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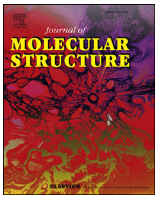

Synthesis, characterization and single crystal structures of chiral Schiff base and its tetranuclear palladium complex with Pd–O–Pd bridging and Pd–Pd bonds

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ABSTRACT

A new chiral Schiff base ligand 2-{*N*-[(2*S*)-(1-hydroxy-3-phenylpropan-2-yl]ethanimidoyl} phenol ((***S***)–**H_2L**) was obtained by acid catalyzed condensation of (2*S*)-(−)-2-amino-3-phenyl-1-propanol with 2′-hydroxyacetophenone. The palladium complex was prepared by treating a solution of **(*S*)–H_2L** in acetone with a solution of Na_2PdCl_4 in water in 1:1 M ratio. The new ligand and its complex were characterized by FT-IR, ^{1}H, ^{13}C{^{1}H} NMR spectroscopy, polarimetry and elemental analysis and their molecular structures were determined by single crystal X-ray diffraction. Both the compounds crystallizes in monoclinic system in the space group $P2_1$. There exists an intra [O–H···N (1.62(5) Å)] and intermolecular [O–H···O (1.53(5) Å) and C–H···O (2.59 Å)] hydrogen bonding and secondary interactions in the crystal of **(*S*)–H_2L**. The structure of the palladium complex was found very interesting wherein the ligand coordinated to metal center as tridentate dianionic (O^-, N, O^-) fashion, **(*S*)-L**, resulting in a tetranuclear palladium cluster, [Pd_4(**(*S*)-L**)$_4$]. In these supramolecular structures phenolate oxygen coordinated to Pd(II) ion as Pd–O terminal bonds [1.934(12) - 1.977(11) Å] and the alkoxide oxygen coordinated as Pd–O–Pd bridging bonds [1.993(11) - 2.012(12) Å]. The Pd–N bond lengths found were in the range of 1.949(13) to 1.919(12) Å. There exists two asymmetric tetranuclear complex molecules in its crystal lattice. There exists very strong metal-metal bond interaction, Pd(2)–Pd(3) [3.0410(18) Å] and Pd(6)–Pd(7) [3.0517(19) Å] respectively in the two asymmetric units.

1. Introduction

The designing, synthesis and study of their coordination behavior, bonding and structure of chiral ligands has been an important strategy towards the development of asymmetric transition metal catalysts and is still a challenging task as it requires a considerable synthetic effort [1].

Schiff bases are excellent class of ligands which bind metal center effectively through highly nucleophilic imine (C=N) group in addition to other donors in hybrid ligands. Chiral Schiff bases derived from chiral β-amino alcohols and salicylaldehyde or its derivatives, known as chiral N-salicyl β-amino alcohol Schiff bases or 'tridentate salen ligands' [1b,2,3] have been attracted in the recent past due to their low molecular weights, high solubility, structural and electronic fine-tunability, prepared by extremely simple synthetic methodology via the condensation reaction of aromatic aldehydes or ketones with chiral amines which are easily available as amino acids or their derivatives and more importantly these ligands in presence of transition metal precursors or polymer supported catalysts have been largely employed as ligands in transition metal catalyzed asymmetric organic synthesis like in sulphide oxidation [1,3], oxidation of disulphides to thiosupfinates [4a] to which can be used to synthesize sulfinyl amines/sulfinamides [4b] and sulfinyl imines/sulfinimdes [4c], alkynylations [5] and trimethylsilyl-cyanations [6].

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The coordination chemistry and structural characterization of Chiral N-salicyl-β-amino alcohol Schiff bases have been explored with metal transition metal ions such as Ti(IV) [7], V(IV/V) [8], Mn(II) [9], Ni(II) [10], Cu(II) [11], Pd(II) [10b]. The structural characterization metal complexes leads to better understanding of their absolute configuration, stereochemistry and ligating capacity. In the complexes of hard metal ions they act as tridentate (O, N, O) type ligands with interesting structural features containing intra and/or inter molecular secondary interactions resulting in supramolecular structures in solid state. These weak non-covalent interactions are expected to play an important role in assessing the catalytic activity [1b].

The synthesis, coordination chemistry and structural characterization of Pd(II) complexes of chiral N-salicyl-β-amino alcohol Schiff bases as ligands is very little explored [10b]. The palladium complexes of these chiral ligands but their catalytic efficiency in various asymmetric organic transformations is yet to be investigated. Therefore it would be worth to explore the synthesis and structural characterization of palladium complexes of chiral N-salicyl-β-amino alcohol Schiff base ligands. Herein we report the synthesis of such ligand ((***S***)−**H₂L**) derived from (2*S*)-(−)-2-amino-3-phenyl-1-propanol and 2′-hydroxy acetophenone and its palladium complex. Both ligand and complex were structurally characterized by ^{1}H and $^{13}C\{^{1}H\}$ NMR and FT-IR spectroscopy, elemental analysis, polarimetry and single crystal X-Ray crystallography.

2. Experimental

2.1. Materials and analytical techniques

(2*S*)-(−)-Amino-3-phenyl-1-propanol, 2′-hydroxy acetophenone, sodium tetrachloro palladate were purchased from Sigma Aldrich Ind. Ltd., and were used as received. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker DPX-400 MHz spectrometer at 400 and 100 MHz respectively. The sample solutions were prepared in DMSO-d_6 as solvent for recording NMR spectra. Specific optical rotation $[\alpha]^{25}$ was determined by polarimetry using Rudolph Autopol-I automatic Polarimeter with a cell of 1 dm path length for solutions of 1 M (c = 1) concentration at room temperature (T = 25–29 °C). Melting points were determined in an open capillary tube and were reported uncorrected. FT-IR spectra were recorded on a JASCO FT-IR-4100 instrument in the range of 400–4000 cm^{-1}. The samples for IR spectroscopy were prepared in the form of discs using dry KBr. Single crystal X-Ray diffraction data of (***S***)−**H₂L** and its palladium complex, $[Pd_4(($**_S_**$)$-**L**$)_4]$ were collected on a Bruker SMART APEX CCD-based X-ray diffractometer with Mo Kα-radiation (λ, 0.71073 Å, at T 193 K). The molecular structures of (***S***)−**H₂L** and $[Pd_4(($**_S_**$)$-**L**$)_4]$ were solved by direct methods and refinement was carried out with SHELXL-97 [12] package and empirical absorption correction has been applied (SADABS). All refinements were made by full-matrix least-squares on F^2 with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were included in the refinement in calculated positions.

2.2. Synthesis of 2-{N-[(2S)-(1-hydroxy-3-phenylpropan-2-yl] ethanimidoyl} phenol, (S)−H₂L

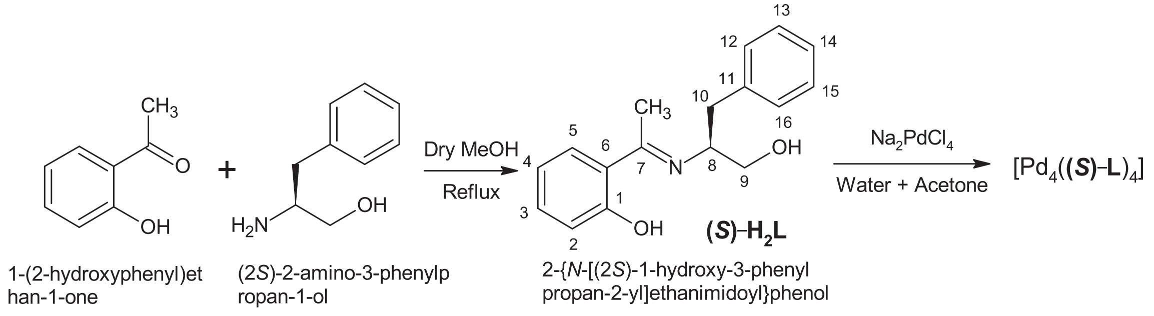
To a stirred solution of 2′-hydroxy acetophenone (1.361 g, 10.0 mmol) in 50 mL dry methanol, a catalytic amount of glacial acetic acid (3–4 drops) was added at room temperature. A solution of (2*S*)-(−)-2-amino-3-phenyl-1-propanol (1.512 g, 10.0 mmol) in 15 mL of dry methanol was added and heated to reflux for about 4 h. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was concentrated under reduced pressure gave yellow solid. This crude solid was purified by flash column chromatography using n-hexane and ethyl acetate mixture (75:25) followed by evaporation of solvent afforded yellow single crystals of the title compound (***S***)−**H₂L**.

Yield: 85%; M.P.: 95–97 °C; $[\alpha]_D^{29} = -50.1°$; Elemental analysis: Found (Calculated): MF, $C_{17}H_{19}NO_2$; C, 75.75 (75.81); H, 7.24 (7.11); N, 5.36 (5.20); FT-IR (ν, cm^{-1}, KBr): 3358, 3324, 2922, 2851, 1683, 1653, 1514, 1154, 697; ^{1}H NMR (DMSO-d_6, 399.65 MHz, δ ppm): 2.060 (s, 3H, CH_3), 2.670–2.725 (dd, 1H, BzCH_2), 3.011–3.056 (dd, 1H, BzCH_2), 3.450–3.504 (qt, 1H, CH_2OH), 3.594–3.750 (qt, 1H, CH_2OH), 4.081 (m, 1H, CHN), 4.911–4.938 (t, *J* = 8.0 Hz, 1H, OH), 6.671–6.709 (t, 2H, Ar*H p* to Ar–OH), 6.732–6.751 (d, *J* = 7.6 Hz, 1H, Ar*H o* to Ar–C=N), 7.147–7.246 (m, 6H, Bz, Ar–H, *m* to Ar–OH), 7.486–7.503 (d, *J* = 6.8 Hz, 2H, Ar*H o* to Ar–OH); $^{13}C\{^{1}H\}$ NMR (DMSO-d_6, 100.638 MHz, δ ppm): 7.66 (CH_3), 28.07 ($BzCH_2$), 54.12 (CH_2OH), 77.87 (CHN), 100.21 (C3), 115.29 (C14), 126.06 (C13, C15), 127.91 (C4), 129.10 (C12, C16), 138.08 (C6), 139.80 (C11, C5), 155.07 (C1), 159.23 (C2), 171.17 (C7).

2.3. Synthesis of [Pd₄((S)-L)₄]

A solution of (***S***)−**H₂L** (0.269 g, 1.0 mmol) in 20 mL of acetone was added to a vigorously stirring solution of $Na_2[PdCl_4]$ (0.294 g, 1.0 mmol) in 10 mL of distilled water. The resulting dark red solution was stirred further for 1 h at room temperature and poured into 50 mL of distilled water. The complex was extracted into dichloromethane (2 × 50 mL). The combined dichloromethane extracts was dried with anhydrous sodium sulphate and then the solvent was evaporated on a rotary evaporator to yield an orange solid. The single crystals of complex were grown by slow evaporation of its solution in a 1:1 mixture chloroform and methanol.

Yield: 60%; M.P. 125 °C (dec); ^{1}H NMR (δ, ppm, DMSO-d_6): $[\alpha]_D^{27} = -254.0°$; Elemental analysis: Found (Calculated): MF, $C_{17}H_{21}NO_2$; C, 75.37 (75.25); H, 7.79 (7.80); N, 5.36 (5.16); FT-IR (ν, cm^{-1}, KBr): 3108, 2962, 1623, 1563, 1523, 1439, 1434, 1383, 1369,



Scheme 1. Synthesis of chiral Schiff base ligand, (***S***)−**H₂L** and its palladium complex, $[Pd_4(($**_S_**$)$-**L**$)_4]$.

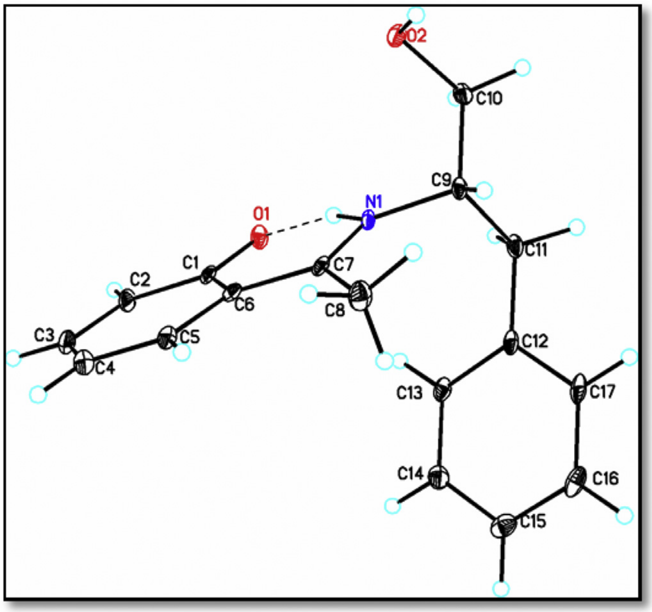


Fig. 1. Molecular structure of **(*S*)—H_2L.**

1346, 1298, 1257, 1237, 1055, 926, 906, 839, 792, 765, 742, 648, 558, 541, 511; ^{1}H NMR (DMSO-d_6, 399.65 MHz, δ ppm): 2.052 (s, 3H, CH_3), 2.638–2.678 (dd, 1H, $BzCH_2$), 2.762–2.811 (dd, 1H, BzCH2), 2.854–2.903 (dd, 1H, CH_2O), 2.948–2.995 (dd, 1H, CH_2O), 5.624–5.670 (qt, 1H, CHN), 6.719–6.805 (m, 1H, ArH *o* to ArC=N)), 6.976–6.998 (d, 1H, ArH *o* to Ar–OH), 7.042–7.556 (m, 5H, ArH), 7.766–7.948 (d, 1H, ArH, *o* to Ar–OH), 7.953–7.970 (d, 1H, ArH, *m* to Ar–OH); ^{13}C{^{1}H} NMR (DMSO-d_6, 100.638 MHz, δ ppm): 11.14 (CH_3), 24.05 ($BzCH_2$), 61.55 (CH_2OH), 78.87 (CHN), 108.98 (C3), 120.38 (C14), 122.82 (C13, C15), 127.53 (C4), 128.84 (C12, C16), 129.80 (C6), 134.80 (C11, C5), 154.50 (C1), 164.52 (C2), 174.21 (C7).

3. Results and discussion

3.1. Synthesis of ligand and complex

The (2*S*)-(−)-2-amino-3-phenyl-1-propanol was prepared by reduction of S-phenylalanine using the reported procedure [13]. The chiral Schiff base type ligand 2-{*N*-[(2*S*)-(1-hydroxy-3-phenylpropan-2-yl] ethanimidoyl} phenol ((***S***)**—H_2L**) and its palladium complex [Pd_4((***S***)**-L**)$_4$] were synthesized as per the reactions given in the Scheme 1. Condensation reaction of 2′-hydroxyacetophenone with (2*S*)-(−)-2-amino-3-phenyl-1-propanol in dry methanol as solvent in the presence of a catalytic amount of glacial acetic acid under refluxing conditions gave ligand (***S***)**—H_2L** in high yield. The complex was obtained by the reaction of (***S***)**—H_2L** with Na_2PdCl_4 as a palladium(II) precursor under green reaction conditions like in solvent water and small amount of acetone at room temperature (300 °C).

The ligand is a yellow crystalline solid, stable, soluble in organic solvents such as methanol, ethanol, propanol, chloroform, dichloromethane, diethyl ether, dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) but insoluble in hexane, heptane, tetrahydrofuran (THF), benzene and toluene. The complex is an orange crystalline solid which is highly soluble in highly polar solvents like dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) and slightly soluble in methanol, ethanol, propanol, chloroform, dichloromethane but insoluble in diethyl ether, hexane,

Table 1
Crystal data and structure refinement parameters for **(*S*)-LH_2** and [Pd_4((***S***)**-L**)$_4$].

Identification code	(*S*)-LH_2	[Pd_4((*S*)-L)$_4$]
Empirical formula	$C_{17}H_{19}NO_2$	$C_{68}H_{68}N_4O_8Pd_4$
Formula weight	269.33	1494.86
Temperature	123(2) K	293(2) K
Wavelength	1.54178 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	P_{21}	P_{21}
Unit cell dimensions	a = 9.3545(2) Å	a = 14.654(3) Å
	b = 6.19930(10) Å	b = 29.067(6) Å
	c = 12.6234(2) Å	c = 14.654(3) Å
	$\alpha = \gamma = 90°$	$\alpha = \gamma = 90°$
	$\beta = 99.9750(10)°$	$\beta = 109.51(3)°$
Volume	720.98(2) Å^3	5884(2) Å^3
Z	2	4
Density (calculated)	1.241 Mg/m^3	1.688 Mg/m^3
Absorption coefficient	0.644 mm^{-1}	1.265 mm^{-1}
F(000)	288	3008
Crystal size	0.32 × 0.18 × 0.11 mm^3	0.23 × 0.11 × 0.08 mm^3
θ range for data collection	3.555–64.435°.	1.401–28.160°.
Index ranges	$-10 \le h<=10, -2 \le k<=7,$ $-14 \le l<=13$	$-19 \le h<=16, -37 \le k<=38,$ $-19 \le l<=19$
Reflections collected	5135	64042
Independent reflections	1436 [R(int) = 0.1268]	21341 [R(int) = 0.0599]
Completeness to theta = 25.500°	95.7%	75.9%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.856 and 0.785	0.795 and 0.657
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1436/1/191	21341/145/1509
Goodness-of-fit on F^2	1.049	1.004
Final R indices [I > 2sigma(I)]	R1 = 0.0537, w*R*2 = 0.1339	R1 = 0.0628, w*R*2 = 0.1523
R indices (all data)	R1 = 0.0545, w*R*2 = 0.1351	R1 = 0.0931, w*R*2 = 0.1755
Absolute structure parameter	−0.1(3)	0.040(12)
Extinction coefficient	0.044(6)	n/a
Largest diff. peak and hole, e.Å^{-3}	0.326 and −0.320	1.297 and −2.205
CCDC No.	1569421	1569422

Table 2
Selected bond lengths [Å] and bond angles [°] for ligand **(*S*)-LH$_2$** and [Pd$_4$((***S***)-**L**)$_4$].

Bond lengths [Å]		Bond angles [°]	
(*S*)-LH$_2$			
O(1)–C(1)	1.306(3)	C(7)–N(1)–C(9)	128.9(2)
N(1)–C(9)	1.451(3)	O(1)–C(1)–C(6)	121.6(2)
O(2)–C(10)	1.417(3)	N(1)–C(7)–C(8)	121.2(2)
N(1)–C(7)	1.304(3)	N(1)–C(9)–C(11)	109.4(2)
		O(1)–C(1)–C(2)	120.0(3)
		N(1)–C(7)–C(6)	117.0(2)
		N(1)–C(9)–C(10)	109.3(2)
[Pd$_4$((***S***)-**L**)$_4$]			
Pd(1)–N(1A)	1.929(14)	N(1A)–Pd(1)–O(1A)	94.4(6)
Pd(1)–O(1A)	1.941(14)	N(1A)–Pd(1)–O(2A)	85.1(5)
Pd(1)–O(2A)	1.965(12)	O(1A)–Pd(1)–O(2A)	178.1(6)
Pd(1)–O(2C)	2.003(11)	N(1A)–Pd(1)–O(2C)	178.5(6)
O(1A)–C(1A)	1.29(2)	O(1A)–Pd(1)–O(2C)	86.6(5)
O(2A)–C(10A)	1.40(2)	O(2A)–Pd(1)–O(2C)	93.9(5)
O(2A)–Pd(2)	2.012(12)	Pd(1)–O(2A)–Pd(2)	134.4(7)
N(1A)–C(7A)	1.28(2)	N(1B)–Pd(2)–O(1B)	92.0(5)
N(1A)–C(9A)	1.48(2)	N(1B)–Pd(2)–O(2B)	84.4(5)
Pd(2)–N(1B)	1.926(13)	O(1B)–Pd(2)–O(2B)	176.2(5)
Pd(2)–O(1B)	1.948(11)	N(1B)–Pd(2)–O(2A)	172.4(5)
Pd(2)–O(2B)	1.957(10)	O(1B)–Pd(2)–O(2A)	93.0(5)
Pd(2)–Pd(3)	**3.0410(18)**	O(2B)–Pd(2)–O(2A)	90.3(5)
O(1B)–C(1B)	1.25(2)	N(1B)–Pd(2)–Pd(3)	103.5(4)
O(2B)–C(10B)	1.398(19)	O(1B)–Pd(2)–Pd(3)	99.0(4)
O(2B)–Pd(4)	1.994(11)	O(2B)–Pd(2)–Pd(3)	83.3(4)
N(1B)–C(7B)	1.28(2)	O(2A)–Pd(2)–Pd(3)	81.3(3)
N(1B)–C(9B)	1.483(19)	Pd(2)–O(2B)–Pd(4)	128.4(6)
Pd(3)–N(1C)	1.926(14)	N(1C)–Pd(3)–O(1C)	93.6(6)
Pd(3)–O(1C)	1.934(12)	N(1C)–Pd(3)–O(2C)	84.8(6)
Pd(3)–O(2C)	1.953(11)	O(1C)–Pd(3)–O(2C)	177.6(5)
Pd(3)–O(2D)	1.993(11)	N(1C)–Pd(3)–O(2D)	171.1(6)
O(1C)–C(1C)	1.271(19)	O(1C)–Pd(3)–O(2D)	92.2(5)
O(2C)–C(10C)	1.393(19)	O(2C)–Pd(3)–O(2D)	89.2(5)
N(1C)–C(7C)	1.29(2)	N(1C)–Pd(3)–Pd(2)	99.9(4)
N(1C)–C(9C)	1.46(2)	O(1C)–Pd(3)–Pd(2)	94.0(4)
Pd(4)–O(1D)	1.905(14)	O(2C)–Pd(3)–Pd(2)	87.9(4)
Pd(4)–N(1D)	1.938(13)	O(2D)–Pd(3)–Pd(2)	86.5(3)
Pd(4)–O(2D)	1.974(12)	Pd(3)–O(2C)–Pd(1)	121.2(6)
O(1D)–C(1D)	1.28(2)	O(1D)–Pd(4)–N(1D)	95.0(6)
O(2D)–C(10D)	1.370(19)	O(1D)–Pd(4)–O(2D)	177.7(6)
N(1D)–C(7D)	1.27(2)	N(1D)–Pd(4)–O(2D)	85.3(5)
N(1D)–C(9D)	1.46(2)	O(1D)–Pd(4)–O(2B)	83.9(5)
Pd(6)–Pd(7)	**3.0517(19)**	N(1D)–Pd(4)–O(2B)	174.6(5)
		O(2D)–Pd(4)–O(2B)	96.1(5)
		Pd(4)–O(2D)–Pd(3)	125.5(6)

Bold values indicates direct palladium-palladium secondary bonding interactions.

heptane, tetrahydrofuran (THF), benzene and toluene.

3.2. FT-IR spectra

The FT-IR spectrum of chiral Schiff base **(*S*)**–**H$_2$L** is shown in Fig. 1. In **(*S*)**–**H$_2$L** the imine group (C=N) has shown a strong band at ν, 1683 cm^{-1}. The broad stretching bands due to phenolic and alcoholic OH groups were appeared at slightly lower wave number ν, 3358 and 3324 cm^{-1} respectively due to strong inter and intra molecular hydrogen bonding [14]. The broad strong absorption at 1514 cm^{-1} could be attributed to be the presence of the ν(C=C) stretching of the aromatic ring backbone. In the complex the C=N stretching band was appeared at 1623 cm^{-1} which has shown red shift of about 60 cm^{-1} in comparison to that band in the ligand. This observation indicates the strong coordination of imine nitrogen to the metal. Other bands in the IR spectrum of complex were found characteristic.

3.3. ^{1}H NMR spectra

In the ^{1}H NMR spectrum of **(*S*)**–**H$_2$L**, the phenolic OH proton was

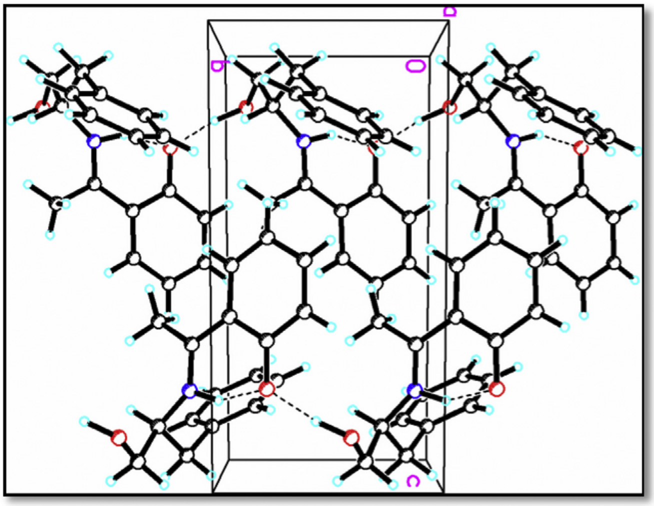


Fig. 2. Intra (O–H···N) and inter (O–H···O) molecular hydrogen bonding in **(*S*)-LH$_2$**.

Table 3
Hydrogen bonds for **(*S*)-LH$_2$** and [Pd$_4$(**(*S*)-L**)$_4$] [Å and °].

D-H ... A	d(D-H)	d(H ... A)	d(D ... A)	<(DHA)
(*S*)-LH$_2$				
O(2)–H(2O)···O(1)#1	1.06(5)	1.62(5)	2.667(3)	172(4)
N(1)–H(1N)···O(1)	1.03(5)	1.53(5)	2.485(3)	152(4)
C(10)–H(10B)···O(2)#2	0.99	2.59	3.568(3)	168.7
[Pd$_4$(**(*S*)-L**)$_4$]				
C(10B)–H(10O)···O(1C)	0.97	2.51	3.33(2)	141.9
C(10B)–H(10P)···O(1D)	0.97	2.47	2.97(2)	111.8
C(10C)–H(10C)···O(1B)	0.97	2.52	3.41(2)	153.7
C(10F)–H(10I)···O(1G)	0.97	2.32	3.23(2)	154.9
C(10G)–H(10K)···O(1F)	0.97	2.55	3.42(2)	149.5

Symmetry transformations used to generate equivalent atoms: #1 x, y+1,z #2 -x, y-1/2, -z.

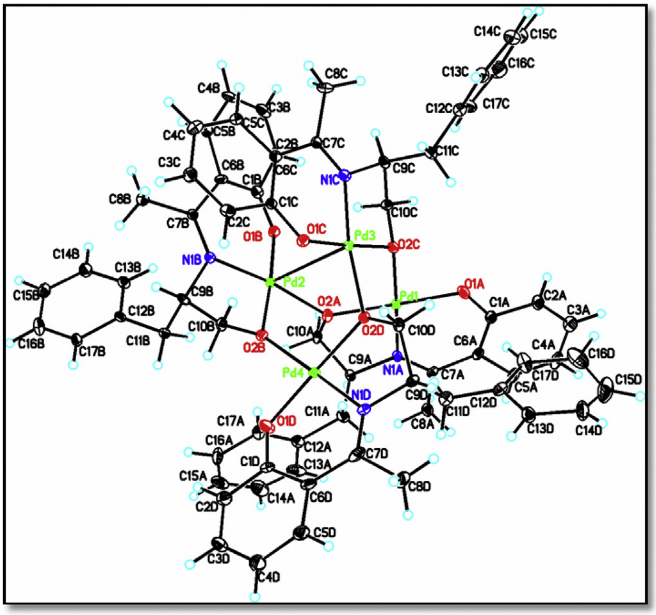


Fig. 3. Molecular structure of [Pd$_4$(**(*S*)-L**)$_4$].

found highly deshielded due to the OH•••N intramolecular hydrogen bonding with imine nitrogen and appeared as a singlet at *δ*, 16.54 ppm as reported for similar Schiff bases [15]. The alcoholic –OH proton was also found deshielded due to intermolecular OH•••O hydrogen bonding obtained a triplet at 4.911–4.938 ppm through the coupling of methylene protons. The aromatic protons (ArH) *ortho* to phenolic OH and *ortho* to imine (>C=N-) groups gave doublets at *δ*, 7.486–7.503 ppm and 6.732–6.751 ppm respectively. A triplet was obtained for ArH proton *para* to phenolic OH at *δ*, 6.671–6.709 ppm. Other ArH protons were appeared as a multiplet between *δ*, 7.147–7.246 ppm. The CH proton coupled with neighboring four methylene protons, appearing as a quintet at *δ*, 4.081 ppm. The methylene protons of CH$_2$OH group are diastereotopic in nature hence gave two quintets between *δ*, 3.450–3.720 ppm on coupling with germinal CH and vicinal OH and CH protons. The benzyl CH$_2$ protons also possess diastereotopic character, hence appeared as doublet of a doublet. The methyl protons were appeared as singlet at *δ*, 2.06 ppm. In the new palladium complex, the signal for phenolic and alcoholic OH protons were absent indicating the deprotonation of both groups forming dianionic ligand due to phenolate and alkoxide. The quintet observed for CH proton has shown deshielding of about 1.34 ppm when compared to that signal in the chiral ligand hence the coordination imine nitrogen to the Pd(II) ion. The CH$_2$OH and benzyl CH$_2$ protons were found shielded due to the coordination of ligand through alkoxide ion. The aromatic protons were also found characteristic shifts such that the ligand coordinated as dianionic tridentate (O$^-$, N, O$^-$) mode.

3.4. ^{13}C{^{1}H} NMR spectra

The proton decoupled carbon-13 NMR spectrum of new chiral Schiff base was found characteristic. The carbon signals of CH$_3$, BzCH$_2$, CH$_2$OH and CH groups were observed at *δ*, 7.7, 28.1, 58.1 and 77.9 ppm respectively due to increased electron withdrawing inductive effect. These carbon signals in its complex were observed deshielded and observed at *δ*, 11, 61 and 79 ppm except the BzCH$_2$ carbon signal which was shielded and obtained at *δ*, 24 ppm. The C=N and Ar–C–OH carbon were appeared highly deshielded and the observed at *δ*, 171.17 and 159.23 ppm respectively. These carbon signals in the palladium complex were found deshielded by about 3.2 and 4.8 ppm when compared those signals in ligand. Other carbon signals were found characteristic shift or no shift in the carbon-13 NMR spectrum of complex. These observations confirmed the coordination behavior of ligand in the complex.

3.5. Single crystal X-Ray diffraction

The single crystals of Schiff base ligand **(*S*)–H$_2$L** and palladium complex, [Pd$_4$(**(*S*)-L**)$_4$] were grown and their absolute molecular structures were determined by single crystal X-ray diffraction. Both

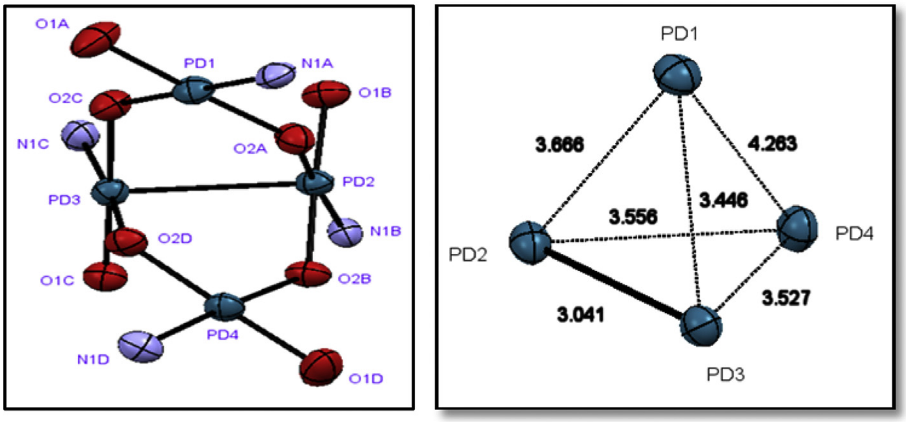


Fig. 4. (a) Bridging Pd–O–Pd, terminal Pd–O and Pd–Pd bonds and (**b**) A core structure of distorted tetrahedral [Pd]$_4$ unit in [Pd$_4$(**(*S*)-L**)$_4$].

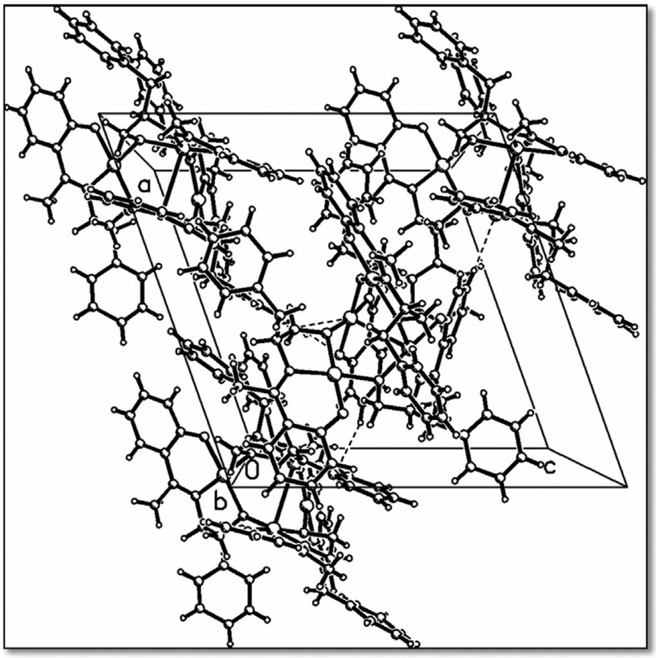


Fig. 5. CH···O type inter molecular hydrogen bonding in [Pd$_4$((***S***)-**L**)$_4$].

(***S***)−**H$_2$L** and its complex crystallizes in monoclinic system with space group *P*2$_1$. The crystal data and refinement parameters of (***S***)−**H$_2$L** and the new palladium complex are given in Table 1. The absolute structure parameters of ligand and complex are 0.1(3) and 0.040(12) respectively indicating that the compounds are enantiomerically pure. The selected bond lengths and bond angles are given in Table 2. The molecular structure of (***S***)−**H$_2$L** is shown in Fig. 1.

The C−N double and single bond lengths found were 1.304(3) and 1.451(3) Å respectively and are comparable with those bond lengths [1.306(3) and 1.466(10) Å] for the similar Schiff base ligand, 2,4-$(HO)_2$−$C_6H_4C(CH_3)$ = N−CH_2CH_2SPh [16]. The ArC−O and RC-O bond lengths are 1.303(4) and 1.417(3) Å as expected for ArC−O and RC-O bond lengths for similar compound [11,16]. In the crystals of ligand (***S***)−**H$_2$L** there exists an intramolecular O−H···N (1.62(5) Å) and intermolecular O−H···O (1.53(5) Å) hydrogen bonding and C−H···O (2.59 Å) secondary bonding interactions as shown in Fig. 2. The secondary bonding intearction parameters are given in Table 3. These bond lengths are in agreement with those present in similar type of Schiff bases [16].

The molecular structure of palladium complex of new chiral Schiff base ligand (***S***)**-LH$_2$** is shown in Fig. 3 and its structure was found very interesting wherein dideprotonated ligand, (***S***)**-L** coordinated to palladium metal center in tridentate dianionic (O^-, N, O^-) fashion resulting in a tetranuclear palladium cluster, [Pd$_4$((***S***)-**L**)$_4$]. In the crystal lattice there were two asymmetric tetranuclear complex molecules. The supramolecular structure were formed by coordination of phenolate oxygen to Pd(II) ion as terminal group and while alkoxide oxygen as bridging group between two Pd(II) centers.

The Pd−N bond lengths found were in the range of 1.949(13) to 1.919(12) Å the Pd−O terminal bond lengths [1.934(12) - 1.977(11) Å] were found shorter than those in the Pd−O−Pd bridging bond lengths [1.993(11) - 2.012(12) Å]. Each palladium acquires square planar geometry coordinated by three oxygen's out of which two are from Pd−O−Pd bridging bonds and one from terminal bond and one nitrogen donors as shown in Fig. 4a resulting in a supramolecular structure. There exists a strong intramolecular palladium-palladium secondary bonding interaction in each asymmetric unit of the complex between the second and third palladium centers such as Pd(2)−Pd(3) and Pd(6)−Pd(7) with a short distance of 3.041(18) and 3.0517(19) Å respectively. This length is intermediate between the sum of the ionic radii (2.75 Å) and the Vander Waal's radii (3.26 Å) [17a] of Pd found in other palladium complexes [17b]. There were no reports on tetranuclear palladium complexes but few of this type complexes found in the literature formed by nickel [10a] and copper [11] by this type of Schiff base ligands containing terminal M − O and bridging M-O-M bonds. The core structure of distorted [Pd]$_4$ tetrahedron in the complex is given in Fig. 4b. All Pd−Pd distances (3.041−3.666 Å) are within the range of sum of Vander Waal's radii of palladium except Pd(1)−Pd(4) which is 4.263 Å. In addition there exists CH···O (2.32−2.55 Å) type inter molecular hydrogen bonding in complex as shown in Fig. 5. The weak secondary interaction may be highly useful in understanding catalytic reaction mechanisms [1].

4. Conclusions

A new chiral Schiff base type ligand (***S***)−**H$_2$L** and its palladium complex were synthesized and both were characterized by FT-IR, ^{1}H, ^{13}C{^{1}H} NMR spectroscopy, polarimetry, elemental analysis and single crystal X-ray diffraction. The ligand contain strong intra O−H···N and intermolecular O−H···O and C−H···O secondary bonding interactions. In the palladium complex the ligand coordinated to palladium metal ion (O^-, N, O^-) donor system resulting in a tetranuclear palladium cluster, [Pd$_4$((***S***)-**L**)$_4$]. Each palladium attained square planar geometry. The four bonds were formed by each of Pd−N and Pd−O terminal bonds through phenolate oxygen and imine nitrogen and two Pd−O−Pd bridging bonds through the alkoxide oxygen. These bonding interaction brought the two alternate palladium centers very near with strong Pd−Pd bonds, resulting tetranuclear palladium cluster complex.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.molstruc.2017.11.112.

References

[1] (a) G.E. O'Mahony, P. Kelly, S.E. Lawrence, A.R. Maguire, ARKIVOC i (2011) 1–110;
(b) C.P. Pradeepa, S.K. Das, Coord. Chem. Rev. 257 (2013) 1699–1715.
[2] (a) L.-Z. Du, J.-F. Gong, C. Xu, Y. Zhu, Y.-J. Wu, M.-P. Song, Inorg. Chem. Commun. 9 (2006) 410–414.
[3] (a) C. Bolm, F. Bienewald, Angew. Chem. Int. Ed. Engl. 34 (1995) 2640–2642;
(b) S.A. Blum, R.G. Bergman, J.A. Ellmann, J. Org. Chem. 68 (2003) 150–155;
(c) Á. Gama, L.Z. Flores-López, G. Aguirre, M. Parra-Hake, L.H. Hellberg, R. Somanathan, ARKIVOC 11 (2003) 4–15;
(d) A. Barbarini, R. Maggi, M. Muratori, G. Sartori, R. Sartorio, Tetrahedron Asymmet 15 (2004) 2467–2473;
(e) Q. Zeng, H. Wang, T. Wang, Y. Cai, W. Weng, Y. Zhao, Adv. Synth. Catal. 347 (2005) 1933–1936;
(f) Y. Wu, F. Mao, F. Meng, X. Li, Adv. Synth. Catal. 353 (2011) 1707–1712;
(g) A.H. Vetter, A. Berkessel, Tetrahedron Lett. 39 (1998) 1741–1744;
(h) E.A. Koneva, K.P. Volcho, D.V. Korchagina, N.I. Komarova, A.I. Kochnev, N.F. Salakhutdinov, A.G. Tolstikov, Russ. Chem. Bull. 57 (1) (2008) 108–117.
[4] (a) G. Liu, D.A. Cogan, J.A. Ellman, J. Am. Chem. Soc. 119 (1997) 9913–9914;

(b) D.A. Cogan, G. Liu, K. Kim, B.J. Backes, J.A. Ellman, J. Am. Chem. Soc. 120 (1998) 8011–8019;
(c) J. Org. Chem. 68 (2003) 3–10.
[5] (a) C. Chen, L. Hong, B. Zhang, R. Wang, Tetrahedron Asymmet 19 (2008) 191–196;
(b) M. Hong, Q. You, Lett. Org. Chem. 4 (2007) 571–575.
[6] (a) Á. Gama, L.Z. Flores-López, G. Aguirre, M. Parra-Hake, R. Somanathan, T. Cole, Tetrahedron Asymmet 16 (2005) 1167–1174;
(b) L.Z. Flores-Lopéz, M. Parra-Hake, R. Somanathan, P.J. Walsh, Organometallics 19 (2000) 2153.
[7] J. Lee, Y. Kim, Y. Do, Inorg. Chem. 46 (2007) 7701–7703.
[8] (a) G. Romanowski, J. Kira, M. Wera, J. Mol. Cat. A Chem. 381 (2014) 148–160;
(b) Polyhedron 67 (2014) 529–539.
[9] C.P. Pradeep, P.S. Zacharias, S.K. Das, J. Chem. Sci. 118 (4) (2006) 311–317.
[10] (a) S. Muche, M. Hołynska, J. Mol. Str. 1142 (2017) 168–174;
(b) B.Y. Waghamare, D.D. Kumbhar, A.G. Pathade, S.K. Pardeshi, IJIRSET 5 (1) (2016) 194–202.
[11] (a) A.K. Sah, T. Tanase, M. Mikuriya, Inorg. Chem. 45 (2006) 2083–2092;
(b) H. Xiang, L. Jiang, H.-Y. Li, X.-D. Zheng, Y. Li, Chin. Chem. Lett. 24 (2013) 49–51;
(c) H. Xiang, Y. Lan, L. Jiang, W.-X. Zhang, Inorg. Chem. Commun. 16 (2012) 51–54.
[12] G.M. Sheldrick, SHELXL 97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
[13] A. Abiko, S. Masamune, Tetrahedron Lett. 33 (1992) 5517–5518.
[14] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, third ed., John Wiley and Sons, Inc, 1978.
[15] (a) P.R. Kumar, A.K. Singh, R.J. Butcher, P. Sharma, R.A. Toscano, Eur. J. Inorg. Chem. (2004) 1107–1114;
(b) P. Barczyński, Z. Dega-Szafran, A. Katrusiak, M. Szafran, J. Mol. Str. 1000 (2011) 127–134.
[16] P.R. Kumar, S. Upreti, A.K. Singh, Polyhedron 27 (2008) 1610–1622.
[17] (a) A. Bondi, J. Phys. Chem. 68 (3) (1964) 441–451;
(b) P.R. Kumar, A.K. Singh, J.E. Drake, M.B. Hursthouse, M.E. Little, Struct. Chem. 18 (2007) 203–207.