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# A Water Soluble Ni-Schiff Base Complex for Homogeneous Green Catalytic C–S Cross Coupling Reactions

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10

11 Abstract: Since the embarkation of C-S cross-coupling from aryl halides with thiols a handful of works have been contemplated in aqueous medium. Herein, we report an example 12 of a water soluble Ni-Schiff base complex as the green catalyst for the synthesis of thioethers. 13 We have synthesized a Ni-Schiff base complex [NiL(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> using N<sub>4</sub>-donor Schiff 14 15 base ligand (1,3-bis(((E)-pyridin-2-ylmethylene)amino)propan-2-ol) and characterized by single crystal X-ray diffraction (SC-XRD) study along with different spectral analyses. The 16 17 complex is mononuclear and cationic in nature having two perchlorate anions. Two water molecules remain coordinated with the Ni(II)-centre. The hydrogen bonding interaction 18 19 through coordinated water and perchlorate anions connect the monomeric units to form 3D 20 supramolecular structure. Based on its aqueous solubility, the complex has been used for the catalytic C-S cross-coupling reaction between aryl iodide and aryl or alkyl thiols using 21 TBAB at 60 °C in aqueous media (yield 92%). At room temperature, an isolated yield of 57% 22 can be achieved. This environmentally benign protocol is paramount in view of the 23 environmental sustainability. 24

Keywords: a) Ni-Schiff base complex, b) green catalyst, c) C–S cross-coupling, d)
thioethers.

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<sup>\*</sup>Both have equal contributions

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- 30

Introduction: Both the reaction kinetics and environmental sustainability are the two major 32 33 parameters of an advanced catalysis reaction [1]. Easy availability of active sites and consequent pronounced interaction of substrates with the active sites boost the kinetics of 34 homogenous catalytic reactions while the usage of organic solvents produces hazardous 35 chemicals against the environmental laws [2]. And thus, there is constant demand to develop 36 new catalytic system that perform under homogeneous condition in green solvents like water, 37 ethanol etc. [3]. In this background, we report a water soluble Ni-Schiff base complex that 38 shows excellent C-S hetero-coupling catalytic reaction in aqueous medium. 39

40 For centuries, sulfur-based therapeutics have been playing a predominant role in material science, food additives to agrochemicals and pharmaceutical industries [4,5]. 41 Therefore, the synthesis of thioether represents significant attention from the scientific 42 community worldwide but C-S cross coupling is quite difficult [6-15] - due to: a) thiols are 43 prone to undergo oxidative dimerization to form disulfides, and b) the organic sulfur centre 44 acts as effective donors, which might lead to catalyst deactivation [16]. Migita et al. first 45 reported the C-S cross-coupling of aryl halides with thiols using [Pd(PPh<sub>3</sub>)<sub>4</sub>] as the catalyst in 46 polar solvents [17-18]. Since then, different catalytic systems utilizing various transition 47 metals, such as Pd [8,17-18], Cu [7-8, 19-20], Co [21-22], Fe [23-24], Mn [25], Rh [26] and 48 Ni [27-43] have been investigated to affect the C-S cross coupling either in zero oxidation 49 state or with appropriate ligands in different oxidation states. Among all these, Ni-complexes 50 are considered as highly potent as Ni is natural abundant, cheap, environment-friendly. 51 52 Again, Ni has emerged as an effective catalyst due to its similar reactivity like that of Pd. Cristau and co-workers first utilized Ni-based coordination compound as catalyst in C-S 53 cross-coupling by employing bis(bipyridine)nickel(II) as catalyst [27]. Kumar et al., and 54 Sikari et al., have reported the adoption of Ni<sup>2+</sup> based coordination polymers on Co<sup>3+</sup> based 55 metallo-ligands and diradical Ni(II) catalyst bearing redox active non-innocent ligand 56 respectively [28, 29]. First observation on the application of Ni-precatalyst compound in C-S 57 cross coupling was reported by Persec et al. [30]. Since then Xu [31], Gehrtz [32], Merchese 58 [33], and Magné group [34] have reported other Ni-based precatalysts in presence of 59 additional reducing agents. Some phosphine and phosphite based Ni-catalysts also emerged 60 in this field [35-37]. Another class of Ni-based catalyst, namely pincer complexes have been 61 found to be effective to catalyse C–S cross couplings [38-40]. N-heterocyclic carbene (NHC) 62 complexes of Ni have also shown efficient catalytic activity [13, 38-40] Recently, 63

photoredox catalysis of Ni-complexes in C–S cross coupling has also been investigated [4143]. Schiff base complexes of transition metals are found to be potent catalyst in many
organic synthesis. Similarly, Ni-Schiff base complexes have also played an active role in
catalyzing C–S coupling reactions utilizing thiols and aryl or alkyl halides.

Almost all of the above catalysis suffers from one or more of the following 68 limitations, namely, use of environmentally harmful organic solvents [34, 44-45], reducing 69 agents [34, 44], air sensitivity [46-47], requirement of inert atmosphere [48-49], high 70 temperature [33, 50-51], high catalyst loading [43], longer time [41] and multi-step tedious 71 synthetic process [24, 41] for catalyst synthesis etc. Thus, we are left with an absolute need of 72 a catalytic system that minimizes the aforementioned limitations to some extent in green 73 solvent so that sustainable environment prevails. Unlike petrochemical solvents, the uses of 74 green solvents solvents are highly beneficial in terms of their low cost, 100% 75 biodegradability, non-toxic nature and non-ozone-depleting behaviours. The use of water as a 76 solvent has been highly recommended because of its non-toxicity and wide availability. 77

In the present work, we have developed a Ni-based Schiff base complex 78 [NiL(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> (Scheme 1) and characterized by SCXRD analysis. The complex has been 79 successfully employed as an efficient catalyst for C–S cross-coupling reactions between aryl 80 81 iodides and aryl/alkyl thiols. Further, we have been able to perform the reactions in water as a solvent under mild reaction conditions with moderate to excellent yields. In aqueous medium 82 the catalyst provided more than satisfactory result by furnishing 57% yield at room 83 temperature and 93% yield at 80 °C. To the best of our knowledge, this is the very first report 84 85 for on-water C–S cross-coupling reactions by a Ni-Schiff base complex with a very simple and efficient protocol. 86



Scheme 1: Detailed synthetic scheme of the ligand and complex

### 89 Experimental section:

Materials and methods: Nickel(II) perchlorate hexahydrate (99%), 1,3-diamino-2-propanol 90 (95%) and 2-pyridinecarboxaldehyde (98%) were purchased from Aldrich and used without 91 further purification. All other chemicals were purchased from Merck chemical company and 92 used as received. All the reagents were used without further purification. PerkinElmer 240C 93 elemental analyzer was employed to perform elemental analysis (C, H, N). The Fourier 94 95 transform infrared (FT-IR) spectra have been recorded by a Nicolet Impact 410 spectrometer using KBr pellets in the range of 400–4000 cm<sup>-1</sup>. Electronic spectra in MeOH were recorded 96 97 in a Perkin Elmer UV-Vis spectrophotometer model Lambda 25.

Synthesis of [NiL(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (1): 20 ml methanolic solution of 4 mmol (428 mg) 2-98 pyridinecarboxaldehyde was added to 10 ml methanolic solution of 2 mmol (180 mg) 1,3-99 diamino-2-propanol with constant stirring for 2 hrs. Now, 20 ml methanolic solution of 100 Ni(ClO<sub>4</sub>)<sub>2</sub>.6H<sub>2</sub>O (2 mmol and 0.732 g) was added dropwise to the ligand solution and stirred 101 for another 12 hrs. The greenish-yellow coloured solution turned red with continuous stirring, 102 then it was filtered and filtrate was kept for crystallization. Red coloured needle shaped 103 crystals (Figure S1) suitable for X-ray diffraction were obtained after few days. Yield: 85%. 104 Anal. Calc. for C<sub>15</sub>H<sub>20</sub>Cl<sub>2</sub>N<sub>4</sub>NiO<sub>11</sub>: C, 32.05; H, 3.58; N, 9.97%. Found: C, 32.10; H, 3.6; N, 105 9.90%. 106

Crystallographic data collection and refinement of 1: Suitable single crystal of the 107 complex was mounted on a Bruker SMART diffractometer equipped with a graphite 108 monochromator and Mo-K<sub>a</sub> ( $\lambda = 0.71073$  Å) radiation. Unit cell parameters were determined 109 by using the APEX2 [52] program. Data reduction was carried out by the SAINT [52], 110 program and correction or absorption was performed using the SADABS, [52], program. The 111 structure was solved using Patterson method by using the SHELXS-2018/3, [53], embedded 112 113 in WINGX software package [54]. Subsequent difference Fourier synthesis and least-square refinement revealed the positions of the remaining non hydrogen atoms. The isopropanol 114 fragment of the ligand (atoms O1/C7/C8/C9) is disordered over two orientations with refined 115 occupancy ratio of 0.557(7): 0.443(7). The oxygen atoms of the perchlorate anions are also 116 disordered over two sets of sites with refined occupancy ratios of 0.667(13):0.333(13) (for 117 atoms O2/O3/O4/O5) and 0.643(14):0.357(14) (for atoms O6/O7/O8/O9). During the 118 refinement, the anisotropic displacement parameters of the disordered perchlorate oxygen 119 atoms were restrained to be nearly isotropic (ISOR instruction in SHELXL-2018/3) and the 120

121 Cl–O bond distances were restrained to be similar (SADI instruction). The water H atoms 122 were located in a difference Fourier map and refined as riding, with  $U_{iso}(H) = 1.5U_{eq}(O)$ . All 123 other H atoms were placed geometrically and refined using a riding atom approximation, with 124 C–H = 0.93-0.98 Å, and with  $U_{iso}(H) = 1.2 U_{eq}(C)$  or 1.5  $U_{eq}(O)$  for hydroxy H atoms. All 125 Figures were drawn by using PLATON, [55] and ORTEP, [56]. Data collection and structure 126 refinement parameters and crystallographic data for complex 1 are given in Table 1.

Catalysis: A round bottomed flask (25 ml) equipped with magnetic spin bar was charged 127 with the catalyst (5 mg, 0.0089 mmol) and H<sub>2</sub>O (2 ml). After stirring the mixture for 10 128 minutes at r.t., alkyl halide (1 mmol), thiol (1 mmol), K<sub>2</sub>CO<sub>3</sub> (2 mmol) and TBAB (10 mol%) 129 130 were added. The reaction vessel was then placed in a pre-heated oil bath at 60 °C and gently stirred for 6 h. After completion of the reaction (monitored by TLC), the reaction mixture 131 was cooled to r.t. and extracted with ethyl acetate (3 x 5 ml). The combined organic layer was 132 dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude product 133 obtained was purified by column chromatography using light petroleum ether as eluent. All 134 products were characterized by <sup>1</sup>H NMR spectroscopy (see Supporting Information). 135

- 136**Table 1:** Crystallographic data collection and refinement parameters of complex 1
- 137

Formula	C <sub>15</sub> H <sub>20</sub> N <sub>4</sub> NiO <sub>3</sub> <sup>-2</sup> (ClO <sub>4</sub> )			
formula weight	561.96			
Crystal system	Monoclinic			
Space group	<i>P</i> 2 <sub>1</sub> /c (No. 14)			
a (Å)	14.7333(14)			
b (Å)	9.8321(10)			
c (Å)	16.6109(15)			
α (°)	90			
β (°)	112.897(4)			
γ (°)	90			
V (Å <sup>3</sup> )	2216.7(4)			
Ζ	4			
$\rho_{calc} (g/cm^3)$	1.681			
$\mu$ (Mo K $\alpha$ ) (mm)	1.181			
F(000)	1132			
crystal size (mm <sup>3</sup> )	0.08 x 0.12 x 0.16			
Temperature, T (K)	300			
θ <sub>min-max</sub> (deg)	3.0, 25.2			

Total data	17560
Unique data	4008
R <sub>int</sub>	0.023
Observed data [I>2.0 $\sigma$ (I)]	3396
N <sub>ref</sub>	4008
N <sub>par</sub>	411
N <sub>restr</sub>	152
R	0.0392
wR <sub>2</sub>	0.1120
S	1.041

139

## 140 **Result and discussions:**

Spectral Characterization of the ligand and complex 1: In the infrared spectrum of the 141 complex (Figure S3) a sharp intense peak centred at 1092 cm<sup>-1</sup> is indicative of ionic 142 perchlorate. Slight deviation from ideal tetrahedral symmetry due to H-bonding is indicated 143 by a splitting in the band as evident from 2D supramolecular sheet structure of the complex. 144 Peak at 1651 cm<sup>-1</sup> of the free ligand (Figure S2) can be attributed to the azomethine group 145 (C=N). This is substantiated by the fact that this peak shifts to lower region at 1644cm<sup>-1</sup>, in 146 the spectrum of the complex, proving the bonding of the group to the metal ion centre. The 147 broad nature of the peak at 3261 cm<sup>-1</sup> in the spectrum of the ligand is not prominent in the 148 complex. A peak at 3344 cm<sup>-1</sup> in the spectrum of the complex is indicative of coordinated 149 water molecules along with the free OH group of the ligand. The broad nature of this peak in 150 the ligand can be explained by the fact that this OH group participates in interaction with the 151 nitrogen atom of the azomethine group. The absorption spectra of the ligand and the complex 152 were collected from methanolic solution. Peaks at lower wave length region are ligand 153 transitions in origin. No peaks which can be denoted d-d transitions are observed in the 154 spectrum which could have been indicative of the regular octahedral geometry of the 155 complex. However, spectrum taken at high concentration shows a slight shoulder like 156 absorption at around 364-366 nm region. The lower region peaks most probably overlaps 157 158 with the charge transfer bands to give a broad nature in general. The longer bond length of the metal centre with the coordinated water molecules indicated that the basic geometry is 159 predominantly square planar with loosely bound water molecules to give an overall six 160 coordinated nature. The d-d transitions expected for octahedral complexes are shifted to 161

lower wavelength region as distortion from regular octahedral geometry increases to give a 162 tetragonally elongated structure. The colour of the complex, therefore, shows a red shift from 163 164 the greenish colour expected for regular octahedral structure. The isolated complex has a brownish red colour which can be attributed to this distortion. In the spectrum of the ligand 165 bands are obtained at 237 nm, 259 nm and 265 nm. The band at 237 nm may be attributed to 166 high energy  $\sigma \rightarrow \sigma^*$  transition whereas the band at 259 nm along with a wide band at 252 nm 167 are probably due to  $\pi \rightarrow \pi^*$  transitions and the coalescence of the band at 265 nm along with 168 the band at 274 nm and 281 nm may be assigned to  $n \rightarrow \pi^*$  transition. 169

Crystal Structure of 1: The SC-XRD analysis shows that the compound crystallizes in 170 monoclinic centro-symmetric  $P2_1/c$  space group (Table 1) and it is a monomeric complex. 171 172 The asymmetric unit contains one Ni(II) ion, one neutral Schiff base ligand L, two coordinated water molecules and two charge neutralizing perchlorate anion (Figure 1). Ni(II) 173 ion shows six coordinated distorted octahedral geometry. The equatorial positions (r.m.s. 174 deviation 0.0254 Å) are occupied by four donor N-atoms (N1, N2, N3 and N4) of the ligand 175 L and two water molecules occupy the two axial sites. Interestingly, the OH group of the L 176 remains uncoordinated to the metal centres. The overall charge of the complex is neutralized 177 by two perchlorate anions. The Ni-N bond lengths (Table S1) fall in the range 2.042(3)-178 2.102(2) Å, while the axial Ni-O bond lengths are: Ni-O1W = 2.094(4) Å and Ni-O2W = 179 2.103(4) Å. The longer Ni-O bond length reflects the tendency of axially elongated 180 compound formation of the Ni(II), a d<sup>8</sup> system. 181

182



Figure 1: ORTEP diagram of 1 with displacement parameters drawn at the 40% probability
 level (the minor component of the disordered isopropanol fragment, perchlorate anions and
 hydrogen atoms are omitted for clarity)

Supramolecular structural analysis reveals that the monomeric units are connected by perchlorate mediated hydrogen bonding interactions (Table S2) to form 1D supramolecular chains parallel to the *b* axis.(Figure 2). Adjacent centrosymmetrically-related chains are further assembled by weak  $\pi$ ... $\pi$  interactions (perpendicular interplanar distance = 3.3550(12) Å, centroid-to-centroid distance = 4.036(2) Å) to form supramolecular ribbons.



Figure 2: Partial crystal packing of complex 1 showing the formation of chains through O-H...Cl hydrogen bonds (purple dashed lines) and ribbons parallel to the *b* axis *via* weak  $\pi...\pi$  stacking interactions (blue dashed lines). Hydrogen atoms not involved in hydrogen bonding are omitted.

206

Catalysis: To test the viability of the newly developed catalyst, we began our initial 207 optimizations using 4-iodoanisole and 4-chlorothiophenol as model substrates and the results 208 209 are presented in Table 2. At the beginning, we investigated the effects of solvent on the reaction and subsequently we varied the base and temperature. The reaction went smoothly in 210 211 presence of polar aprotic solvents like CH<sub>3</sub>CN and DMF using 5 mg (0.0089 mmol) of the monomeric complex (Table 2, entries 1 and 2). The reaction when carried out in aqueous 212 213 medium in presence of tetrabutylammonium bromide (TBAB) as additive resulted in the formation of the desired product in excellent yield (entry 3, 93%). Lowering the temperature 214 to 60 °C and keeping all other parameters same resulted in almost similar conversion (entry 215 4, 92%). The use of  $Na_2CO_3$  as base also formed the corresponding thioether in slightly lower 216 217 yield (entry 5, 84%). We even carried out the reaction at room temperature which further reduced the yield of the product (entry 6, 57%). The reaction when conducted in the absence 218

- of TBAB, formed the product in 39% yield (entry 7). This might be due to the poor solubility
- of the substrates in water.
- 221

# **Table 2:** Optimization of the reaction condition<sup>a</sup>

223	MeO + HS (I + HS) (				
	Entry	Solvent	Base	Temp (°C)	Yield (%) <sup>b</sup>
	1	CH <sub>3</sub> CN	K <sub>2</sub> CO <sub>3</sub>	80	68
	2	DMF	$K_2CO_3$	80	73
	3	$H_2O$	$K_2CO_3$	80	93
	4	H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	60	92
	5	$H_2O$	Na <sub>2</sub> CO <sub>3</sub>	80	84
	6	$H_2O$	$K_2CO_3$	r.t.	57
	7	$H_2O$	$K_2CO_3$	60	39

<sup>a</sup>Reaction conditions: 4-iodoanisole (1 mmol), 4-chlorothiophenol (1 mmol), catalyst (5 mg, 0.0089
mmol), solvent (2 mL) and base (2 mmol). For reaction in H<sub>2</sub>O as solvent, TBAB (10 mol%) have
been used.

<sup>b</sup>Isolated yield.

228

With the optimized reaction condition in hand we explored the scope of the reaction with 229 different substrates (Table 3). Substitution pattern on both the reacting partners did not affect 230 the course of the reaction and corresponding products were obtained in 92-74% yield (entries 231 1-8). We have tested the reactivity of aryl iodides, aryl bromide and aryl chloride under the 232 standard reaction conditions (entry 1). Aryl iodides showed better results compared to other 233 aryl halides in terms of product yield. Aryl chloride did not react at all during the course of 234 the reaction. Electron donating groups (-OMe and -Me) as well as electron withdrawing 235 groups (-NO<sub>2</sub> and -F) on the both the reacting partners were tolerated under the reaction 236 conditions. Moreover, the reaction when carried out with aliphatic thiol (heptanethiol) also 237 afforded the desired product in 79% yield (entry 8). 238

**Table 3:** [NiL(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> catalysed C–S cross coupling reaction<sup>a</sup>





<sup>a</sup>Reaction conditions: aryl iodide (1 mmol), thiol (1 mmol), catalyst (5 mg, 0.0089 mmol), K<sub>2</sub>CO<sub>3</sub> (2 mmol), H<sub>2</sub>O (2 mL) and TBAB (10 mol%) were stirred at 60 °C for 6 h.
<sup>b</sup>Isolated yield.

On the basis of previous mechanistic studies, a plausible mechanism for C–S cross-coupling reaction has been proposed (Scheme 2) [57]. Initially, oxidative addition of aryl halide with the catalyst leads to the formation of the intermediate **I**. Subsequent addition of thiol to intermediate **I** generates another intermediate **II** along with the elimination of HX. Finally, intermediate II undergoes reductive elimination to form the desired C–S cross-coupled product while regenerating the NiL catalytic species.

251



Scheme 2: Plausible mechanism for C–S cross-coupling reaction

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253

255 **Conclusion:** In this contribution, we have shown the catalytic homogeneous C–S coupling in water by using Ni-Schiff base complex. A tetradentate N<sub>4</sub>-Schiff base ligand based Ni-256 complex has been synthesized by one pot chemical reaction and characterized by SC-XRD 257 analysis. The ready solubility of this mononuclear and cationic complex in water allows us to 258 investigate the homogeneous C-S coupling reaction in water. Coupling reaction were 259 successful for both alkyl and aryl thiols with their yields between 74 to 92%. To the best of 260 our knowledge (Table S3), this is the first ever example of Ni(II)-Schiff base complex which 261 is highly competent and productive green catalyst in catalysing C–S cross coupling from aryl 262 iodide and alkyl or aryl thiols in aqueous medium. Our next goal is to find the condition to 263 increase the yield (>90%) in room temperature using this catalyst in greener way. 264

Supporting information: CCDC number of complex is 2051558. Figures showing the packing of compound, tables with bond distances, angles and intermolecular interaction parameters for complex, IR spectra of the ligand and complex, UV-Vis spectra of the ligand and complex and NMR spectra of organic compounds are provided in the supporting information.

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