Synthesis, characterization and antimicrobial activity of new paladium and nickel complexes containing Schiff bases

C.E. Satheesh, P. Raghavendra Kumar, P. Sharma, K. Lingaraju, B.S. Palakshamurthy, H. Rajanaika

PII: S0020-1693(15)00571-X
DOI: http://dx.doi.org/10.1016/j.ica.2015.11.017
Reference: ICA 16775

To appear in: *Inorganica Chimica Acta*

Received Date: 22 August 2015
Revised Date: 11 November 2015
Accepted Date: 12 November 2015

Please cite this article as: C.E. Satheesh, P. Raghavendra Kumar, P. Sharma, K. Lingaraju, B.S. Palakshamurthy, H. Rajanaika, Synthesis, characterization and antimicrobial activity of new paladium and nickel complexes containing Schiff bases, *Inorganica Chimica Acta* (2015), doi: http://dx.doi.org/10.1016/j.ica.2015.11.017

Synthesis, characterization and antimicrobial activity of new paladium and nickel complexes containing Schiff bases

Satheesh C.E.[1], Raghavendra Kumar P. [1]*, Sharma P.[2], Lingaraju K.[4], Palakshamurthy B.S.[3], Rajanaika H.[4]

[1]Department of Chemistry, University College of Science, Tumkur University, Tumkur 572 103

[2]Instituto de Quimica, UNAM, Circuito Exterior, Coyoacan, D. F. 04510, Mexico

[3]Department of Physics, University College of Science, Tumkur University, Tumkur 572 103

[4]Department of Studies and Research in Environmental Science, Tumkur University, Tumkur 572 103

*Corresponding author: raghukp1@gmail.com, Ph. No. +91-9901511112

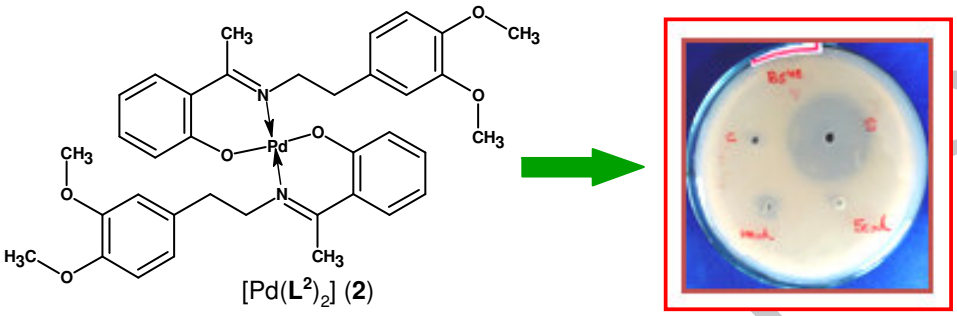
Keywords: Schiff's base, 2-(3,4-Dimethoxyphenyl) ethanamine, Palladium, Nickel, Complex, Antimicrobial activity

Abstract:

New Schiff base ligands were synthesized by condensation of 2-(3,4-dimethoxyphenyl) ethanamine with 2-hydroxy benzaldehyde (**L^1H**) and 2'-hydroxy acetophenone (**L^2H**) respectively. Reaction of **L^1H** or **L^2H** with Na_2PdCl_4 or $NiCl_2.6H_2O$ in 2:1 ratio obtained four new coordination complexes $[M(L^{1-2})_2]$ (where M = Pd(II); **1** and **2** and M = Ni(II); **3** and **4**). Both the ligands and four complexes were characterized by elemental analysis, FT-IR and UV-Vis., spectroscopy. **L^1H**, **L^2H**, **1** and **2** were also characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The molecular structures of **1** and **3** were determined by single crystal X-ray diffraction. The spectroscopic and crystal structure data showed that the ligands coordinated to M(II) ion in a bidentate monoanionic (O^-, N) fashion. The Pd-O and Pd-N bond lengths in **1** are 1.984(11) and 2.020(12) Å in **3** the Ni-O and Ni-N bond lengths are 1.8222(13) and 1.9262(15) Å respectively. The C=N bond length in **3** found 1.290(2) Å which was shorter than 1.310(19) Å in **1**. The bond angles provided square planar geometry around Pd(II) and Ni(II) in both **1** and **3**. There exists C-H···O type (2.50 – 2.52 Å) intermolecular hydrogen bonding in both **1** and **3** resulting in supramolecular structures. The antimicrobial activity of new Schiff base ligands and their Pd(II) and Ni(II) complexes against pathogenic microbial strains by agar well diffusion method was conducted. All the ligands and complexes showed significant antibacterial and antifungal activities. The bacterial and fungi growth inhibition activity of ligands has been

increased on complexation as well as among complexes palladium complexes were found better antibacterial and antifungal agents than the nickel complexes of corresponding ligands. Ligand **L^1H** and the complex **2** showed highest antibacterial activity against *P. desmolyticum* and highest antifungal activity against *C. Albicans.*

Graphical Abstract:



Antibacterial activity of [Pd(L^2)$_2$] (**2**) by agar well diffusion method

Highlights:

- Pd(II) and Ni(II)) complexes, [M(**L**)$_2$] of Schiff base ligands were synthesised from 2-(3,4-dimethoxyphenyl) ethanamine, a dimethyl derivative of dopamine, a starting material for many nuerotransmitting agents.
- FT-IR, ^{1}H, ^{13}C{^{1}H} NMR and UV-Vis., spectroscopy, elemental analysis and single crystal X-ray diffraction have been used as characterization techniques.
- The spectroscopic data and single crystal X-ray diffraction studies on complexes revealed that the ligands coordinated to M(II) ions in bidentate monoanionic (O^-, N) mode. In the crystals of complexes [Pd/Ni($\mathbf{L^1}$)$_2$] (**1** and **3**) contain C-H$\cdots$O intermolecular secondary interactions.
- New ligands and the complexes were screened for their antibacterial and antifungal activities by agar well diffusion method. The antimicrobial activity of complexes was higher than the free ligands and in particular the Pd complexes are better inhibitors than Ni.
- The **L^1H** and **2** are among the ligands and complexes showing highest antifungal and antibacterial activity especially against *P. desmolyticum* and highest antifungal activity against *C. Albicans.*

1. Introduction

Transition metal complexes of Schiff base ligands have been extensively studied due to their ease of preparation, availability of low cost raw materials, and formation of stable and chelated coordination complexes with most of the transition metals [1]. Applications of Schiff bases and their transition metal complexes have been largely investigated in the fields of biochemistry [2], catalysis [3] and medicine [4].

Schiff base ligands synthesized generally by condensation of aldehydes or ketones with aliphatic or aromatic amines. Their transition metal complexes have been evaluated for their variety of biological properties [5] such as antibacterial [6], antioxidant [8], antifungal and anti-HIV [7], anticancer [9], antiamoebic [10a], herbicidal [11] activities. Investigation of biological activities Schiff bases derived from compounds (amines, aldehydes or ketones) of biologically important, for example isatin [7], 2-azetidinone [12a], cephalothin [12b] and their metal complexes have been the current interest. In this regard metal complexes of Schiff bases never been prepared from 2-(3,4-dimethoxyphenyl) ethanamine, a dimethyl derivative of dopamine, which is a starting material for many nuerotransmitting agents [13] and other biologically important compounds [14] and investigated their biological activities.

Transition metal complexes are potential to show biological activity and are the current area of research [8c]. Schiff base ligands derived are very effective metal chelators on coordination, chelated complexes enhance the biological activity under the identical experimental conditions [15].

Azomethine (>C=N-) group of Schiff bases play an important role in the antimicrobial activities. The actual mechanism of increased activity of complexes is expected due to other than structural factors like solubility, dipole moment and cell permeability [16] and also their enzymatic action. A possible mode of increased toxicity may be considered in the light of Tweedy's chelation theory [17].

Therefore we have reported herein the synthesis, characterization and evolution of antimicrobial activities such as antibacterial and antifungal activities of Schiff base ligands $\mathbf{L^1H}$ and $\mathbf{L^2H}$ derived from 2-(3,4-dimethoxyphenyl) ethanamine, 2-hydroxy benzaldehyde and 2-hydroxy acetophenone and their Pd(II) and Ni(II) complexes $[M(\mathbf{L^{1\text{-}2}})_2]$ (**1-4**).

2. Experimental

2.1. Materials

2-(3,4-dimethoxyphenyl) ethylamine (97%) and Na_2PdCl_4 (98%) were obtained from Sigma Aldrich, India. 2-Hydroxy benzaldehyde (99.5%) and 2'-Hydroxy acetophenone (99%) were purchased from Merck Specialities Pvt. Ind. Ltd. $NiCl_2.6H_2O$ was obtained from S.D. Fine-Chem Ltd., India. All solvents (EtOH, MeOH, Pet-ether, Hexane, $CHCl_3$ and MDC) were of reagent grade and used without further purification. The microorganisms used in this study are *Klebsiella aerogenes* (*K. aerogenes*) [NCIM-2098], *Escherichia coli* (*E. coli*) [NCIM-5051], *Pseudomonas desmolyticum* (*P. desmolyticum*) [NCIM-2028] and *Staphylococcus aureus (S. aureus)* [NCIM-5022] as pathogenic bacterial strains and *Aspergillus flavus* (*A. flavus*) [NCIM-544] and *Candida albicans* (*C. albicans*) [NCIM-3100] as pathogenic fungal strains. These microorganisms were purchased from National Chemical Laboratory (NCL), Pune, India. These strains were maintained on nutrient agar slant at 4 °C. Standard antibiotics Ciprofloxacin and Fluconazole were purchased from Hi Media, Mumbai, India.

2.2 Analytical methods

Elemental analysis (C, H and N) was performed on a LECO–CHSNO – 9320 type elemental analyser. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of ligands and Pd(II) complexes were recorded in $CDCl_3$ or DMSO-d_6 solutions on a Bruker WM-400 spectrometer (400 MHz) using TMS as an internal standard. The FT-IR spectra of all the compounds were recorded by scan method in the range of 4000–500 cm^{-1} with an Agilent FT-IR spectrometer. UV–Vis., spectra were recorded on UNI-CAM-UV 2-100 spectrophotometer. Melting points of ligands and complexes were determined with a Gallenkamp melting point apparatus in an open capillary and are reported uncorrected. Single crystal X-Ray diffraction data of **1** and **3** 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 **1** and **3** were solved by direct methods and refinement was carried out with SHELXL-97 [18] 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.

2.3 Synthesis of ligands L^1H *and* L^2H

2-(3,4-dimethoxyphenyl) ethanamine (200 mg, 1.1 mmol) was dissolved in 20 ml of dry ethanol and this solution was stirred for 0.5 h at room temperature. 2-hydroxy benzaldehyde

(0.115 ml, 1.1 mmol) or 2'-hydroxy acetophenone (0.133 ml, 1.1 mmol) dissolved in 20 ml of dry ethanol was added to the above solution drop wise with stirring. The mixture was stirred further for 1.5–2.0 h at room temperature during which the solution changes to yellow colour. The progress of the reaction was monitored on TLC using pet-ether and ethyl acetate (70:30 %) as mobile phase. After completion, the reaction solution was concentrated by rotary evaporator which resulted yellow precipitate. The yellow precipitate was washed with hexane or petroleum ether (10 ml X 2) and then dried under vacuum. The dry solid was recrystallized from a mixture (1:1) of chloroform and hexane gave yellow single crystals of $\mathbf{L^1H}$ or $\mathbf{L^2H}$.

L^1H: Yellow Crystalline solid; **Yield:** 290 mg (93%); **M.P.:** 122-123 °C; **Element. Anal. Calcd. (Found)** for $C_{17}H_{19}NO_3$: C, 71.56(71.16); H, 6.71(6.63); N, 4.91(4.96); **FT-IR** (ν, cm^{-1}): 3418, 2992, 2957, 2835, 1634, 1588, 1515, 1333, 1261, 1138, 1025, 851, 761, 655, 554; **UV-Vis.,** λ_{max} in nm: 261, 279, 315, 408; **^{1}H NMR** ($CDCl_3$, δ ppm): 13.44 (s, 1H, OH), 8.18 (s, 1H, CH=N), 7.270-7.313 (t, 1H, H4), 7.160-7.184 (d, 1H, H6), 6.864-6.962 (d, 1H, H3), 6.707-6.848 (m, 4H, H5, H11, H14, H15), 3.849 (s, 3H, -OCH_3), 3.807 (s, 3H, -OCH_3), 3.817-3.837 (q, 2H, =NCH_2), 2.934-2.968 (t, 2H, -CH_2Ar); **^{13}C{^{1}H} NMR** ($CDCl_3$, δ, ppm): 36.241 (C9), 55.222 (OCH_3), 55.412 (OCH_3), 59.909 (C8), 111.748 (C5), 112.725 (C11), 116.458 (C14), 118.372 (C15), 118.557 (C10), 120.587 (C4), 131.528 (C3), 131.765 (C1), 132.192 (C6), 147.176 (C13), 148.492 (C12), 160.772 (C2), 165.849 (C7).

L^2H: Yellow Crystalline solid; **Yield:** 310 mg (94 %); **M.P.:** 125-126 °C. **Element. Anal. Calcd. (Found)** for $C_{18}H_{21}NO_3$: **C**, 72.22(72.32); H, 7.07(7.08); N, 4.68(4.75); **FT-IR** (ν, cm^{-1}): 3392, 2934, 2912, 2836, 1607, 1516, 1454, 1230, 1137, 1024, 857, 816, 763, 653, 566, 527; **UV-Vis.:** λ_{max} in nm: 257.6, 277, 319, 392; **^{1}H NMR** ($CDCl_3$, δ ppm): 16.55 (s, 1H, OH), 7.443-7473 (d, 1H, H6), 7. 249-7.292 (t, 1H, H4), 6.907-6.937 (d, 1H, H3), 6.723-6.825 (m, 4H, H5, H11, H14, H15), 3.853 (s, 3H, OCH_3), 3.815 (s, 3H, OCH_3), 3.785-3.802 (t, 2H, =NCH_2), 2.993-3.027 (t, 2H, ArCH_2), 2.180 (s, 3H, CH_3); **^{13}C{^{1}H} NMR** ($CDCl_3$, δ ppm): 14.211 (CH_3), 35.605 (C9), 50.222 (C8), 55.257 (OCH_3), 55.454 (OCH_3), 111.848 (C5), 112.819 (C11), 116.429 (C14), 118.093 (C15), 118.703 (C10), 120.582 (C4), 128.608 (C3), 131.924 (C1), 132.252 (C6), 147.230 (C13), 148.537 (C12), 163.883 (C2), 172.402 (C7).

2.4 Synthesis of palladium complexes, $[Pd(L^{1-2})_2]$ (1-2)

The $Na_2[PdCl_4]$ (100 mg, 0.3 mmol) was dissolved in 10 ml of water and the solution was stirred for 5 min. A solution of ligand $\mathbf{L^1H}$ (194 mg, 0.68 mmol) or $\mathbf{L^2H}$ (203 mg, 0.68 mmol) made in 20 ml of acetone was added to the above solution with vigorous stirring and the stirring was continued further for 1.5–2.0 h. The progress of the reaction was monitored by TLC using pet-ether and ethyl acetate (50:50) as mobile phase. The resulting orange solution was extracted into 100 ml of chloroform. The chloroform layer was washed with water (25 ml x 3) and treated with anhydrous sodium sulfate crystals. The solvent was evaporated to dryness on rotary evaporator to obtain an orange-red powder. The orange-red powder subjected to recrystallization in a 1:1 mixture of chloroform and hexane gave yellowish-orange coloured crystals of **1** or **2** after 24 h.

1: Yellow**-**Orange crystalline solid**; Yield:** 390 mg (85 %); **M.P.:** 190-192 °C; **Element. Anal. Calcd.(Found)** for $C_{34}H_{36}N_2PdO_6$: C, 60.49(60.30); H, 5.38(5.27); N, 4.15(4.18); **FT-IR:** (ν, cm^{-1}): 3444, 2921, 1618, 1599, 1514, 1447, 1321, 1231, 1143, 1023, 912, 760, 583, 438; UV-Vis., λ_{max} in nm: 257.8, 280.7, 392; **^{1}H NMR** ($CDCl_3$, δ ppm): 7.383 (s, 1H, CH=N), 7.219-7.544 (t, 1H, H4), 7.059-7.083 (d, 1H, H3), 6.905-6.926 (d, 1H, H6), 6.782-6.832 (m, 3H, H11, H14, H15), 6.537-6.576 (t, 1H, H5) 3.951-3.987 (t, 2H, NCH_2) 3.853 (s, 3H, OCH_3), 3.777 (s, 3H, OCH_3), 3.067-3.103 (t, 2H, CH_2Ar).

2: Yellow-orange crystalline solid**; Yield:** 400 mg (84 %); **M.P.:** 191-192 °C; **Element. Anal. Calcd.(Found)** for $C_{36}H_{40}N_2PdO_6$: **C**, 61.49(61.42); H, 5.73(5.65); N, 3.98(3.98); **FT-IR:** (ν, cm^{-1}): 3444, 2951, 2833, 1595, 1515, 1436, 1317, 1235, 1143, 1023, 859, 816, 761, 590; **^{1}H NMR** ($CDCl_3$, δ ppm): 7.409-7.429 (d, 1H, H6), 7.082-7.112 (t, 1H, H4), 7.002 (s, 1H, H11), 6.800-6.895 (m, 2H, H5, H15), 6.708-6.769 (d, 1H, H14), 6.528-6.565 (d, 1H, H3), 4.001-4.112 (t, 2H, $=NCH_2$), 3.675 (s, 3H, $-OCH_3$), 3.617 (s, 3H, $-OCH_3$), 3.227-3.333 (t, 2H, $ArCH_2$), 2.201 (s, 3H, CH_3); **^{13}C{^{1}H} NMR** ($CDCl_3$, δ ppm): **^{13}C{^{1}H} NMR** ($CDCl_3$, δ ppm): 14.094 (CH_3), 38.224 (C9), 55.644 (OCH_3), 55.825 (OCH_3), 59.851 (C8), 111.157 (C5), 112.557 (C11), 115.002 (C14), 120.164 (C4, C10), 121.061 (C15), 131.476 (C1), 134.127 (C6), 134.497 (C3), 147.447 (C13), 148.649 (C12), 162.077 (C2), 164.456 (C7).

2.5 Synthesis of nickel complexes, $\mathbf{[Ni(L^{1\text{-}2})_2]}$ **(3-4)**

To a solution of $NiCl_2.6H_2O$ (100 mg; 0.42 mmol) and triethylamine (0.117 ml; 0.84 mmol) made in 20 ml of methanol, added slowly a methanolic solution (50 mL) of $\mathbf{L^1H}$ (240

mg, 0.84 mmol) or **L^2H** (252 mg, 0.84mmol). The reaction mixture was stirred at room temperature for 6-7 h. The progress of the reaction was monitored by TLC using pet ether and ethyl acetate (50:50) as mobile phase. The resulting green solution was evaporated to dryness using rotary evaporator gave a green powder. This powder was dissolved in chloroform, filtered, washed with small volume of ether and then dried under vacuum resulted a green solid. This solid was recrystallized from a mixture of chloroform and hexane (1:1) and obtained crystals of **3** or **4**.

3: Green crystalline solid. **Yield**: 424 mg (80 %); **M.P.:** 189-191 ^oC; **Element. Anal. Calcd. (Found)** for $C_{34}H_{36}N_2NiO_6$: **C**, 65.09(65.24); **H**, 5.78(5.82); **N**, 4.47(4.61); **FT-IR** (ν, cm^{-1}): 3444, 2922, 1614, 1541, 1514, 1470, 1417, 1330, 1278, 1232, 1143, 1025, 915, 845, 807, 761, 602, 441; **UV-Vis.:** λ_{max} in nm: 259, 372.

4: Pale brown crystalline solid; **Yield: 468 mg (**85 %); M.P.: 196-197 ^oC; **Element. Anal. Calcd. (Found)** for $C_{36}H_{40}N_2NiO_6$: **C**, 65.97(65.83); H, 6.15(6.11); **N**, 4.27(4.26); **FT-IR** (ν, cm^{-1}): 3418, 2950, 2832, 1597, 1539, 1514, 1442, 1363, 1335, 1284, 1224, 1142, 1023, 929, 863, 817, 761, 592, 526; **UV-Vis.:** λ_{max} in nm: 260, 274, 319 and 390.

2.6 Evaluation of antimicrobial activity

The antimicrobial activity of new Schiff base ligands and their Pd(II) and Ni(II) complexes were screened by agar well diffusion method [24-27] against four bacterium namely Gram -ve bacteria *K. aerogenes*, *E. coli, P. desmolyticum*, Gram +ve bacteria *S. aureus* and two fungi such as *A. flavus* and *C. albicans*.

Nutrient and potato dextrose broth was used to culture the bacteria and fungi respectively. Nutrient agar plates were prepared and swabbed using sterile L-shaped glass rod with 100 µl of 24 h mature broth culture of individual bacterial strains. The wells of 6 mm were created into the each petri plate using sterile cork borer. Two test solutions of each **L^1H**, **L^2H**, **1**, **2**, **3** and **4** were prepared by dissolving 500 and 1000 µg in 50 and 100 µl of sterile water respectively to get 10 µg / µl concentration of each compound and assessed their antibacterial activity. Similarly a standard antibiotic solution was prepared by dissolving 5 µg Ciprofloxacin (as positive control) in 50 µl of sterile water to get 0.1 µg / µl concentration. These solutions were added into the wells by sterile micropipettes. The plates were incubated at 37 °C for 36 h. After the incubation period, the zone of inhibition of each well was measured

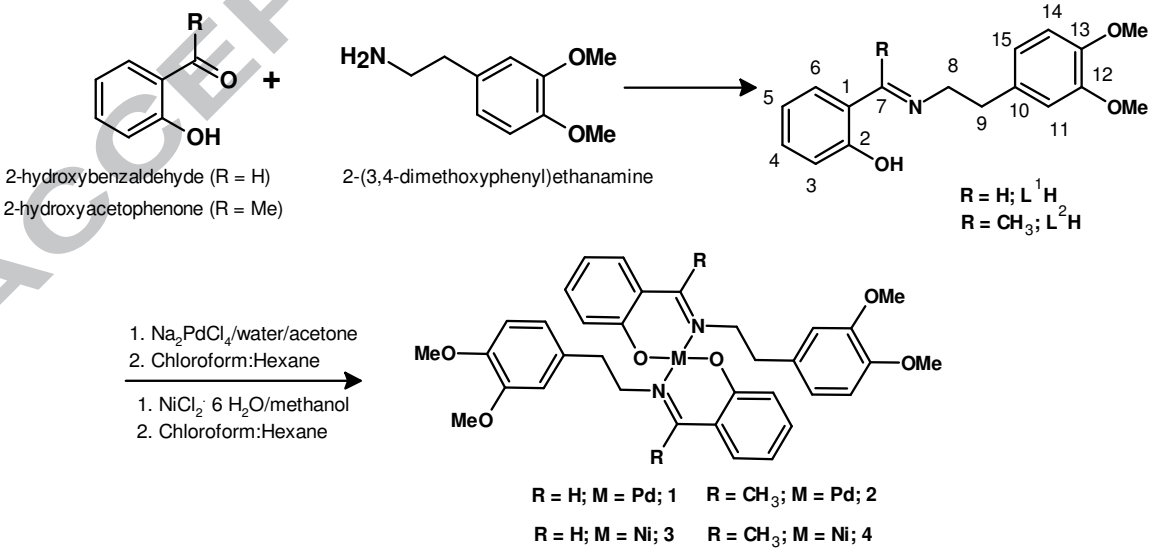
and the values were noted. The measurements were made in triplicate for each compound and their average values are reported.

Antifungal activity of the culture strains of fungi performed on potato dextrose agar (PDA) slant at 27±0.2 °C for 48 - 96 h, till sporulation. Spore of strains were transferred into 5 mL of sterile, 1% saline solution. 100 µL of each fungal spore suspension was spread on each sterile PDA plate. Using the sterile cork borer, wells of 6 mm were made into the each petri plate. The solutions of compounds **L^1H**, **L^2H**, **1**, **2**, **3** and **4** were made by dissolving 250, 500 and 750 µg of in 25, 50, 75 µL in sterile water to get 10 µg / µl concentration and these solutions were used to assess the dose dependent activity of each compound. Similarly a solution of standard antifungal drug solution was made by dissolving 200µg of Fluconazole (as positive control) in 50 µL in sterile water to get 10 µg / µl concentration. The plates were incubated for 72 h at 27 °C. After the incubation period, the zone of inhibition of each well was measured and the values were noted. Triplicates were maintained for each compound and the average values are reported.

3. Results and discussion

3.1 Synthesis of ligands and complexes

Schiff base ligands **L^1H** and **L^2H** were obtained in high yields (90-95 %) by condensation reaction of 2-(3,4-dimethoxyphenyl) ethanamine with 2-hydroxy benzaldehyde and 2'-hydroxy acetophenone respectively in equi-molar ratio in dry ethanol as a solvent.



Scheme 1: Synthesis of Schiff base ligands L^1H and L^2H and complexes $[M(L^{1-2})_2]$ (1-4)

The mononuclear Pd(II) (**1** and **2**) and Ni(II) (**3** and **4**) complexes were obtained by direct reaction of ligands ($\mathbf{L^1H}$ and $\mathbf{L^2H}$) with metal ion precursors (Na_2PdCl_4 and $NiCl_2.6H_2O$) in 1:2 molar ratio. The equations for the reactions of the synthesis of ligands and complexes are given in the **Scheme 1**.

The ligands are yellow crystalline solids and are freely soluble in some of the common polar organic solvents such as $CHCl_3$, CH_2Cl_2, CH_3OH, DMSO and DMF whereas partially soluble in diethyl ether, while they are insoluble in non-polar solvents like hexane, heptane, benzene and toluene at room temperature. The yields of the complexes (85-90 %) are also as high as that of ligands. The ligands and complexes were recrystallized in mixture solvents. Single crystals of complexes **1** and **3** suitable for the X-Ray diffraction studies were grown and their molecular structures were determined.

3.2 FT-IR Spectra

Bands in the region of 3418 and 3392 cm^{-1} are due to ν(O-H) stretching vibration for $\mathbf{L^1H}$ and $\mathbf{L^2H}$. The strong bands at 1634 and 1607 cm^{-1} were assigned to ν(C=N) stretching mode of the imine group for ligands. These bands showed a red shift of about 15-20 cm^{-1} in all the complexes, thus indicating there is a strong coordination of imine nitrogen to the metal ions [19]. Ligands also display bands at 1261 and 1230 cm^{-1} which were assigned to ν(C–O) stretching vibration. These bands were strongly affected due to the chelation ligands through the phenoxide (O^-) group and the bands shifted to higher wave numbers and hence indicated the coordination of phenoxide [20]. The strong absorption bands between 1550 and 1500 cm^{-1} in all ligands and complexes could be reasonably attributed to the presence of the ν(C=C) stretching vibration of the aromatic ring backbone.

3.3 UV-Vis. Spectra

In the UV-Vis., spectra of ligands, in DMSO, there were intense absorption bands at λ, 261, 279, 315 and 408 nm in $\mathbf{L^1H}$ and at 258, 277, 319 and 392 nm in $\mathbf{L^2H}$. In both the ligands the first two absorptions observed at 261, 279 nm and 257, 277 nm in $\mathbf{L^1H}$ and $\mathbf{L^2H}$ respectively can be assigned to the π– π* transitions of the aromatic rings. The latter absorption bands at 315, 319 and 392, 408 nm in $\mathbf{L^1H}$ and $\mathbf{L^2H}$ respectively can be attributed to the charge transfer transitions within the delocalized π system [10b]. In the electronic spectra of complexes **1**, **3** and **4** the intense higher-energy bands observed at around 260 nm were attributed to an intra-ligand

charge transfer ($\pi \rightarrow \pi^*$). The shoulder at λ, 392 nm in **1** was blue-shifted relative to its free ligand $\mathbf{L^1H}$ which expected due to charge transfer from the phenolate to metal ion. Similar spectra were observed for Ni(II) complexes **3** and **4** [10b] . The combined UV-Vis. spectra of ligands and complexes are shown in **Fig. 1**.

3.4 NMR Spectroscopy

The proton NMR spectra of ligands are characteristic. In the proton NMR spectra of $\mathbf{L^1H}$ and $\mathbf{L^2H}$ the $ArCH_2$ and CH_2N protons were appeared as triplets at δ, 2.93-3.02 and 3.78-3.83 ppm respectively and they were matches with the reported values of 2.87 and 3.82 ppm for the similar Schiff bases of 2-hydroxy arylaldehydes and 4-hydroxy phenylethylamine [21a]. The methoxy protons gave two singlets at δ, 3.849 and 3.807 in $\mathbf{L^1H}$ whereas in $\mathbf{L^2H}$ these protons are slightly deshielded and obtained at 3.853 and 3.815 ppm [21b]. The OH signal in $\mathbf{L^1H}$ and $\mathbf{L^2H}$ was observed at 13.44 and 16.50 ppm respectively as these protons are highly deshielded due to intramolecular O-H···N hydrogen bonding [21c]. A singlet for CH=N proton in $\mathbf{L^1H}$ was obtained at 8.18 ppm. In the proton spectra of Pd(II) complexes (**1** and **2**) the signals due to OH protons were absent that indicated the coordination ligands to the metal in the deprotonated phenoxide ion (O^-) fashion. The $ArCH_2$ and CH_2N protons were slightly deshielded (0.1 ppm) whereas these protons in **2** showed higher deshielding effect (0.2 ppm). The CH=N proton in **1** was shielded by 0.8 ppm and this indicated strong coordination of $\mathbf{L^1H}$ to Pd(II).

In the 13-C NMR spectrum of $\mathbf{L^1H}$ and $\mathbf{L^2H}$, the $ArCH_2$ carbon signals were appeared at δ, 36.24 and 38.22 ppm respectively whereas the NCH_2 signals were highly deshielded and observed at δ, ~59.9 ppm [21a-b]. In **2**, the $ArCH_2$ carbon was shielded by about 3 ppm and the NCH_2 carbon was by 9.8 ppm. The CH=N carbon was appeared at 165.85 ppm in **2**.

3.5 Single crystal X-ray diffraction

The molecular structures of **1** and **3** were confirmed by single crystal X-ray diffraction. Crystal data and structure refinement parameters of $[Pd(\mathbf{L^1})_2]$ (**1**) and $[Ni(\mathbf{L^1})_2]$ (**3**) are given in **Table 1**. The selected bond lengths and bond angles of **1** and **3** are given in **Table 2**. Both the compounds **1** and **3** were crystallized in monoclinic crystal system. The Pd-O and Pd-N bond lengths in **1** are 1.984 (11) and 2.020(12) Å. These bond lengths are comparable with the values, 1.983(3) and 2.020(4) Å, reported for the similar complex [22]. The C=N bond length in **1** was found 1.310(19) Å. The O1—Pd1—O1(i) and N1—Pd1—N1(i) angles are 180.0°. Therefore

the structure of the complex **1** was square planar as expected. The molecular structure of compound **1** is shown in **Fig. 2**.

The molecular structure of **3** is given in **Fig. 3**. In **3** the Ni-O and Ni-N bond lengths are 1.8222(13) and 1.9262(15) Å respectively. The bond lengths and bond angles matches with those reported for the complex [Ni(**L**)$_2$].2DMF, where **L** is a Schiff base of 4-hydroxy phenylethylamine and 2-hydroxy naphthaldehyde [21a]. The C=N bond length in **3** was found 1.290(2) Å which was slightly shorter than that found in **1** (1.310(19) Å) [21d]. This suggested that the ligand **L^{1}H** is coordinated to Pd(II) ion strongly in **1** than to Ni(II) in **3**. The O1(i)—Ni1—O1 and N1—Ni1—N1(i) bond angles are 180.0° each which also suggested square planar geometry around Ni in **3**.

The crystals of both **1** and **3** contain C—H···O (2.50(0) and 2.52(0) Å, respectively as given in **Table 3**) intermolecular hydrogen bonding [23a] which is shorter than their sum of the vander Waal's radii (2.60 Å) [23b]. These secondary interactions resulted supramolecular structure in **1** and **3** as depicted in **Fig. 4** and **Fig. 5** respectively. The spectral data of **1** – **4** and single crystal data of **1** and **3** complexes revealed that the ligands coordinated to M(II) ion through (N, O$^-$) donor set forming two coplanar six-membered chelated rings so that the overall molecular structure of **1** to **4** is square planar. The attempts made to grow single crystals of **2** and **4** in various solvents like chloroform, dichloromethane does not gave the crystals suitable for X-ray diffraction.

3.6 Antibacterial activity and Antifungal activity

The antimicrobial properties of new Schiff base ligands, **L^{1}H** and **L^{2}H** and their complexes, **1**, **2**, **3** and **4** were evaluated by Agar well diffusion method. To assess the biological potential of synthesised compounds, the antibacterial activity against four bacteria strains such as *K. aerogenes, E. coli, P. desmolyticum*, *S. aureus* and antifungal activity against two fungi strains *A. flavus* and *C. albicans* were performed. Nutrient agar and potato dextrose agars were used to culture the bacteria and fungi respectively.

The experimental details and zone of inhibition in respect of both antibacterial and antifungal activity of compounds **L^{1}H, L^{2}H**, **1-4** against the pathogenic microbial strains with different concentration are given in **Table 4** and **Table 5** and their graphical representations are shown in **Fig. 6** and **Fig. 7** respectively. These experimental observations indicated that the new ligands and complexes have been shown significant antibacterial activity in *P. desmolyticum* and *S. aureus* and whereas they showed moderate activity in *K. aerogenes* and *E. coli.*

Antifungal activities of above compounds were also found significant effect in *A. flavus* and but moderate activity in *C. albicans*. The synthesized complexes were found to be more toxic compared with their parent free ligands against the same micro-organism and under the identical experimental conditions. The enhanced biological activity of the chelated metal complexes may be due to the effect of the metal ion on the normal cell process.

The bacterial and fungi inhibition was also found to be metal dependent. The palladium complexes have shown better inhibition than the nickel complexes. Among these new compounds screened the ligand $\mathbf{L^1H}$ and the complex **2** showed highest antibacterial and antifungal activity. Schiff bases which contain azomethine (>C=N-) group played an important role in these antimicrobial activities such as antibacterial and antifungal and as chelation increases, the bacterial and fungal growth inhibition also increases. Previously reported [28-29] that, compounds containing heterocyclic ring damaged the cell wall but which was not observed with the present compounds.

Chelation considerably reduces the polarity of the metal ion because of partial sharing of its positive charge with the donor group and possible π-electron delocalization within the whole chelate ring system that is formed during coordination. Such chelation could enhance the lipophilic character of the central metal atom and hence increase the hydrophobic character and liposolubility of the complex favouring its permeation through the lipid layers of the cell membrane. The enhanced biological activity of the chelated metal complexes may be due to the effect of the metal ion on the normal cell process.

Conclusions

New Schiff's base ligands have been synthesized via condensation of 2-(3,4-dimethoxyphenyl) ethanamine with 2-hydroxy benzaldehyde (**$\mathbf{L^1H}$**) and 2-hydroxy acetophenone (**$\mathbf{L^2H}$**) respectively. Pd(II) and Ni(II) complexes [M($\mathbf{L^{1\text{-}2}}$)$_2$] (**1** to **4**) have been synthesized. The ligands and complexes were characterized by elemental analysis, FT-IR, UV-Vis., ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. The molecular structures of Pd(II) and Ni(II) complexes of $\mathbf{L^1H}$ were determined by single crystal X-ray diffraction. The crystal and spectroscopic data revealed that the ligands bind Ni(II) and Pd(II) ions in **1-4** in bidentate monoanionic (O^-, N) mode. The bond lengths Pd-O [1.984(11) Å] and Pd-N [2.020(12) Å] in **1** and Ni-O [1.8222(13) Å] and Ni-N [1.9262(15) Å] in **3** are comparable with the reported values. The >C=N bond length in **3** found 1.290(2) Å which was shorter than that in **1,** 1.310(22) Å indicating strong coordination of ligand to Pd(II) than to Ni(II). The complexes

have square planar geometry around Pd and Ni in **1** - **4**. The crystals of **1** and **3** contain C—H···O (2.50(0) and 2.52(0) Å respectively) intermolecular hydrogen bonds which results in supramolecular structure.

The antimicrobial activity of new Schiff base ligands $\mathbf{L^1H}$ and $\mathbf{L^2H}$ and their complexes, **1** to **4** was evaluated by agar well diffusion method against pathogenic bacterial and fungal strains. Nutrient and potato dextrose agars were used to culture the bacteria and fungi respectively. The antibacterial activity against *K. aerogenes, E. coli, P. desmolyticum*, *S. aureus* strains and antifungal activity against *A. flavus* and *C. albicans* strains was investigated. The new ligands and complexes have shown higher antibacterial activity against *P. desmolyticum*, and *S. aureus* and moderate activity in *K. aerogenes* and *E. coli* bacteria. Furthermore, Schiff bases and their derived complexes also showed higher antifungal activity against *A. flavus* than *C. albicans*. The inhibition of growth of bacteria and fungi has been enhanced on Complexation of ligands. The palladium complexes have shown better inhibition than the nickel complexes. Among these new compounds screened the ligand $\mathbf{L^1H}$ and the complex **2** showed highest antibacterial and antifungal activity.

Acknowledgements

Raghavendra Kumar P., thank CSIR, New Delhi, India for funding the project No. 01(2701)/12/EMR-II.

Supplementary data:

More details on the structural determinations have been deposited with the Cambridge Crystallographic Data Centre under the deposition number CCDC 1417813 and 1417818.

Table 1 Crystal data and structure refinement parameters of $[Pd(L^1)_2]$ (1) and $[Ni(L^1)_2]$ (3)

Complex	**$[Pd(L^1)_2]$ (1)**	**$[Ni(L^1)_2]$ (3)**
Formula	$C_{34}H_{36}N_2PdO_6$	$C_{34}H_{36}N_2NiO_6$
Molecular weight	675.05	627.36
Temperature (K)	293	296
Wavelength (Mo Kα radiation)	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions		
a (Å)	10.7959 (5)	10.8616 (7)
b (Å)	5.8833 (3)	5.8893 (4)
c (Å)	23.3478 (11)	23.1314 (17)
α and γ (°)	90.00	90.00
β (°)	93.106 (4)	93.419 (6)
Volume (Å^3)	1480.77 (12)	1477.02 (18)
Z	2	2
Calculated density (mg/m^3)	1.514	1.411
μ (mm^{-1})	0.68	0.71
F(000)	696	660
Crystal size (mm)	0.30 × 0.26 × 0.24	0.38 × 0.34 × 0.26
θ_{min} - θ_{max} range (°)	3.2 to 25.0	3.5 to 25.0
Index ranges	-12 ≤ h ≥ 12,	-12 ≤ h ≥ 12,
	-6 ≤ k ≥ 6,	-6 ≤ k ≥ 7,
	-27 ≤ l ≥ 27	-27 ≤ l ≥ 27
Reflections collected	30650	23474
Independent reflections [R_{int}]	2634 [0.074]	2581 [0.039]
Reflections observed [I > 2σ(I)]	2378	2180
Absorption correction Integration		
Max. and min. transmissions	0.9158 and 0.7757	0.9158 and 0.7757
Reflections/Parameters/Restraints	2634/200/0	2581/198/0
Goodness-of-fit (S) on F^2	1.15	1.04
Final *R* indices [F^2>2σ(F^2)]	R_1 = 0.136; wR_2 = 0.392	R_1 = 0.028; wR_2 = 0.071
Largest diff. peak and hole	4.84 and -1.25	0.19 and -0.21
Δρ (min and max) (e Å^3)		
$(\Delta/\sigma)_{max}$	< 0.001	< 0.001
Extinction coefficient*	0.007(3)	--
CCDC No	912128	912128

*Extinction correction: SHELXL2014/7 (Sheldrick-2014, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)^{1-1/4}$

Table 2 Bond lengths (Å) and bond angles (°) of $[Pd(L^1)_2]$ (1) and $[Ni(L^1)_2]$ (3)

$[Pd(L^1)_2]$ (1)		$[Ni(L^1)_2]$ (3)	
Bond lengths (Å)			
Pd1—O1	1.984 (11)	Ni1—O1(i)	1.8222 (13)
Pd1—O1i	1.984 (11)	Ni1—O1	1.8222 (13)
Pd1—N1	2.020 (12)	Ni1—N1	1.9262 (15)
Pd1—N1i	2.020 (12)	Ni1—N1(i)	1.9262 (15)
N1—C8	1.481 (17)	N1—C7	1.290 (2)
C7—N1	1.310 (19)	N1—C8	1.489 (2)
O2—C16	1.40 (2)	O3—C13	1.369 (2)
O3—C17	1.43 (2)	O3—C17	1.426 (2)
O1—C2	1.30 (2)	O1—C2	1.313 (2)
O2—C12	1.381 (18)	O2—C12	1.371 (2)
O3—C13	1.381 (17)	O2—C16	1.421 (2)
Bond angles (°)			
O1—Pd1—O1^i	180.0 (11)	O1(i) —Ni1—O1	180.00 (10)
O1—Pd1—N1	92.9 (5)	O1—Ni1—N1	93.31 (6)
O1^i—Pd1—N1	87.1 (5)	O1(i) —Ni1—N1	86.69 (6)
O1—Pd1—N1^i	87.1 (5)	O1—Ni1—N1(i)	86.70 (6)
O1^i—Pd1—N1^i	92.9 (5)	O1(i) —Ni1—N1(i)	93.30 (6)
N1—Pd1—N1^i	180.0 (5)	N1—Ni1—N1(i)	180.0(0)
C7—N1—Pd1	121.8 (9)	C2—O1—Ni1	130.32 (12)
C8—N1—Pd1	121.6 (9)	C7—N1—Ni1	124.05 (12)
C2—O1—Pd1	125.8 (11)	C8—N1—Ni1	121.64 (11)
N1—C7—C1	129.7 (14)	C7—N1—C8	114.25 (15)
N1—C8—C9	112.4 (12)	N1—C8—C9	112.55 (15)
O2—C12—C13	115.1 (13)	N1—C7—C1	127.30 (17)
C14—C13—O3	127.0 (15)	O1—C2—C1	122.77 (16)
O3—C13—C12	115.0 (13)	O1—C2—C3	118.84 (18)
C7—N1—C8	116.4 (12)	O2—C12—C11	125.07 (16)
C12—O2—C16	117.2 (13)	O2—C12—C13	114.99 (15)
C13—O3—C17	116.0 (13)	O3—C13—C14	125.37 (17)
O1—C2—C1	126.7 (13)	O3—C13—C12	115.75 (15)
O1—C2—C3	116.3 (16)	C12—O2—C16	117.55 (14)
C11—C12—O2	124.7 (14)	C13—O3—C17	117.43 (15)
Symmetry code: (i) -*x*+1, -*y*+1, -*z*+2..		Symmetry code: (i) −x, −y+1, −z.	

Table 3 Secondary interactions in $[Pd(L^1)_2]$ (1) and $[Ni(L^1)_2]$ (3)

Complex	D—H···A	D—H	H···A	D ···A	D—H···A
$[Pd(L^1)_2]$ (1)*	C4—H4···O3$^{(ii)}$	0.95	2.50	3.39 (2)	155
$[Ni(L^1)_2]$ (3)**	C4—H4···O3$^{(ii)}$	0.93	2.52	3.405 (2)	158(0)
*Symmetry code: (ii) *x*-1, -*y*+3/2, *z*-1/2; **Symmetry codes: (ii) x+1, −y+1/2, z+1/2.					

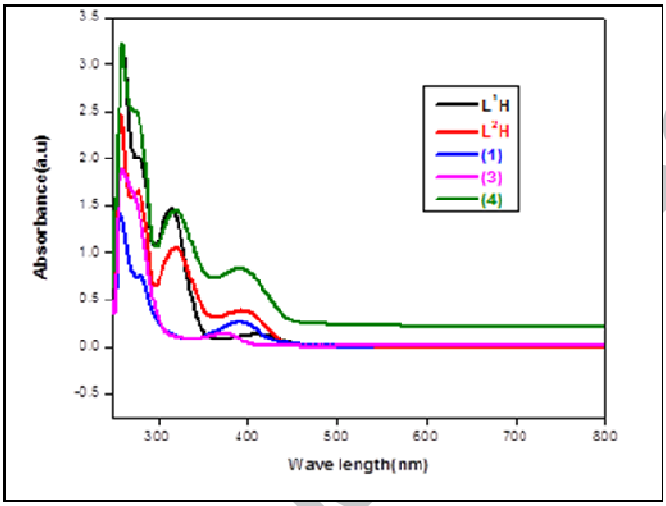


Fig. 1 UV-Vis. Spectra of L^1H, L^2H, 1, 3 and 4

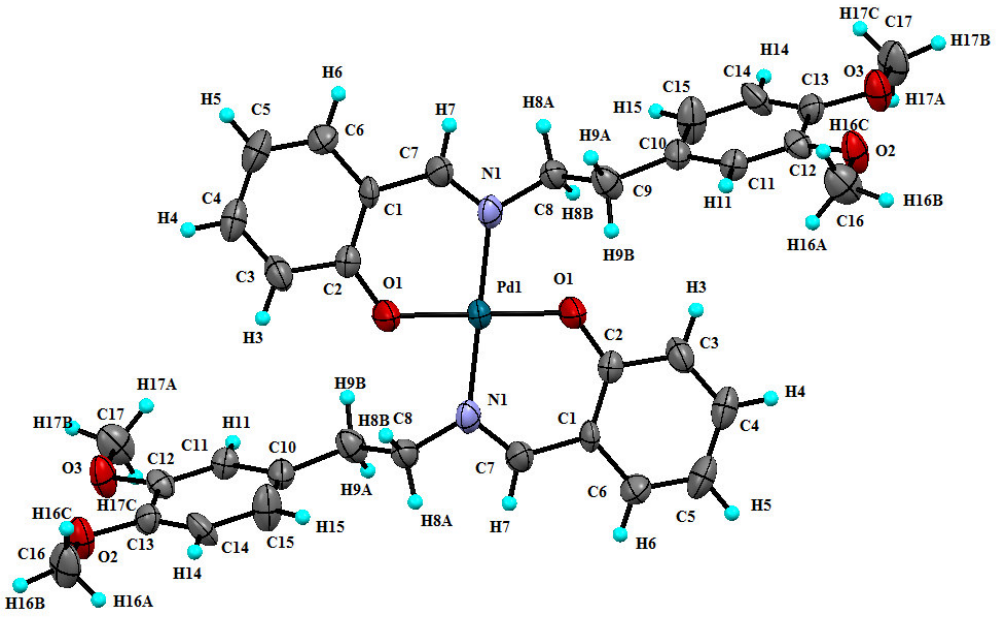


Fig. 2 ORTEP of $[Pd(L^1)_2]$ (1)

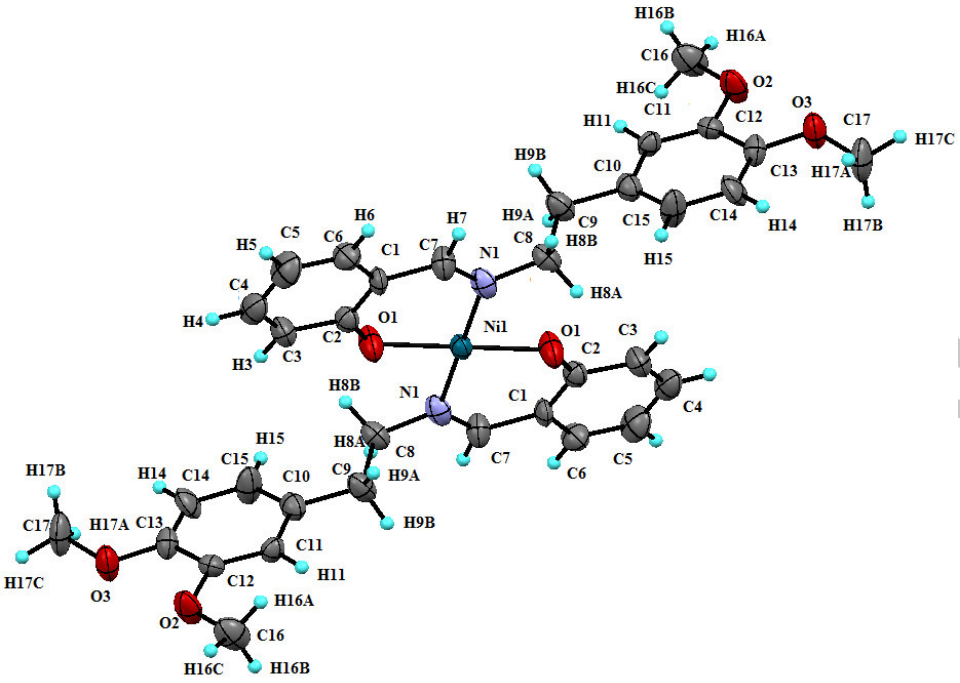


Fig. 3 ORTEP of $[Ni(L^1)_2]$ (3)

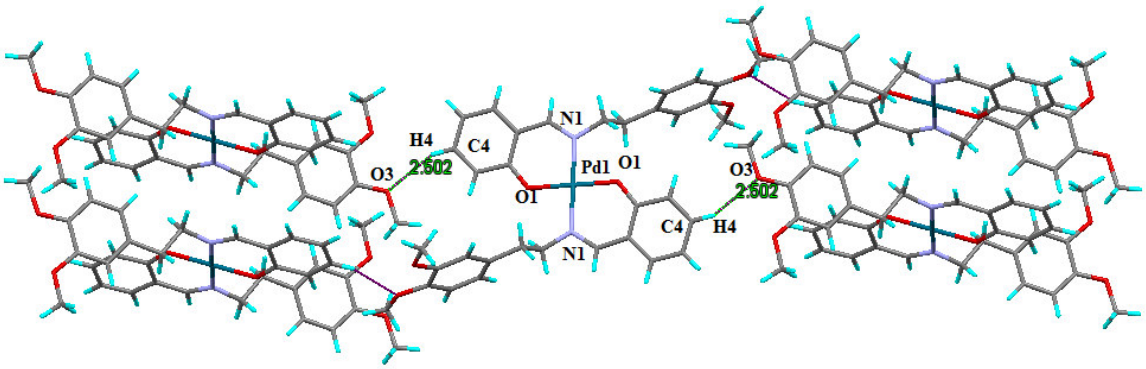


Fig. 4 C-H…O Intermolecular secondary interactions in $[Pd(L^1)_2]$ (1)

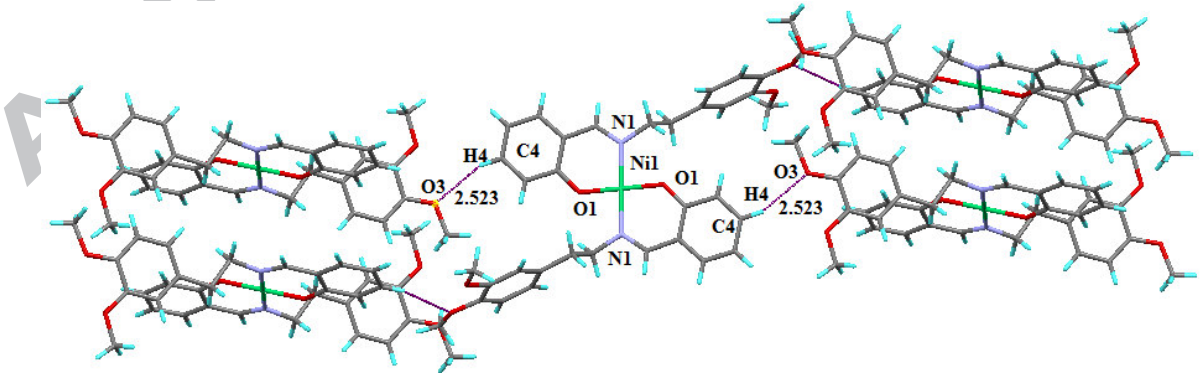


Fig. 5 C-H…O Intermolecular secondary interactions in $[Ni(L^1)_2]$ (3)

Table 4: Antibacterial activity of L^1H, L^2H, 1, 2, 3 and 4

Sample	Treatment	*K. aerogenes* (Mean±SE)	*E. coli* (Mean±SE)	*S. aureus* (Mean±SE)	*P. desmolyticum* (Mean±SE)
Ciprofloxacin	5 µg/50 µL	12.33±0.03	13.67±0.03	14.00±0.00	15.60±0.03
L^1H	500 µg/50 µL	1.60±0.06	1.33±0.12	1.00±0.00	1.60±0.06
	1000 µg/100 µL	2.53±0.03	1.67±0.17	1.67±0.17	3.67±0.17
L^2H	500 µg/50 µL	1.00±0.00	0.50±0.00	1.00±0.00	2.00±0.00
	1000 µg/100 µL	2.00±0.00	1.67±0.17	2.67±0.17	3.23±0.07
1	500 µg/50 µL	1.00±0.00	1.00±0.00	1.00±0.00	1.00±0.00
	1000 µg/100 µL	2.37±0.09	2.60±0.06	3.00±0.00	3.67±0.17
2	500 µg/50 µL	2.00±0.00	1.00±0.00	1.00±0.00	4.67±0.17
	1000 µg/100 µL	3.43±0.23	1.67±0.17	2.50±0.07	6.67±0.17
3	500 µg/50 µL	1.00±0.00	1.10±0.06	2.07±0.07	1.00±0.00
	1000 µg/100 µL	2.50±0.07	2.00±0.00	3.23±0.07	2.53±0.03
4	500 µg/50 µL	0.50±0.00	1.30±0.06	1.10±0.06	2.00±0.00
	1000 µg/100 µL	1.17±0.17	2.53±0.03	3.43±0.12	4.00±0.00

Values are the mean ± SE of inhibition zone in mm.

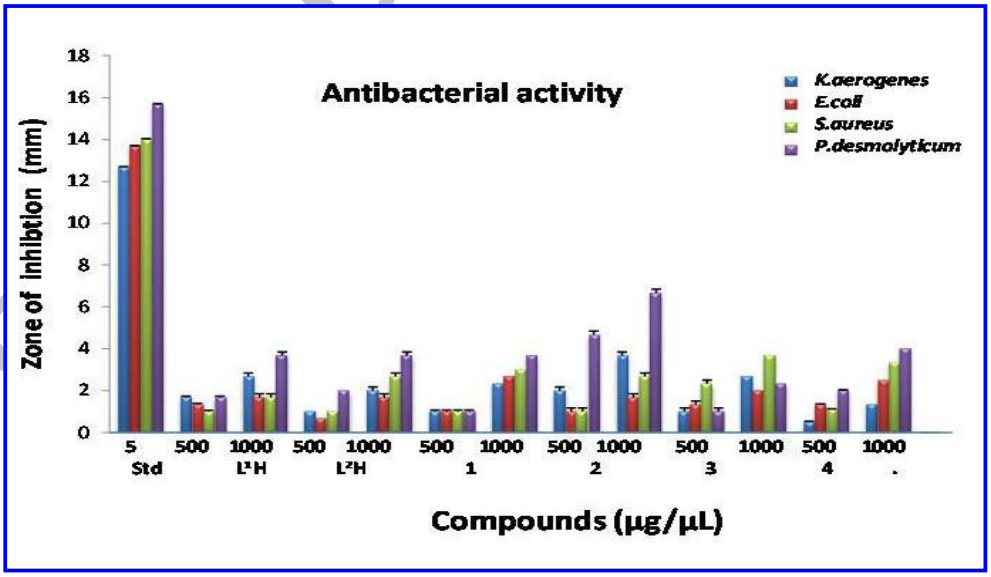


Fig. 6 Antibacterial activity of compounds L^1H, L^2H, 1, 2, 3 and 4

Table 5: Antifungal activity of L^1H, L^2H, 1, 2, 3 and 4

Sample	Treatment	*A. flavus* (Mean±SE)	*C. albicans* (Mean±SE)
Fluconazole	(200 µg/50 µL)	10.27±0.03	11.50±0.06
L^1H	(250 µg/25 µL)	1.33±0.03	0.55±0.00
	(500 µg/50 µL)	3.57±0.03	2.27±0.03
	(750 µg/75 µL)	5.23±0.03	3.20±0.06
L^2H	(250 µg/25 µL)	1.50±0.06	1.00±0.00
	(500 µg/50 µL)	2.33±0.03	2.50±0.06
	(750 µg/75 µL)	4.57±0.03	4.27±0.03
1	(250 µg/25 µL)	1.60±0.03	1.37±0.03
	(500 µg/50 µL)	2.33±0.03	2.17±0.03
	(750 µg/75 µL)	5.00±0.00	3.50±0.06
2	(250 µg/25 µL)	1.57±0.03	0.00±0.00
	(500 µg/50 µL)	3.67±0.03	1.00±0.00
	(750 µg/75 µL)	6.33±0.03	1.67±0.03
3	(250 µg/25 µL)	1.50±0.06	1.00±0.00
	(500 µg/50 µL)	2.00±0.00	2.33±0.33
	(750 µg/75 µL)	3.67±0.03	3.00±0.00
4	(250 µg/25 µL)	1.00±0.00	1.33±0.03
	(500 µg/50 µL)	1.67±0.03	2.67±0.03
	(750 µg/75 µL)	2.37±0.09	3.17±0.09

Values are the mean ± SE of zone of inhibition in mm.

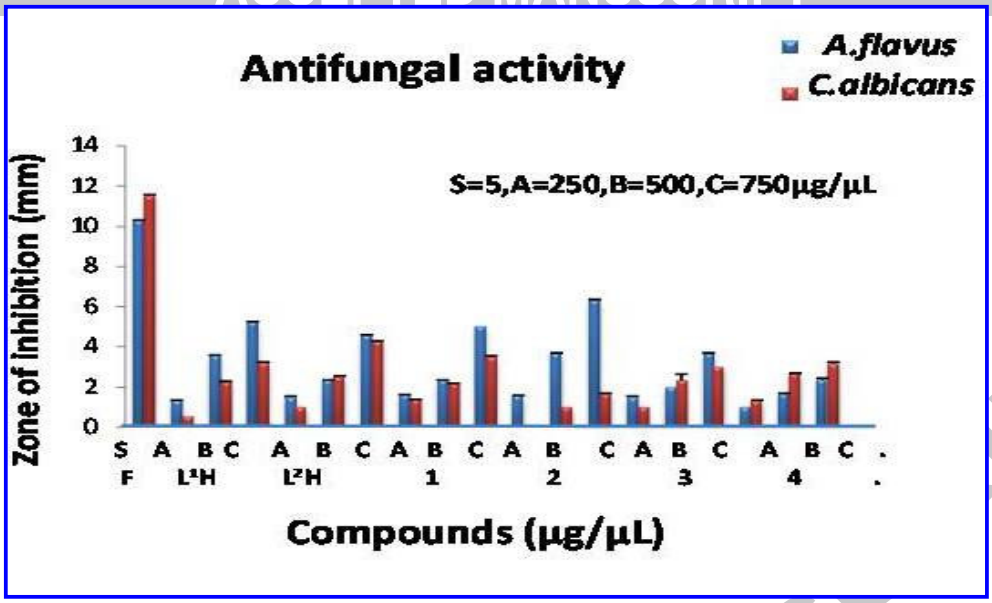


Fig. 7 Antifungal activity of compounds L^1H, L^2H, 1, 2, 3 and 4

References:

1. K.C. Gupta, A.K. Sutar, *Coord. Chem. Rev.* 252 (**2008**) 1420–1450.
2. A. Garoufis, S.K. Hadjikakou, N. Hadjiliadis, *Coord. Chem. Rev.* 253 (**2009**) 1384–1397.
3. (a) S.A. Sadeek, M.S. Refat, S.M. Teleb, *Bull. Chem. Soc. Ethiopia,* 18 (**2004**) 149-156; (b) A. Garoufis, S.K. Hadjikakou, N. Hadjiliadis, in: M. Gielen, E.R.T. Tiekink (Eds.), Metals in Medicine, Palladium (Pd), in Metallotherapeutic Drugs and Metal-based Diagnostic Agents: The Use of Metals in Medicine, John Wiley & Sons, Ltd., **2005**, p. 399 (Ch. 21).
4. (a) M. Sarv, O. Atakol, N. Yilmaz, D. Ulku, *Anal. Sci.* 15 (**1999**) 401-402; (b) M. Bagherzadeh, M. Amini, A. Ellern, L. K. Woob, *Inorg. Chim. Acta* 383 (**2012**) 46–51.
5. (a) D. Sinha, A.K. Tiwari, S. Singh, G. Shukla, P. Mishra, H. Chandra, A.K. Mishra, *Eur. J. Med. Chem.* 43 (**2008**) 160–165; (b) B. Witkop, L.K. Ramachandran, *Metabolism* 13 (**1964**) 1016–1025; (c) K. Singh, M.S. Barwa, P. Tyagi, *Eur. J. Med. Chem.* 41 (**2006**) 147–153; (d) D. Sinha, A.K. Tiwari, S. Singh, G. Shukla, P. Mishra, H. Chandra, A.K. Mishra, *Eur. J. Med. Chem.* 43 (**2008**) 160–165; (e) A.M. Asiri, S.A. Khan, *Molecules* 15 (**2010**) 6850–6858.
6. (a) C. Gerdemann, C. Eicken, B. Krebs, *Chem. Res.* 35 (**2002**) 183–191; (b) M. Tumer, N. Deligonul, A. Golcu, E. Akgun, M. Dolaz, H. Demirelli, M. Dıgrak, *Transit. Met. Chem.* 31 (**2006**) 1–12; (c) A.M. Asiri, S.A. Khan, *Molecules* 15 (**2010**) 4784–4791.
7. S.N. Pandeya, D. Sriram, G. Nath, E. De-Clercq, *Arzneimittelforschung* 50 (**2000**) 55–59;
8. (a) L.X. Cheng, J.J. Tang, H. Luo, X.L. Jin, F. Dai, J. Yang, Y.P. Qian, X.Z. Li, B. Zhou, *Bioorg. Med. Chem. Lett.* 15 (**2010**) 2417–2420; (b) M.S. Alam, J.H. Choi, D.U. Lee, *Bioorg. Med. Chem.* 20 (**2012**) 4103–4108; (c) S. Medici, M. Peanaa, V.M. Nurchi, J.I. Lachowicz, G. Crisponi, M.A. Zoroddua, *Coord. Chem. Rev.* 284 (**2015**) 329–350; (d) M.N. Patel, C.R. Patel, H.N. Joshi, *Inorg. Chem. Commun*. 27 (**2013**) 51–55; (e) R.R. Coombs, M.K. Ringer, J.M. Blacquiere, J.C. Smith, J.S. Neilsen, Y.-S. Uh, J.B. Gilbert, L.J. Leger, H. Zhang, A.M. Irving, S.L. Wheaton, C.M. Vogels, S.A.Westcott, A. Decken, F.J. Baerlocher, *Transition Met. Chem.* 30 (**2005**) 411-418; (f) H. Zhang, D.W. Norman, T.M. Wentzell, A.M. Irving, J.P. Edwards, S.L. Wheaton, C.M. Vogels, S.A. Westcott, F.J. Baerlocher, A. Decken, *Transition Met. Chem.* 30 (**2005**) 63-68; (g) X. Dong, Y. Li, Z. Li, Y. Cui, H Zhu, *J. Inorg. Biochem.* 108 (**2012**) 22–29.
9. (a) E.I. Solomon, M.D. Lowery, *Science* 259 (**1993**) 1575-1581; (b) M. Tumer, E. Akgun, S. Toroglu, A. Kayraldız, L. Donbak, *J. Coord. Chem.* 61 (**2008**) 2935-2949; (c) A. Golcu, M. Tumer, H. Demirelli, R.A. Wheatley, *Inorg. Chim. Acta*, 358 (**2005**) 1785–1797.

10. (a) N. Bharti, M.R. Maurya, F. Naqvi, A. Azam, *Bioorg. Med. Chem.* 10 (**2010**) 2243–2245; (b) Z. Chu, W. Huang, *J. Mol. Str.* 837 (**2007**) 15–22.

11. M. Tumer, H. Koksal, S. Serin, M. Dıgrak, *Transit. Met. Chem.* 24 (**1999**) 13–17.

12. (a) B.K. Ishwar, S.K. Mishra, P.J. Jainey, C.S. Shastry, *J. Chem. Pharm. Res.* 3 (**2011**) 114–118; (b) J.R. Anacona, N. Noriega, J. Camus, *Spectrochim. Acta Part A: Mol. Biomol. Spectroscopy* 137 (**2015**) 16-22.

13. (a) M.R. Gluck, G.D. Zeevalk, *J. Neurochem.* 91 (**2004**) 788–795; (b) M.-J. Oliva-Madrid, J.-A. Garcıa-Lopez, I. Saura-Llamas, D. Bautista, J. Vicente, *Organometallics* 31 (**2012**) 3647−3660; (c) K.N. Kumar, R. Ramesh, *Spectrochim. Acta Part A*, 60 (**2004**) 2913-2918; (d) G. Venkatachalam, R. Ramesh, *Spectrochim. Acta Part A*, , 61 (**2005**) 2081-2087; (e) V.P. Daniel, B. Murukan, B.S. Kumari, K. Mohanan, *Spectrochim. Acta Part A*, 70 (**2008**) 403-410; (f) M.M. Abd-Elzaher, *Appl. Organomet. Chem.* 18 (**2004**) 149-155; (g) B.K. Singh, U.K. Jetley, R.K. Sharma, B.S. Garg, *Spectrochim. Acta Part A*, 68 (**2007**) 63-73.

14. (a) K. Neuvonen, F. Fulop, H. Neuvonen, A. Koch, E. Kleinpeter, K Pihlaja, *J. Org. Chem.* 70 (**2005**) 10670-10678; (b) E.J. Cony, J.O. Link, *J. Org. Chem.* 56 (**1991**) 442-444; (c) J.-X. Gu, Z.-Y. Li, G.-Q. Lin, *Chin. J. Chem.* 13 (**1995**) 475-480. d) M.D. Rozwadowskar, A. Sulima, *Tetrahedron* 57 (**2001**) 3499-3506. (e) R. Quevedo, E. Baquero, M. Rodriguez, *Tetrahedron Lett.* 51 (**2010**) 1774–1778.

15. (a) K.R. Grunwald, G. Saischek, M. Volpe, F. Belaj, N.C. Mosch-Zanetti, *Eur. J. Inorg. Chem.* 15 (**2010**) 2297–2305; (b) M. Shebl, S.M.E. Khalil, S.A. Ahmed, H.A.A. Medien, *J. Mol. Struct.* 980 (**2010**) 39–50; (c) A. Bodakoti, M. Abid, A. Azam, *Eur. J. Med. Chem.* 41 (**2006**) 63–70.

16. G. Shen, J. Li, *J. Appl. Polym. Sci.* 78 (**2000**) 676-684.

17. B.G. Tweedy, *Phytopathology,* 55, (**1964**) 910-917.

18. G.M. Sheldrick, SHELXL 97, Program for Crystal Structure Refinement, University of Go ¨ ttingen, Germany, **1997**.

19. (a) U. Ozdemir, P. Guvenç, E. Sahin, F. Hamurcu, *Inorg. Chim. Acta* 362 (**2009**) 2613-2618; (b) U. Ozdemir, F. Arslan, F. Hamurcu, *Spectrochim. Acta, Part A* 75 (**2010**) 121-126; (c) U.O. Ozdemir, G. Olgun, *Spectrochim. Acta, Part A* 70 (**2008**) 641-645.

20. (a) E. Keskiog˘lu, A.B. Gündüzalp, S. Çete, F. Hamurcu, B. Erk, *Spectrochim. Acta, Part A* 70 (**2008**) 634-640; (b) Z. Chu, W. Huang, *J. Mol. Str.* 837 (**2007**) 15–22.

21. (a) X. Dong, Y. Li, Z. Li, Y. Cui, H. Zhu, *J. Inorg. Biochem.* 108 (**2012**) 22–29; (b) A.A. Vitale, A.E. Stahl, P.C.S. Claro, M.A.F. Addato, R.P. Diez, A.H. Jubert, *J. Mol. Str.* 881

(**2008**) 167–174; (c) P.R. Kumar, A.K. Singh, R.J. Butcher, P. Sharma, R.A. Toscano, *Eur. J. Inorg. Chem.* (**2004**) 1107-1114.

22. M. Bagherzadeh, M. Amini, A. Ellern, L.K. Woob, *Inorg. Chim. Acta* 383 (**2012**) 46–51.
23. (a) P.R. Kumar, B.S. Palakshamurthy, U. Shailesh, *Heteroatom Chem.* 00 (**2015**) 000-000 (Published online) (b) S.S. Batsanov, *Inorg. Mat.* 37 (**2001**) 871–885.
24. C. Perez, M. Paul, P. Bazerque, *Actabiologiaeet Med. Experimentalis,* 15 (**1990**) 113-115.
25. Raja Naika, K. Lingaraju, K. Manjunath, D. Kumar, G. Nagaraju, H. Nagabhushana, D. Suresh, *J. Taibah Uni. Sci.* 9 (**2015**) 7–12.
26. J. Meletiadis, J.W. Mouton, J. Meis, B.A. Bouman, P.E. Verweij, N. Eurofung., *J. Clinic. Microbio.* 40 (**2002**) 2876-2885.
27. S. Sahoo, P.K. Panda, S. Tripathy, S.K. Nayak, S.K. Dash., *Ind. Drugs* 44 (**2007**) 352-356.
28. R. Dabur, A.K. Chhillar, V. Yadav, K. Kamal, P. Gupta, G.L. Sharma., *J. Med. Micro.* 54 (**2005**) 549-552.
29. N. Kawabata, *Prog. Polym. Sci.* 17 (**1992**) 1-34.

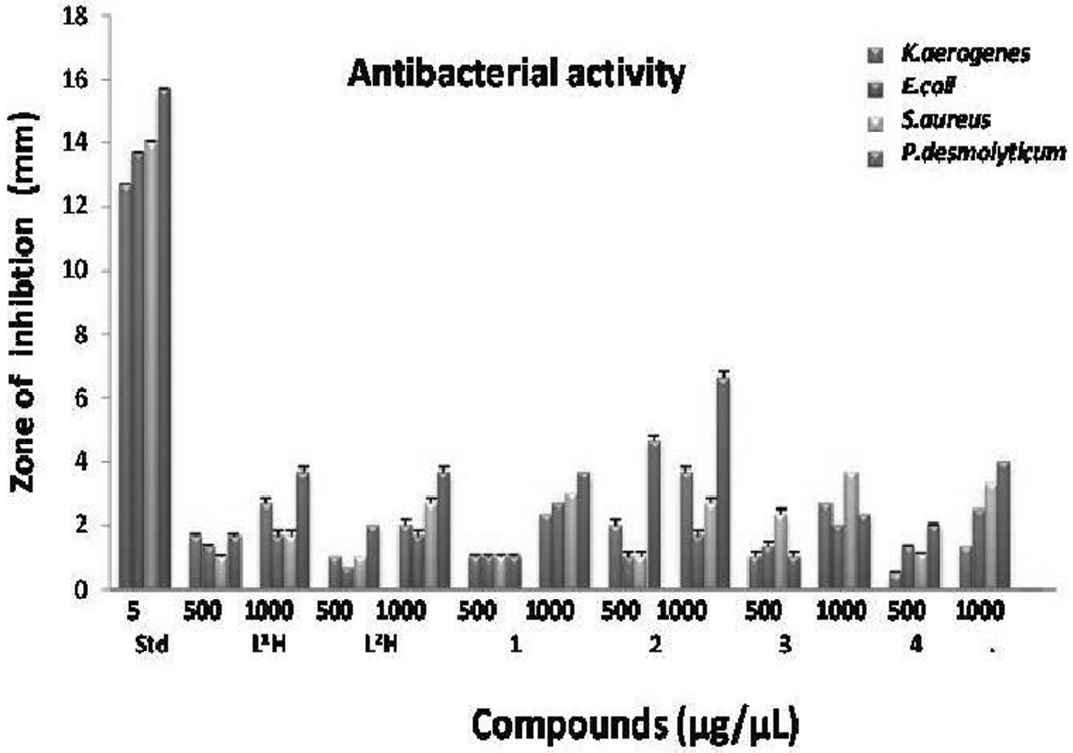

Antibacterial activity
K.aerogenes
E.coli
S.aureus
P.desmolyticum
Zone of inhibtion (mm)
18
16
14
12
10
8
6
4
2
0
5
Std
500
1000
L¹H
500
1000
L²H
500
1000
1
500
1000
2
500
1000
3
500
1000
4
Compounds (µg/µL)

Fig. 6