier syntheses and refined with SHELXL97 package incorporated in WinGX 1.64 crystallographic collective package [17]. All the hydrogen positions for the compound were initially located in the difference Fourier map, and for the final refinement, the hydrogen atoms were placed geometrically and held in the riding mode. The last cycles of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all non - hydrogen atoms and isotropic thermal parameters for all the hydrogen atoms. Full - matrix - least - squares structure refinement against $|F^2|$. Molecular geometry calculations were performed with PLATON [18], and molecular graphics were prepared using ORTEP - 3 [19].

3. Results and Discussion

We have already reported the synthesis of palladium (II) compound with tridentate naphtholato - O, N, O ligand, 1 - (2' - hydroxy - 1' - naphthylazo) - 2 - hydroxynaphthalene (H₂L) ligand, [Pd (L) (D)] (**1a** and **1b**) in presence of neutral Lewis base, D [D = 4 - picoline or PPh₃] (Scheme 1).



Scheme 1: (i) Na₂ [PdCl₄], EtOH, room temperature, 8 h; (ii) 4 - picoline or PPh₃, room temperature, 2 h

The cyclopalladates have been characterized by single crystal X - ray crystallography. Single crystals of complexes were grown by slow diffusion of n - hexane into dichloromethane solution of the complexes. The structures of divalent cyclopalladates (**1a** and **1b**) derived from the reaction of H₂L and Na₂ [PdCl₄] in presence of neutral donor (D) are shown in Figures 1 and 2 respectively. The selected bond parameters are given in Tables 1 and 2 respectively.

The structure of **1a** shows that the palladium (II) is bonded to N1 of diazene group, O1 and O2 of naphthalato function and N3 of donor 4 - picoline. Therefore, 1 - (2' - hydroxy - 1' - naphthylazo) - 2 - hydroxynaphthalene (H₂L) binds palladium (II) as a dianionic tridentate [O, N, O] fashion forming a five membered chelate ring and a six - membered chelate ring. The tetra co - ordination around Pd (II) is almost planar. The maximum deviation is represented by the 'bite' angle O (2) - Pd (1) - N (1) of 93.83 (13) °. Similarly the palladium (II) center in **1b** is found to be bonded to N1 of diazene group, O1 and O2 of naphthalato function and P1 of triphenylphosphine.

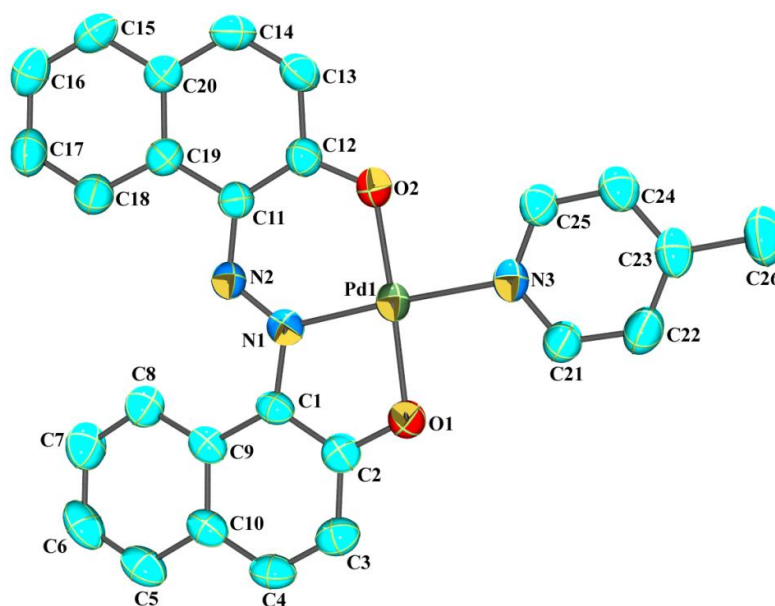


Figure 1: Molecular structure of **1a** with ellipsoids drawn at the 50% probability level

Table 1: Selected bond lengths (Å) and bond angles (°) for **1a**

	Bond lengths (Å)		Bond angles (°)
Pd (1) - N (1)	1.961 (3)	N (1) - Pd (1) - O (1)	83.41 (13)
Pd (1) - O (1)	1.987 (3)	N (1) - Pd (1) - O (2)	93.83 (13)
Pd (1) - O (2)	1.954 (3)	O (1) - Pd (1) - N (3)	93.77 (13)
Pd (1) - N (3)	2.078 (4)	O (2) - Pd (1) - N (3)	88.99 (13)
N (1) - N (2)	1.269 (5)		
N (1) - C (1)	1.415 (5)		
N (2) - C (11)	1.392 (5)		
O (1) - C (2)	1.311 (5)		
O (2) - C (12)	1.302 (5)		

In both the structures, the C - O bond lengths [1.311 (5) and 1.302 (5) Å in **1a**; 1.328 (8) and 1.312 (8) Å in **1b**] are shorter than the C - O bond length found in naphthols (1.385 Å) [20]. The shortening of the C - O bond length in azonaphthalato chelate ring may be ascribed to favourable conjugation of a lone pair p - orbital on the naphthalato oxygen atom with the π - system of the chelate ring [21]. The crystal data and structure refinement data for **1a** and **1b** has been compiled in Table 3.

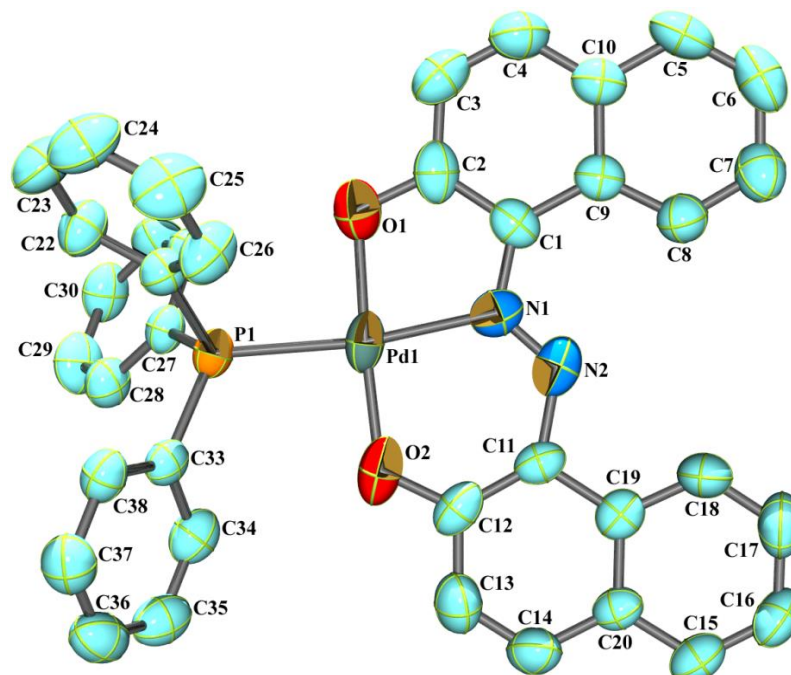


Figure 2: Molecular structure of **1b** with ellipsoids drawn at the 50% probability level

Table 2: Selected bond lengths (Å) and bond angles (°) for **1b**

	Bond lengths (Å)		Bond angles (°)
Pd (1) - N (1)	2.043 (6)	N (1) - Pd (1) - O (1)	81.1 (2)
Pd (1) - O (1)	1.983 (5)	N (1) - Pd (1) - O (2)	95.5 (2)
Pd (1) - O (2)	1.944 (6)	O (1) - Pd (1) - P (1)	91.11 (15)
Pd (1) - P (1)	2.3024 (16)	O (2) - Pd (1) - P (1)	92.29 (15)
N (1) - N (2)	1.207 (7)		
N (1) - C (1)	1.387 (8)		
N (2) - C (11)	1.477 (9)		
O (1) - C (2)	1.328 (8)		
O (2) - C (12)	1.312 (8)		

Table 3: Crystal data and structure refinement for **1a** and **1b**

Identification Code	1a	1b
Empirical formula	C ₂₆ H ₁₉ N ₃ O ₂ Pd	C ₃₈ H ₂₇ N ₂ O ₂ P Pd
Formula weight	511.84	680.99
Temperature	293 (2) K	293 (2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, Space Group	Orthorhombic, P _{bca}	Triclinic, P - 1
Unit cell dimensions	a = 8.275 (2) Å b = 18.111 (5) Å c = 28.216 (8) Å α = 90.00° β = 90.00° γ = 90.00°	a = 9.038 (2) Å b = 12.990 (3) Å c = 14.575 (3) Å α = 78.877 (3)° β = 84.288 (3)° γ = 70.974 (3)°
Volume	4229 (2) Å ³	1586.2 (6) Å ³
Z, Calculated density	8, 1.608 Mg/m ³	2, 1.426 Mg/m ³
Absorption coefficient	0.907 mm ⁻¹	0.672 mm ⁻¹
F (000)	2064	692
Crystal size	0.24 x 0.22 x 0.12 mm	0.24 x 0.16 x 0.09 mm
Theta range for data collection	2.25 to 25 deg.	2.01 to 25 deg.
Limiting indices	- 9 ≤ h ≤ 9, - 21 ≤ k ≤ 21, - 33 ≤ l ≤ 33	- 10 ≤ h ≤ 10, - 15 ≤ k ≤ 15, - 17 ≤ l ≤ 17
Reflections collected/unique	38675/3721 [R (int) = 0.0589]	15436/5532 [R (int) = 0.0295]
Completeness to theta	25 deg., 100.0%	25 deg., 98.9%
Refinement method	Full - matrix least - squares on F ²	Full - matrix least - squares on F ²
Data/restraints/parameters	3721/0/289	5532/0/404
Goodness - of - fit on F ²	1.010	1.149
Final R indices [I > 2σ(I)]	R1=0.0441, wR2=0.1134	R1= 0.0741, wR2= 0.1788
R indices (all data)	R1=0.0581, wR2=0.1238	R1=0.0808, wR2= 0.1831
Largest diff. Peak and hole	1.856 and - 0.423 e. Å ⁻³	2.676 and - 1.364 e. Å ⁻³

Crystallographic Analysis

Solid state structures of palladium (II) complexes have been thoroughly investigated by X - ray crystallography. A detailed analysis revealed several interactions in the solid state structures of the cyclopalladates.

Structure of **1a** and Intra - /intermolecular Interaction in Solid State

The ortep diagram of **1a** is presented in Figure 1 and the packing diagram is presented in Figure 3. The crystal packing has been found to be stabilized by two

intermolecular C - H... π interaction: C6 - H6...Cg7 [where Cg7 is the centroid of the C15 - C20 ring at $-1/2 - X, -1/2+Y, Z$] and C13 - H13...Cg4 [where Cg4 is the centroid of the C1 - C9 ring at $1/2 - X, 1/2+Y, Z$] [Figure 4, Table 4]. Moreover, the crystal packing has been found to be further stabilized by one intermolecular C - H...O interaction (C4 - H4...O1 distance being 2.58 Å; symmetry operator is $-1/2+X, 1/2 - Y, -Z$). Further, the solid state structure of **1a** is characterized by four intramolecular interactions (C8 - H8...N2, C18 - H18...N2, C21 - H21...O1 and C25 - H25...O2) [Figure 5, Table 5].

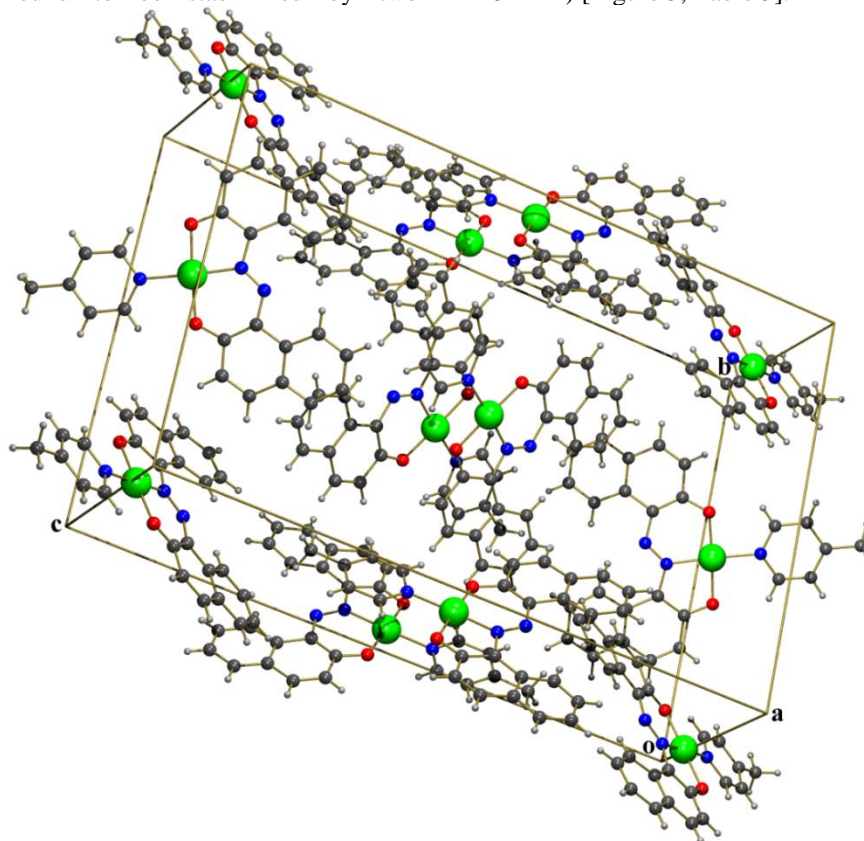


Figure 3: Packing diagram of **1a**

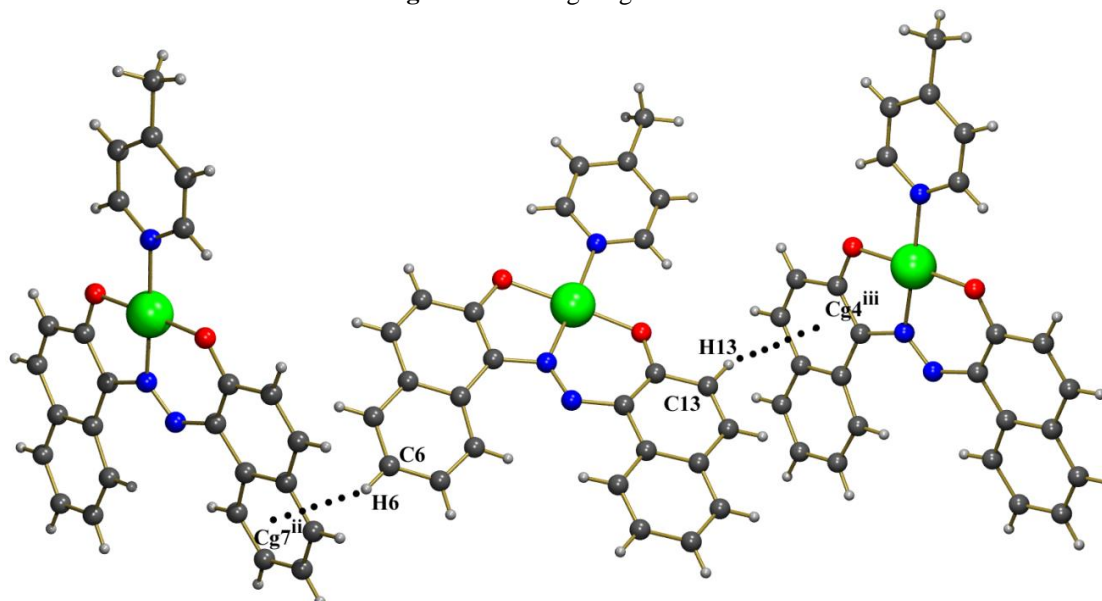


Figure 4: C - H... π interactions in **1a** [Cg (4) and Cg (7) are the centroids of C1 - C9 and C15 - C20 rings respectively. Symmetry operators are (i) $1/2 - X, 1/2+Y, Z$ (ii) $-1/2 - X, -1/2+Y, Z$]

Table 4: Geometric parameters of the C - H... π interactions

		H...Cg/Å	γ^a	C - H...Cg/ $^\circ$	H...Cg/Å	Symm. Operation on Cg
1a^b	C6 - H6...Cg (7)	2.83	11.99	157	3.700 (6)	- 1/2 - X, - 1/2+Y, Z
	C13 - H13...Cg (4)	2.86	21.94	158	3.737 (5)	1/2 - X, 1/2+Y, Z
1b^c	C7 - H7...Cg (8)	2.92	18.14	161	3.813 (8)	- X, 1 - Y, - Z
	C30 - H30...Cg (9)	2.83	10.71	140	3.597 (9)	- 1+X, Y, Z

^a γ = angle defined by a line connecting center of gravity of the aromatic ring with H atom and the normal to the aromatic ring

^bCg (4) and Cg (7) are the centroids of C1 - C9 and C15 - C20 rings respectively

^cCg (8) and Cg (9) are the centroids of C27 - C32 and C33 - C38 rings respectively

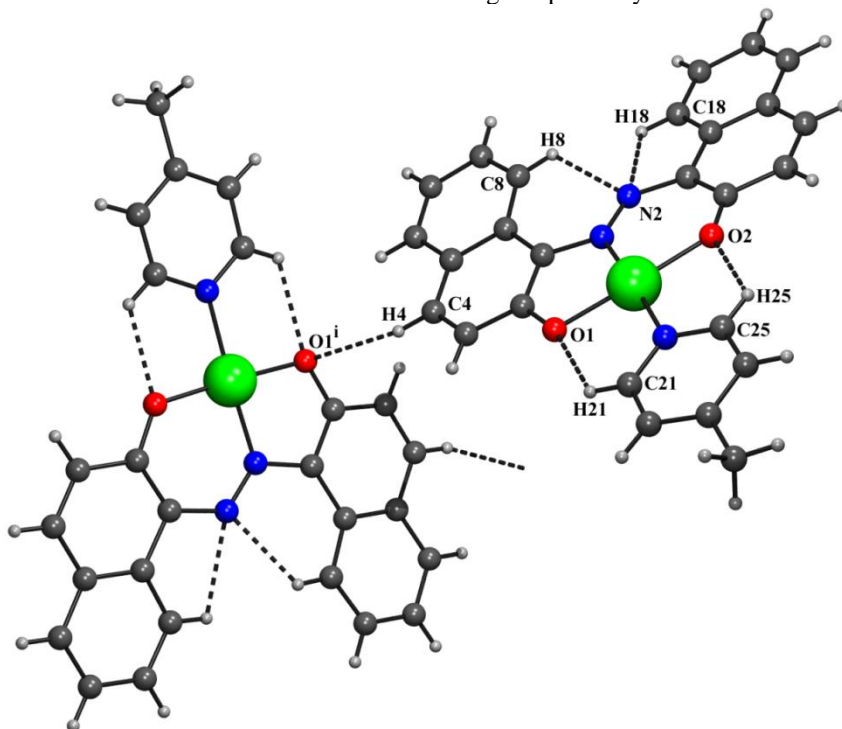


Figure 5: C - H...O interactions in **1a**; Possible hydrogen bonds C4 - H4...O1; Symmetry operator is - 1/2+X, 1/2 - Y, - Z and other intramolecular hydrogen bonds [C8 - H8...N2, C18 - H18...N2, C21 - H21...O1 and C25 - H25...O2]

Table 5: Geometric parameters of the hydrogen bonding interactions

		d (D - H) /Å	d (H...A) /Å	d (D...A) /Å	D - H...A/ $^\circ$	Symm. operation on A
1a	C4 - H4...O1	0.93	2.58	3.479 (5)	162	- 1/2+X, 1/2 - Y, - Z
	*C8 - H8...N2	0.93	2.31	2.897 (5)	121	X, Y, Z
	*C18 - H18...N2	0.93	2.46	2.779 (6)	100	X, Y, Z
	*C21 - H21...O1	0.93	2.42	3.010 (6)	121	X, Y, Z
	*C25 - H25...O2	0.93	2.29	2.870 (5)	120	X, Y, Z
1b	*C8 - H8...N2	0.93	2.32	2.916 (10)	121	X, Y, Z
	*C18 - H18...N2	0.93	2.41	2.763 (11)	103	X, Y, Z
	*C34 - H34...O2	0.93	2.59	2.993 (10)	107	X, Y, Z

*Intramolecular hydrogen bond.

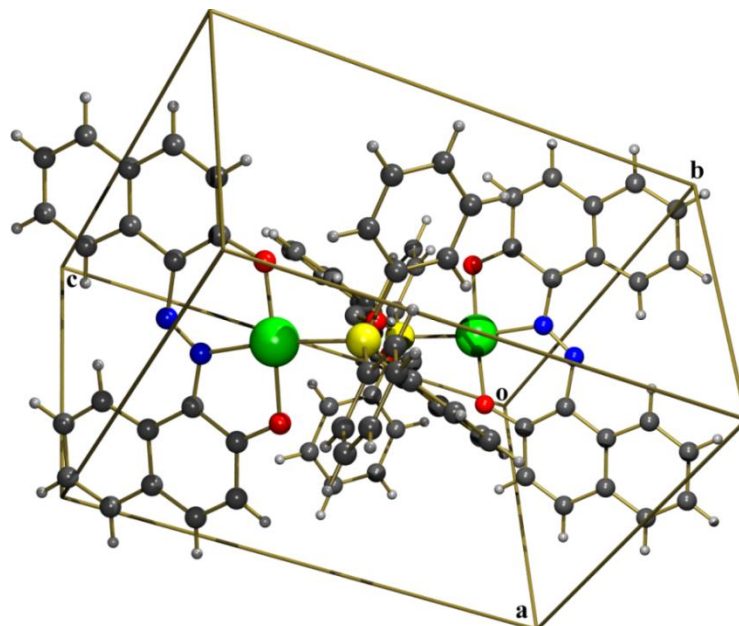


Figure 6: Packing arrangement in **1b**

Structure of **1b** and Intra - /intermolecular Interaction in Solid State

The crystal packing arrangement in the cyclopalladate **1b** is shown in Figure 6. The crystal packing has been found to be stabilized by two intermolecular C–H... π interactions. The intermolecular C–H... π interactions involve the centroids of the rings C27→C32 (Cg8) and C33→C38 (Cg9) [symmetry

codes: (i) - X, 1 - Y, - Z; (ii) - 1+X, Y, Z] with the hydrogen H7 and H30; the H...Cg bond distances are 2.92 and 2.83 Å respectively [Figure 7, Table 4]. The solid state structure of **1b** is characterized by three intramolecular interactions (C8 - H8...N2, C18 - H18...N2 and C34 - H34...O2) [Figure 8, Table 5].

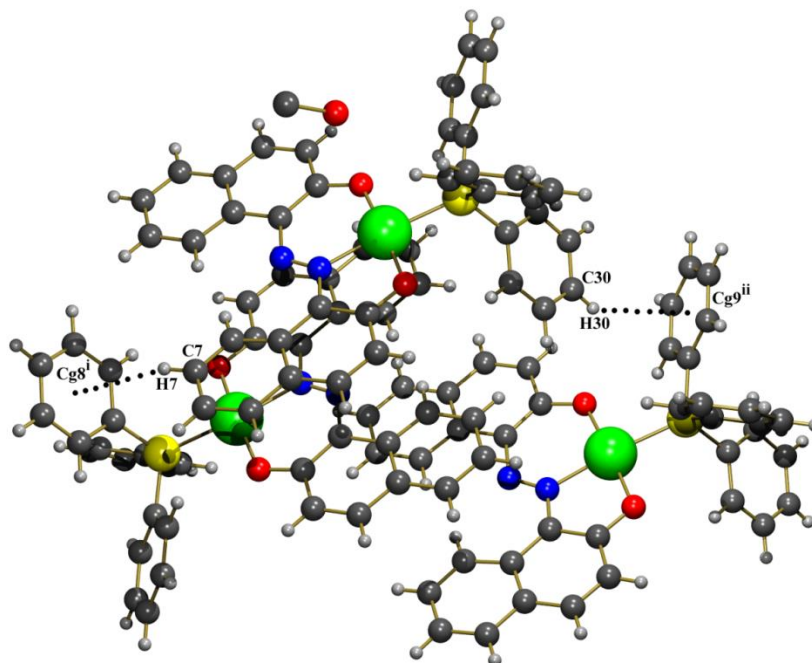


Figure 7: C - H... π interactions in **1b** [Cg (8) and Cg (9) are the centroids of C27 - C32 and C33 - C38 rings respectively. Symmetry operators are (i) - X, 1 - Y, - Z (ii) - 1+X, Y, Z]

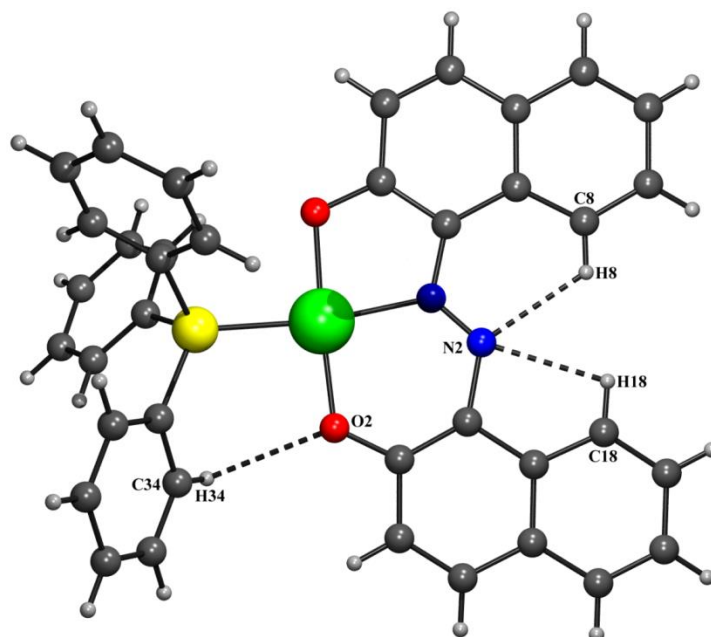


Figure 8: Intramolecular hydrogen bonds [C8 - H8...N2, C18 - H18...N2 and C34 - H34...O2]

4. Conclusion

Molecular structure of cyclopalladates with different donor, 4 - picoline and PPh_3 , has been successfully established by single crystal X - ray crystallography. In both the structures, the ligand 1 - (2' - hydroxy - 1' - naphthylazo) - 2 - hydroxynaphthalene (H_2L) binds palladium (II) as a dianionic tridentate [O, N, O] fashion and the fourth position is occupied by donor D. The crystal packing has been found to be stabilized by intermolecular C-H... π interactions.

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