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# Synthesis, crystal structure, bioactivities of Ni(II), Cu(II), Co(II) and

Pd(II) complexes with unsymmetrical thioether donor Schiff base:

Phosphine free Pd(II) complex catalyzed Suzuki reaction

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#### Abstract

A series of new Ni(II), Cu(II), Co(II) and Pd(II) complexes were synthesized from the reaction of thioether containing Schiff base ligand with corresponding metal salts by a simple environmentally benign procedure. The molecular formulae of ligand and their complexes are  $C_{21}H_{19}NO_2S_{2}$ , **1**, [Ni( $C_{21}H_{18}NO_2S_{2}$ ].CH<sub>3</sub>OH.H<sub>2</sub>O,**2**, [M( $C_{21}H_{18}NO_2S_{2}$ ] (**3 & 4**), where (M=Cu(II) and Co(II)) and [Pd( $C_{21}H_{18}NO_2SC_{1}$ ](**5**). All complexes were characterized by

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elemental analysis, FT-IR, UV-Visible spectroscopy and single crystal X-ray diffraction analysis. The ligand was characterized by same techniques and with <sup>1</sup>HNMR spectroscopy. X ray diffraction study reveals that copper complex adopts square planar geometry by coordinating via deprotonated hydroxyl oxygen, azomethine nitrogen of ligand to the copper centre and sulfur atoms remain unligated. As expected, nickel complex acquired a distorted octahedral geometry coordinating via deprotonated hydroxyl oxygen, azomethine nitrogen and thioether sulphur atoms of ligands. Interestingly, one water and one methanol molecule are attached at the out sphere of the nickel complex. Suzuki reaction was carried out in open atmospheric conditions using palladium complex as catalyst. The significant features of the palladium complex catalyzed reaction are good yield, simple workup procedure, easy purification and easy recovery technique of the catalyst. The reported palladium complex is phosphine free, air stable, moisture insensitive. The ligand and complexes show very good biological activities against *Mycobacterium abscessus, Bacillus subtilis, Staphylococcus aureus, Proteus vulgaris, Mycobacterium smegmatis* and *Escherichia coli*.

**Keywords:** Thioether; Crystal structure; Schiff Base; Phosphine free ligand; Suzuki reaction; Bioactivity

#### Introduction

In recent years, interest in coordination chemistry of Schiff base ligand with ONS donating sites have increased due to capabilities of forming stable complexes [1] and have a wide range of antifungal [2], antibacterial [3, 4], anticancer properties [5]. The combination of thioether with imine moiety escalates such properties [6]. So, attempts to design model complexes which can possibly mimic such activity with reported biologically active compounds. Nickel with N/S coordinating sphere is present in several metalloenzymes and this property encourages in

synthesizing N/S coordinated nickel complexes [7]. Incorporation of thioether atom in copper complex is important due to presence of N/S atoms in most copper containing mettaloenzymes. Cobalt complexes with thioether are also interesting as they can mimic the role of sulfur donor site around cobalt in enzyme like nitrile hydratase [8]. Apart from biological activities they gain interest in varied catalytic activities due to their deep involvement in organic synthesis with several ligand systems [9]. There have been different notable examples on activity of Schiff base complexes in heterogeneous as well as homogeneous catalysis [6, 10, 11, 12, 13, 14, 15, 16]. Palladium complex catalyzed Heck reaction, Suzuki reaction etc. are important tool for construction of aryl-carbon bond [17]. However, phosphine containing palladium complexes failed to catalyze C-C coupling raection with aryl chlorides [18]. Now a days, researchers are given interest in simpler, faster, cheaper and more efficient methodologies for such coupling reactions [19].

The present article deals with the synthesis of tridentate N-(4-metoxy phenol)-2methyliden-2-benzylthiophenyl amine **HL**, ligand and its Ni(II), Cu(II), Co(II) and Pd(II) complexes of composition [NiL<sub>2</sub>].CH<sub>3</sub>OH.H<sub>2</sub>O,**2**, [CuL<sub>2</sub>],**3**, [CoL<sub>2</sub>],**4**, and [PdLCl],**5**. The complex formations have been authenticated by X-ray diffraction studies, UV-Visible spectroscopy and elemental analyses. The ligand formation was confirmed by same techniques and <sup>1</sup>HNMR spectroscopy. The synthesized phosphine free palladium complex shows excellent catalytic activities towards Suzuki reaction under mild conditions. All compounds show considerable antibacterial and antifungal properties *Mycobacterium abscessus, Bacillus subtilis, Staphylococcus aureus, Proteus vulgaris, Mycobacterium smegmatis* and *Escherichia coli*.

#### 2. Experimental

#### 2.1. Physical measurement

Nickel acetate tetrahydrate (Merck), copper nitrate trihydrate (Merck), cobalt sulphate heptahydrate (Merck), 2-hydroxy-5-methoxy benzaldehyde (Alfa Aeser), sodium tetrachloropalladate (Alfa Aeser) were used as obtained. 2-(benzylthio) aniline was prepared according to literature method [20]. Elemental analyses were recorded on Perkin-Elmer Model 240C elemental analyzer. Electrical conductivities were measured on CM-180 Conductivity meter (Elico India). Electronic spectra were measured on Cary 100 Bio UV-Visible spectrophotometer. Magnetic susceptibilities were measured on conventional Gouy balance using freshly prepared Hg[Co(NCS)<sub>4</sub>] as calibrant by Magway MSB MK1 Magnetic susceptibility balance, Sherwood Scientific, Cambridge, UK. Infrared spectra of the ligand and complexes were recorded on IR-affinity-I FTIR Spectrometer SHIMADZU as KBr Pellet. Melting points were recorded on a Veego melting point apparatus and were uncorrected. The <sup>1</sup>H NMR spectrum was recorded on a Bruker 400 DRX spectrometer in CDCl<sub>3</sub> solution, using TMS as the internal standard. All other reagents and solvents used were of commercially grade and employed as received or purified by standard methods prior to use. All reactions were carried out at open atmosphere.

#### 2.2. Preparation of N-(4-metoxy phenol)-2-methyliden-2-benzylthiophenyl amine (1)

In a simple procedure, 2-hydroxy-5-methoxy benzaldehyde (0.1 mL, 1 mmol) was added drop wise with continuous stirring to a 30 ml ethanolic solution of 2-(Benzylthio) aniline (0.215 g, 1 mmol). The solution was stirred for another 30 minutes and the color of the solution changes to orange yellow. The solution was kept in freezing condition for 6 hours. The orange yellow

crystalline product formed was filtered off, washed several times with 25% ethanol-water solution to remove the impurities and dried in vacuum ( $10^{-2}$ torr) (Purity was checked by TLC). Yield 89.2%. M.P. 180°C. IR (KBr pellet, cm<sup>-1</sup>): 3413(m), 1695(s), 1604(s), 1429(s), 1109(s), 735(s). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  13.70 (1H, s, OH), 8.41 (1H, s, CH=N), 7.08-7.32 (13 H, m, Ar-H), 4.11 (3H, s, OCH<sub>3</sub>) and 3.81 (2H, s, CH<sub>2</sub>). UV-Vis [DCM,  $\lambda_{max}$ , nm( $\epsilon_{max}$ , Lmol<sup>-1</sup>cm<sup>-1</sup>)]: 259 (37881), 396 (26385). Anal. Calc. for C<sub>21</sub>H<sub>19</sub>NO<sub>2</sub>S, M.W.: 349.45, C, 72.18; H, 5.48; N, 4.01; S, 9.18. Found: C, 72.09; H, 5.40; N, 3.92; S, 9.05 %. The reaction scheme for synthesis of ligand is shown in **Scheme 1**.



Scheme 1: Synthesis of ligand

#### 2.3. Preparation of [NiL<sub>2</sub>].CH<sub>3</sub>OH.H<sub>2</sub>O complex (2)

In a simple procedure, the ligand, **1** (0.698g, 2 mmol) was dissolved in boiling methanol (30 mL) followed by addition of 2 mmol methanolic (10 ml) NaOH solution. Then a methanolic solution (30 ml) of nickel acetate tetrahydrate (0.248g, 1 mmol) was added drop wise to above solution with continuous stirring. The solution was stirred for 30 minutes. The color of the solution changed to brown-black. Then the solution was kept undisturbed for 3 days. The black-brown needle like crystals suitable for single crystal X-ray diffraction study formed was filtered off,

washed with 25% methanol-water solution for several times to remove the impurities and dried under vacuum (10<sup>-2</sup>torr) (Purity was checked by TLC). Yield 69.8%. MP 286°C. IR (KBr,cm<sup>-1</sup>): 2929(s), 1734(s), 1591(s), 1456(s), 1149(s), 1011(s), 680(s), 582(m). UV-Vis [DCM,  $\lambda_{max}$ , nm( $\epsilon_{max}$ , Lmol<sup>-1</sup>cm<sup>-1</sup>)]: 273 (35798), 308 (26741), 501 (8120). Anal. Calc. for C<sub>43</sub>H<sub>42</sub>N<sub>2</sub>NiO<sub>6</sub>S<sub>2</sub>, M.W.: 805.63, C, 64.11; H, 5.25; N, 3.48; S, 7.96. Found: C, 64.01; H, 5.14; N, 3.23; S, 7.84 %.

#### 2.4. Preparation of [CuL<sub>2</sub>] complex (3)

The preparation of complex **3** follows the same procedure as that of **2** except that copper nitrate trihydrate (0.241g 1 mmol) was used. The resulting solution was kept undisturbed for 24 hours after color changes to bluish black. The bluish black needle like crystals suitable for single crystal X-ray diffraction study formed was filtered off, washed with 25% methanol-water solution for several times to remove the impurities and dried under vacuum ( $10^{-2}$ torr) (Purity was checked by TLC). Yield 70.6 %. MP 246°C. IR (KBr,cm<sup>-1</sup>): 2983(s), 1734(s), 1593(s), 1465(s), 1255(s), 756(s), 663(m), 567(m). UV-Vis [DCM,  $\lambda_{max}$ , nm( $\varepsilon_{max}$ , Lmol<sup>-1</sup>cm<sup>-1</sup>)]: 272 (35009), 445 (7402), 503 (6763). Anal. Calc. for C<sub>42</sub>H<sub>36</sub>CuN<sub>2</sub>O<sub>4</sub>S<sub>2</sub>, M.W.: 760.42, C, 66.34; H, 4.77; N, 3.68; S, 8.43. Found: C, 66.21; H, 4.69; N, 3.56; S, 8.38%.

#### 2.5. Preparation of [CoL<sub>2</sub>] complex (4)

The preparation of complex **4** follows the same procedure as that of **3** except that cobalt sulphate heptahydrate (0.281g 1 mmol) was used. The resulting solution was kept undisturbed for 2 days after color changes to black. Black micro crystals were collected by filtration and washed with 25% methanol-water solution for several times to remove the impurities and dried under vacuum  $(10^{-2}\text{torr})$  (Purity was checked by TLC). Yield 64.7%. MP 239°C. IR (KBr,cm<sup>-1</sup>): 2918(s), 1729(m), 1589(s), 1456(s), 1153(m), 1031(m), 752(s), 686(s). UV-Vis [DCM,  $\lambda_{max}$ , nm( $\epsilon_{max}$ ,

Lmol<sup>-1</sup>cm<sup>-1</sup>)]: 275 (38726), 306 (29820), 506 (7391). Anal. Calc. for C<sub>42</sub>H<sub>36</sub>CoN<sub>2</sub>O<sub>4</sub>S<sub>2</sub>, M.W.: 755.81, C, 66.74; H, 4.80; N, 3.71; S, 8.48. Found: C, 66.61; H, 4.69; N, 3.67; S, 8.42%.

#### 2.6. Preparation of [PdLCl] complex (5)

Sodium tetrachloropalladate (250 mg, 0.85 mmol) is dissolved in 15 ml ethanol. It was added drop wise to a boiling ethanolic solution (15 ml) of ligand, HL (258 mg, 0.81 mmol). The solution was stirred in water bath at  $90^{\circ}$ c for 1 hour. The color of the solution changed to bright red. The resulting solution was kept undisturbed for 1 hour. The red micro crystals were collected by filtration and washed with 25% ethanol-water solution for several times to remove the impurities and dried under vacuum  $(10^{-2}$ torr) (Purity was checked by TLC). Yield 83.2%. MP: above 300°C. IR (KBr,cm<sup>-1</sup>): 3290(m), 2990(m), 1710(m), 1630(s), 1439(s), 1140(s), 1040(s), 725(s), 651(s). UV-Vis [DCM,  $\lambda_{max}$ , nm( $\epsilon_{max}$ , Lmol<sup>-1</sup>cm<sup>-1</sup>)]: 264 (32473), 328 (28398), 495 (5466). Anal. Calc. for C<sub>21</sub>H<sub>18</sub>ClNO<sub>2</sub>PdS, M.W. 490.31 C, 51.44; H, 3.70; N, 2.86; S, 6.54. Found: C, 51.32; H, 3.61; N, 2.77; S, 6.43 %. The reaction scheme for the synthesis of metal complexes is shown in Scheme 2. 





Scheme 2: Synthesis of metal complexes

#### 2.7. General experimental procedure for the Suzuki reaction:

A mixture of aryl boronic acid (3.5 mmol), aryl halide (3.5 mmol), the palladium complex (0.001 mmol) and potassium carbonate (8.0 mmol) in methanol (10 ml) were heated to reflux for 24 hours. After evaporation of solvent, the residue was poured into water and extracted with diethyl ether. The ether solution was dried over  $Na_2SO_4$  to remove trace water content and filtered. The ether solution was passed through silica column (60–120 mesh) and catalyst remains trapped. After extraction of desired compound, catalyst was extracted using dichloromethane. Pure product was obtained upon evaporation of the ether. The yields of the products were determined.

#### 2.8 Antibacterial activity analysis:

The antibacterial assay was performed against test pathogens *Mycobacterium abscessus*, *Bacillus subtilis*, *Staplylococcus aureus*, *Proteus vulgaris*, *Mycobacterium smegmatis* and *Escherichia coli* by adopting agar diffusion assay method **[21]**. The presence of inhibition zone (in mm) around the well was observed. All bacterias were cultured in Mueller Hinton broth (MHB) at 37  $^{\circ}$ C for 24 h. Experiments were carried out in a laminar flow by strictly maintaining aseptic conditions. 100 µL of fresh inoculum from each culture was added on the plates and spread using sterilized spreader. Wells were punctured on freshly spread bacterial culture on MHA. A stock solution of 10 mg/ml of each compound was prepared in DMF solvent and each compound (20 µg) was added to the wells. Four wells were bored on each plate, each filled with same compound and two plates for each test compound were taken. All the plates were incubated at 37°C for 24 h. Growth inhibition of test organisms was measured with standard scale, the mean values of inhibition zones were taken and the data were compared with standard drug kanamycin acid sulphate.

#### 2.9. X-ray data collections, crystal structure solutions and refinement:

Single-crystal X-ray Diffraction data collections for compound 2 and 3 at 296 K were performed with Mo K $\alpha$  radiation ( $\lambda$ =0.71073Å) using a Bruker Smart Apex II CCD diffractometer equipped with graphite monochromator. The SMART [22] software was used for data collection and also for indexing the reflections and determining the unit cell parameters. Collected data were integrated using SAINT [22] software. The structures were solved by direct methods and refined by full-matrix least-square methods using SHELXTL [23] software. Absorption corrections were done by multi-scan method (SADABS) [22]. All the non-H atoms were refined in the anisotropic

approximation against  $F^2$  of all reflections. The H-atoms were placed at their calculated positions and refined in the isotropic approximations. Details of crystal analysis, data collection and g sch structure refinement data are summarized in Table 1. The same atom numbering scheme was

#### Table 1: Crystal structure refinement details for the two complexes 2 and 3.

Compound	Nickel complex	Copper complex
CCDC entry no.	1020519	1020520
Empirical formula	C43 H42 N2 Ni O6 S2	C42 H36 Cu N2 O4 S2
Formula weight	805.60	760.40
T (K)	296(2) K	296(2)
$\lambda$ (Å)	0.71073 Å	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	$Pca_2(1)$	Pbca
Unit cell dimensions		
a (Å)	21.1584 (7) Å	20.4740 (6) Å
b (Å)	11.3032 (3) Å	7.5475 (2) Å
c (Å)	15.9419(6) Å	22.2830 (6) Å
$\alpha$ (°)	90°	90°
β(°)	90°	90°
γ (°)	90°	90°
$V(A^3)$	3812.6 (2) Å <sup>3</sup>	3443.34(16) Å <sup>3</sup>
Z	4	4
$D_{calc}$ (Mg/m <sup>3</sup> )	1.404 g/cc	1.467 g/cc
$\mu (mm^{-1})$	$0.670 \text{ mm}^{-1}$	$0.804 \text{ mm}^{-1}$
F (0 0 0)	1688	1580
Crystal size (mm <sup>3</sup> )	$0.32 \ge 0.21 \ge 0.16 \text{ mm}^3$	$0.31 \ge 0.18 \ge 0.12 \text{ mm}^3$
$\theta$ range for data collection (°)	2.31 to 20.55°	1.83 to 26.28°.
Index ranges	-25 < h < 26	-25 < h < 20
0	-13 < k < 13	-9 < k < 9
	-11 < 1 < 19	-23 <1 < 27
Reflections collected	15941	14235
Independent reflections (R <sub>int</sub> )	5151 [R(int) = 0.0707]	3485 [R(int) = 0.0447]
Completeness (%)	100.0 %	98.3 %
Absorption correction	Semi-empirical from	Semi-empirical from
	equivalents	equivalents
Max and min transmission	0.9003 and $0.8141$	0.9710 and 0.5904
Refinement method	Full-matrix least-squares	Full-matrix least-squares on
	on $F^2$	$F^2$
Data/restraints/parameters	5151 / 0 / 502	3485 / 0 / 233
Goodness-of-fit on F <sup>2</sup>	1.004	1.113
Final R indices $[I > 2\sigma(I)]$	R1=0.0430, wR2=0.0828	R1 = 0.0382, w $R2 = 0.1050$
R indices (all data)	$R_{1-0.0596} = 0.0912$	$R_1 = 0.0502$ , $wR_2 = 0.1210$

#### 3. Results and discussion

#### **3.1 Characterization**

#### **3.1.1.** <sup>1</sup>H NMR spectrum of ligand (1)

The <sup>1</sup>H NMR (400 MHz) spectrum of ligand (HL) **1** was recorded in CDCl<sub>3</sub> in the range 0-15 (ppm). The <sup>1</sup>H NMR spectrum shows signal as singlet  $\delta$  13.70 ppm downfield for phenolic proton. Another singlet appears at  $\delta$  8.41 ppm due to benzilidemine proton (CH=N). The multiplet, singlet and singlet appear at  $\delta$  7.08-7.32,  $\delta$  4.11 and  $\delta$  3.81 ppm for aromatic (Ar—H), methoxy proton and benzylic protons (CH<sub>2</sub>) respectively.

#### **3.1.2. Infrared spectroscopy**

The ligand exhibits characteristics v(O-H), v(C=C), v(C-S), v(C=N) bands at 3413, 1604, 1429, 735 cm<sup>-1</sup> respectively. The absence of v(O-H) band in all metal complexes indicates the deportation of ligand. The appearance of a band for v(C=N) in the range of 1600-1589 cm<sup>-1</sup> which shows a shifting to the lower frequencies by 7-5 cm<sup>-1</sup> compared to ligand (**HL**) suggesting the complexion of ligand with metal atom through nitrogen atom. Moreover, in complexes phenolic v(C-O) stretching is shifted by 20-32 cm<sup>-1</sup> towards lower wave numbers compared to ligand indicating coordination of the phenolic oxygen to the metal ion [24]. The metal complexes show bands in the range 750-756 cm<sup>-1</sup> for v(C-S) band shifted to higher frequencies compared to ligand confirmed the M-S bond [25]. The new band for complexes in the range 651-680 cm<sup>-1</sup> tentatively assigned coordination with oxygen atom [24]. Metal sulfur stretching frequencies occur in the (480± 210 cm<sup>-1</sup>) range but are often difficult to detect as they tend to be weak and quite broad [9].

#### 3.1.3. Electronic spectroscopy

The electronic spectra of ligand and complexes are recorded in dichloromethane medium. The bands for ligand, 1 at 259 nm and 396 nm due to  $n-\pi^*$  transition of the imine moietv and  $\pi-\pi^*$ transition of phenyl rings respectively [26]. Nickel(II) complex, 2 shows two peaks in 273 nm and 308 nm which are due to  $n-\pi^*$ ,  $\pi-\pi^*$  transitions respectively. The presence of only one band in 500-800 nm region in the electronic spectrum of nickel(II) complex shows evidence of octahedral coordination [27]. The intense band at 501 nm in spectrum of nickel(II) complex is probably combination of a d-d transition and S-Ni charge transfer band [28]. The electronic spectrum of copper(II) complex, **3** shows bands at 267 nm and 427nm suggesting  $n-\pi^*$ ,  $\pi-\pi^*$ transitions respectively. In copper(II) complex the d-d transition cannot be observed as it is obscured by strong charge transfer transition [29]. The appearance of band at 509 nm show the evidence of square based geometry around Cu(II) centre [30, 31]. Again, the Cobalt(II) complex, 4 shows bands at 275 nm and 306 nm due to  $n-\pi^*$ ,  $\pi-\pi^*$  transitions respectively. The low energy absorption for cobalt(II) complex is appeared around 506 nm due to due to a MLCT transition [32]. It is interesting to observe that palladium(II) complex, 5 shows a low energy band in the range 502 nm and a structured band within the range 330 nm for MLCT transitions [33, 34].

#### **3.1.4. Molar conductivity**

The molar conductivity of complexes is taken in acetonitrile medium. The values of complexes **2**, **3**, **4** and **5** are 25.9, 20.7, 33.4 and 39.7 s cm<sup>2</sup> mol<sup>-1</sup> respectively. The molar conductivity values in the range 20.7-39.7 s cm<sup>2</sup> mol<sup>-1</sup> confirm non-electrolytes nature of complexes [**35**].

#### **3.1.5.** Magnetic measurement

The magnetic moment ( $\mu_{eff}$ ) for nickel complex, 2 was found to be 2.79 BM. This value is quite good agreement to the spin only value of 2.83 BM for d<sup>8</sup> system with O<sub>h</sub> symmetry. Copper complex. **3** show 1.69 BM and confirmed  $d^9$  configuration with square planar geometry [36]. The magnetic moment of the cobalt complex, 4 is 5.17 BM. This value almost closes with high spin octahedral cobalt(II) complex [37]. ,C

#### **3.2. X-ray crystallography**

#### 3.2.1. Structure description of nickel complex, 2

The molecular structure of Nickel complex, 2 shows octahedral geometry (Figure 1). The complex is a six coordinated centrosymmetrical mononuclear complex. It crystallizes in the orthorhombic space group  $Pca_2(1)$ . Interestingly, one methanol and one water molecule resides in the asymmetric unit. The methanol and water molecules are hydrogen bonded to the phenolic oxygen atoms of each of the coordinated ligand molecules. Nickel atom is in axially distorted octahedron condition. The equatorial plane is satisfied by two thioether atoms and two hydroxyl oxygen atoms. The two imine nitrogen atoms are remained in axial position. The Ni-O distances are 2.000(3) Å, 2.007(3) Å. Whereas Ni-S distances are 2.433(14) Å, 2.476(13) Å. Ni—N distances are 2.035(4) Å, 2.035(4) Å **[9].** The bite angles are O2—Ni1—O1 (88.74(12) °), O1-Ni1-S2 (95.33(10) °), S2-Ni1-S1 (82.92(4) °), O2-Ni1-S1 (93.39(9) °). The bond angles N2-Ni1-N1 (175.35(16) °) indicates distortion from ideal octahedral geometry. Some selected bond lengths and bond angles are summarized in Table 2.



Figure: 1 Molecular structure of the nickel complex, 2 shown with 35 % probability ellipsoids.

#### 3.2.2. Structure description of copper complex, 3

Copper complex, **3** adopts square planar geometry. The perspective view of the crystal structure is shown in **Figure 2.** An approximately square planar geometry is formed around Cu atom by two deprotonated hydroxyl nitrogen atoms and two imine nitrogen atoms. However, two sulfur atoms are remained unligated. This may be due to soft nature of sulfur atoms. Moreover, most copper complexes interested to form tetradentate complexes. Bulkiness of the ligand also favored in this regard. The bond angles O1—Cu1—N1, O1—Cu1—N1, O1—Cu1—N1, O1—Cu1—N1 are 87.86(7) °, 92.14(7) °, 92.13(7) °, 87.87(7) °. The significant discrepancies in bond angles

show the deviation from square planar geometry. The bond lengths Cu1—O1, Cu1—O1, Cu1—N1, Cu1—N1 are 1.8716(17) Å, 1.8717(17) Å, 2.0137(19) Å, 2.0137(19) Å respectively [38]. Some selected bond lengths and bond angles are summarized in Table 3.



Figure: 2 Molecular structure of copper complex, 3 shown with 35 % probability ellipsoids

#### **3.2.3. Hydrogen bonding in nickel and copper complexes (2 & 3)**

The hydrogen bonds along with equivalent positions are summarized in **Table 4.** The water and methanol molecules in nickel complex are connected by O—H...O interactions forming one dimensional chain along c-axis (**Figure 3**). 1D chain is connected by C—H...O and C—H... $\pi$  interactions between host molecules that fulfill the crystal packing (**Figure 4**). In copper complex, molecules are stacked via C—H... $\pi$  and C—H...O interactions along b-axis (**Figure** 

5). Columnar stacks are connected by C—H...O interactions that complete the 3D packing (Figure 6).



Figure: 3 Water and methanol connected through O—H...O interactions in nickel complex, 2.



Figure: 4 C—H...O and C—H...  $\pi$  interactions in nickel complex, **2**.



Figure: 5 C—H...  $\pi$  and C—H...O interactions in copper complex, **3**.



Figure: 6 C—H...O interactions in copper complex, **3**.

|--|

Bond length		Bond angle	
Ni1—O2	2.000(3)	02—Ni1—O1	88.74(12)
Ni1-01	2.007(3)	O2—Ni1—N2	90.59(14)
Ni1—N2	2.035(4)	01—Ni1—N2	94.38(14)
Ni1—N1	2.035(4)	O2—Ni1—N1	91.94(14)
Ni1—S2	2.433(14)	01—Ni1—N1	89.58(14)
Ni1—S1	2.476(13)	N2—Ni1—N1	175.35(16)
O1—C1	1.309(5)	O2—Ni1—S2	173.63(10)
O4—C43	1.274(8)	O1—Ni1—S2	95.33(10)
N1C7	1.309(5)	N2—Ni1—S2	84.23(12)
N1	1.399(5)	N1—Ni1—S2	92.98(11)
N2-C27	1.294(6)	O2	93.39(9)
N2C28	1.427(5)	S1—Ni1—S1	171.18(10)
S1—C13	1.772(4)	N2—Ni1—S1	94.03(11)
S1-C14	1.830(5)	N1—Ni1—S1	81.91(11)
S2—C33	1.785(5)	S2—Ni1—S1	82.92(4)
S2-C34	1.834(5)		

Table 3: Selected bond lengths (Å) and bond angles (°) for 3

Bond length		Bond angle	
Cu1—01	1.871(17)	01—Cu1—O1	180.0
Cu1—N1	2.013(19)	01—Cu1—N1	87.86(7)
S1—C14	1.775(2)	N1—Cu1—N1	180.0(5)
S1—C15	1.830(3)	C14—S1—C15	97.92(11)
O2—C4	1.385(3)	C4—O2—C7	116.45(18)
O2—C7	1.428(3)	C1	130.64(16)
01—C1	1.319(3)	C8—N1—C9	114.8(2)
N1—C8	1.306(3)	C8—N1—Cu1	123.97(17)
N1—C9	1.441(3)	C9—N1—Cu1	121.01(15)
		N1—C8—C6	126.8(2)

 Table 4: Hydrogen bond geometries.

H Bond	D-H(Å)	d (Å)	D (Å)	Angle (°)	Equivalent positions			
Nickel complex, 2								
O5- H5A…O1	0.98	1.67	2.646 (6)	171	1/2+x,1-y,z			
O6- H6A…O5	0.98	1.90	2.859(6)	163	-			
O6– H6B…O3	0.98	1.94	2.856(6)	155	1/2-x,y,1/2+z			
C11–H11…O2	1.08	2.38	3.408(5)	158	1/2+x,1-y,z			
C14-H14B…O6	1.08	2.28	3.356(6)	173	1/2-x,y,-1/2+z			
С36- Н35А…О5	1.08	2.38	3.445(6)	166	-1/2+x,1-y,z			
Copper complex, <b>3</b>								
C11– H11…O2	1.08	2.42	3.405 (6)	150	-x,1/2+y,1/2-z			
C15-H15B…O1	1.08	2.45	3.477 (4)	158	-x,1-y,-z			

NP

#### 3.3. Palladium complex catalyzed phosphine free Suzuki reaction

Suzuki reaction is most important palladium catalyzed C–C coupling reaction in organic synthesis. In this case, phosphine moiety containing palladium complex are widely used. But, most palladium complexes of phosphine ligands are air and moisture sensitive and therefore P—C bond decomposition occurs at elevated temperature which poisons the metal, leading to decomposition of the catalyst and affects in conversion and selectivity of Suzuki reaction [**39**]. The reported thioether containing palladium complex is thermally stable and insensitive to oxygen and moisture. The apparent stability of present complex has led to precise mode of action. A few works has been reported with thioether containing palladium catalyzed Suzuki reaction. The synthesized palladium complex show very good catalytic activity towards Suzuki reaction (Scheme 3). We have tried for the ability of the catalyst for optimization of coupling

reaction between iodobenzene and phenylboronic acid with different amounts of the catalyst, solvents, bases and at different temperatures (65, 85 and 100  $\circ$ C) (**Table 5**). The effect of bases (Et<sub>3</sub>N, Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>), solvents (nonpolar, protic and aprotic) and catalyst amount are summarized (Table 6). Among the bases, K<sub>2</sub>CO<sub>3</sub> was found to be the most effective. Our investigation show methanol is found to be best choice. 1 mol% of palladium complex gave the optimum results using methanol as solvent and 65°C as the reaction temperature. Thus, the optimum conditions are: iodobenzene (1 mmol), phenylboronic acid (1.1 mmol), palladium complex (1 mol %) methanol (2 mL), K<sub>2</sub>CO<sub>3</sub> (2 mmol) and 65°C as the reaction temperature. Adopting the optimized reaction condition coupling reactions of various substituted aryl halides and phenylboronic acids were carried out using 1 mol% palladium complex as catalyst at 65°C (Table 7). Most of the reactions completed in 24–34 hours with moderate to excellent yields. The yields vary with the substrates having either electron-donating groups or electronwithdrawing groups. Under optimized conditions, phenyl iodide and bromide were reacted efficiently with phenylboronic acid (Table 7). Both electron-withdrawing and releasing groups with phenylboronic acid afforded the corresponding products with high yields (Table 7). It was found that present catalyst exhibited higher conversions and yields [40].

$$\mathbf{F}_{\mathbf{H}} = \mathbf{F}_{\mathbf{H}} + (\mathbf{H}_{\mathbf{O}})_{2}\mathbf{B} - \mathbf{F}_{\mathbf{K}} + \mathbf{F}_{\mathbf{C}}\mathbf{C}_{\mathbf{O}}, \mathbf{M}_{\mathbf{O}}\mathbf{H}, \mathbf{24} \, \mathrm{hrs}, 65^{\circ}\mathrm{C}$$
**Scheme 3:** Palladium complex catalyzed Suzuki reaction

Scheme 3: Palladium complex catalyzed Suzuki reaction

Entry	Solvent	Base	Temp (°C)	Time(hrs)	Conversion
1	DMF	Et <sub>3</sub> N	100	24	0
2	DMF	$Na_2CO_3$	100	24	48
3	DMF	$K_2CO_3$	100	24	64
4	CH <sub>3</sub> CN	Et <sub>3</sub> N	85	24	0
5	CH <sub>3</sub> CN	$Na_2CO_3$	85	24	58
6	CH <sub>3</sub> CN	$K_2CO_3$	85	24	68
7	Methanol	Et <sub>3</sub> N	65	24	0
8	Methanol	$Na_2CO_3$	65	24	77
9	Methanol	$K_2CO_3$	65	24	92

Table 5: Optimization of the reaction conditions for the Suzuki reaction of iodobenzene with
phenylboronic acid

**Table 6:** Optimization of the catalyst concentration on the reaction of iodobenzene with phenylboronic acid

Entry	Cat (mol %)	Time(hrs)	Conversion
1	None	34	0
2	0.1	32	55
3	0.2	30	64
4	0.3	28	73
5	0.4	26	84
6	0.5	24	92
2			



Fable 7: Suzuki	reaction wit	h the	catalyst	[PdLCl] <sup>[xyz]</sup>	]
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<sup>x</sup>Solvent= Methanol, <sup>y</sup>Base=K<sub>2</sub>CO<sub>3</sub>, <sup>z</sup>Time=24-34 hrs

#### 3.4. Antibacterial activities of compounds:

Antibacterial activities of the ligand and complexes are evaluated by adopting the literature method [21] and compared with standard drug kanamycin acid sulphate [41]. Individually 10 mg/ml of ligand and complexes in DMF are tested qualititavely for vitro antibacterial activities

against the gram positive and gram negative bacterias using disc diffusion assay. The ligand and complexes exhibit activity against all bacterias. DMF do not exhibit any antibacterial properties. The biological activities of compounds depend on metal atom, geometry of the complex, charge of the metal ion, chelate effect of the ligand. The results are shown in Table 8. It is observed that ligand is more active against Mycobacterium abscessus and palladium complex show very good activity against Bacillus subtilis, Staphylococcus saureus, Proteus vulgaris, Mycobacterium follow smegmatis Escherichia The bacterial activity the and coli. order Pd(II)>Cu(II)>Ni(II)>ligand. The increasing activity may be explained by Tweedy's chelation theory [42]. Chelation decreases the polarity of the metal center by neutralizing partial positive charge of metal ion and delocalization of pi electron within the chelate ring. Chelation increases the lipophilic nature of metal centre. As a result, hydrophobic nature and liposolubility of the complex increases and favors permeability through the lipid layers of the cell membrane. It enhances the up taking/entrancing tendency. Hence antimicrobial activity of the testing compounds [43]. Accordingly, the antimicrobial activity of the complexes increases lipophilic nature which deactivates enzymes responsible for respiration processes and other cellular enzymes also. These are important in various metabolic pathways of micro-organisms.

Table 8: Antibacterial activity of ligand and complexes

			Zone of inhibition <sup>a</sup> (cm)				
Compounds	Concentration	Bacillus	Staphylococcus	Proteus	Escherichia	Mycobacterium	Mycobacterium
	(µg/ml)	subtilis	aureus	vulgaris	coli	smegmatis	abscessus
Ligand(1)	10	1.6	0.6	1.9	1.7	1.5	2
$NiL_2(2)$	10	1.7	0.7	1.2	1.4	1	1.4
$CuL_2(3)$	10	1.8	0.6	1.7	1.6	1.3	1.1
PdLCl(5)	10	1.9	0.9	1.9	1.8	1.9	1.8
Kanamycin	10	1.15	1.32	1.28	1.29		

<sup>a</sup>Kanamycin (20 µg/well) was used as positive reference, synthesized compounds (20 µg /well).

#### 4. Conclusion

A new sterically and electronically tunable mixed hydroxyl-imine-thioether tridentate ligand and its four mononuclear Ni(II), Cu(II), Co(II), Pd(II) complexes were prepared. These were characterized by physio-chemical analysis. Single crystal X-ray diffraction data, elemental analyses and electronic spectra revealed slightly distorted octahedral arrangement for complex 2 and slightly distorted square planar geometry for complex 3. The phosphine free palladium complex show very good catalytic activity towards and Suzuki reaction. All compounds show very good antibacterial activity. 

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#### Appendix A. Supplementary data

It contains <sup>1</sup>H NMR, FT-IR and UV-Visible spectra of compounds **1-5**, which can be found via the "supplementary data" section of this article's webpage. CCDC 1020519 and 1020520 contain the supplementary crystallographic data for nickel complex, 2 and copper complex, 3. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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#### **Graphical Abstract**

A series of new Ni(II), Cu(II), Co(II) and Pd(II) complexes were synthesized from the reaction of thioether containing Schiff base ligand with corresponding metal salts by a simple environmentally benign procedure. Copper forms square planar geometry. As expected, nickel complex acquired a distorted octahedral geometry. The reported palladium complex is phosphine free, air stable, moisture insensitive. Ligand and complexes show very good activity against *Mycobacterium abscessus, Bacillus subtilis, Staphylococcus aureus, Proteus vulgaris, Mycobacterium smaamatis* and *Escharishia aoli* 

Mycobacterium smegmatis and Escherichia coli.

