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A water soluble Ni-Schiff base complex for homogeneous green catalytic C S cross-coupling reactions

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

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10  
11 **Abstract:** Since the embarkation of C–S cross-coupling from aryl halides with thiols a  
12 handful of works have been contemplated in aqueous medium. Herein, we report an example  
13 of a water soluble Ni-Schiff base complex as the green catalyst for the synthesis of thioethers.  
14 We have synthesized a Ni-Schiff base complex  $[\text{NiL}(\text{H}_2\text{O})_2](\text{ClO}_4)_2$  using N<sub>4</sub>-donor Schiff  
15 base ligand (1,3-bis(((*E*)-pyridin-2-ylmethylene)amino)propan-2-ol) and characterized by  
16 single crystal X-ray diffraction (SC-XRD) study along with different spectral analyses. The  
17 complex is mononuclear and cationic in nature having two perchlorate anions. Two water  
18 molecules remain coordinated with the Ni(II)-centre. The hydrogen bonding interaction  
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  
21 catalytic C–S cross-coupling reaction between aryl iodide and aryl or alkyl thiols using  
22 TBAB at 60 °C in aqueous media (yield 92%). At room temperature, an isolated yield of 57%  
23 can be achieved. This environmentally benign protocol is paramount in view of the  
24 environmental sustainability.

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

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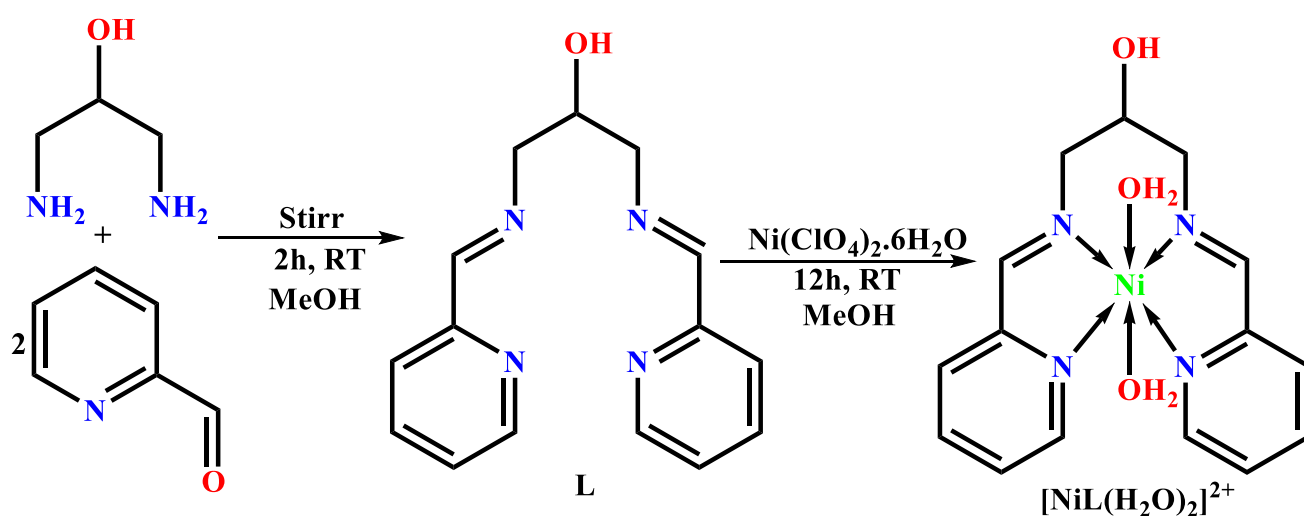
32 **Introduction:** Both the reaction kinetics and environmental sustainability are the two major  
33 parameters of an advanced catalysis reaction [1]. Easy availability of active sites and  
34 consequent pronounced interaction of substrates with the active sites boost the kinetics of  
35 homogenous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

40 For centuries, sulfur-based therapeutics have been playing a predominant role in  
41 material science, food additives to agrochemicals and pharmaceutical industries [4,5].  
42 Therefore, the synthesis of thioether represents significant attention from the scientific  
43 community worldwide but C-S cross coupling is quite difficult [6-15] - due to: a) thiols are  
44 prone to undergo oxidative dimerization to form disulfides, and b) the organic sulfur centre  
45 acts as effective donors, which might lead to catalyst deactivation [16]. Migita et al. first  
46 reported the C–S cross-coupling of aryl halides with thiols using  $[\text{Pd}(\text{PPh}_3)_4]$  as the catalyst in  
47 polar solvents [17-18]. Since then, different catalytic systems utilizing various transition  
48 metals, such as Pd [8,17-18], Cu [7-8, 19-20], Co [21-22], Fe [23-24], Mn [25], Rh [26] and  
49 Ni [27-43] have been investigated to affect the C–S cross coupling either in zero oxidation  
50 state or with appropriate ligands in different oxidation states. Among all these, Ni-complexes  
51 are considered as highly potent as Ni is natural abundant, cheap, environment-friendly.  
52 Again, Ni has emerged as an effective catalyst due to its similar reactivity like that of Pd.  
53 Cristau and co-workers first utilized Ni-based coordination compound as catalyst in C–S  
54 cross-coupling by employing bis(bipyridine)nickel(II) as catalyst [27]. Kumar et al., and  
55 Sikari et al., have reported the adoption of  $\text{Ni}^{2+}$  based coordination polymers on  $\text{Co}^{3+}$  based  
56 metallo-ligands and diradical Ni(II) catalyst bearing redox active non-innocent ligand  
57 respectively [28, 29]. First observation on the application of Ni-precatalyst compound in C–S  
58 cross coupling was reported by Persec et al. [30]. Since then Xu [31], Gehrtz [32], Merchese  
59 [33], and Magné group [34] have reported other Ni-based precatalysts in presence of  
60 additional reducing agents. Some phosphine and phosphite based Ni-catalysts also emerged  
61 in this field [35-37]. Another class of Ni-based catalyst, namely pincer complexes have been  
62 found to be effective to catalyse C–S cross couplings [38-40]. N-heterocyclic carbene (NHC)  
63 complexes of Ni have also shown efficient catalytic activity [13, 38-40] Recently,

64 photoredox catalysis of Ni-complexes in C–S cross coupling has also been investigated [41-  
65 43]. Schiff base complexes of transition metals are found to be potent catalyst in many  
66 organic synthesis. Similarly, Ni-Schiff base complexes have also played an active role in  
67 catalyzing C–S coupling reactions utilizing thiols and aryl or alkyl halides.

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

78 In the present work, we have developed a Ni-based Schiff base complex  
79  $[\text{NiL}(\text{H}_2\text{O})_2]^{2+}$  (Scheme 1) and characterized by SCXRD analysis. The complex has been  
80 successfully employed as an efficient catalyst for C–S cross-coupling reactions between aryl  
81 iodides and aryl/alkyl thiols. Further, we have been able to perform the reactions in water as a  
82 solvent under mild reaction conditions with moderate to excellent yields. In aqueous medium  
83 the catalyst provided more than satisfactory result by furnishing 57% yield at room  
84 temperature and 93% yield at 80 °C. To the best of our knowledge, this is the very first report  
85 for on-water C–S cross-coupling reactions by a Ni-Schiff base complex with a very simple  
86 and efficient protocol.



87  
88

**Scheme 1:** Detailed synthetic scheme of the ligand and complex

89 **Experimental section:**

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

98 **Synthesis of  $[\text{NiL}(\text{H}_2\text{O})_2](\text{ClO}_4)_2$  (1):** 20 ml methanolic solution of 4 mmol (428 mg) 2-  
99 pyridinecarboxaldehyde was added to 10 ml methanolic solution of 2 mmol (180 mg) 1,3-  
100 diamino-2-propanol with constant stirring for 2 hrs. Now, 20 ml methanolic solution of  
101  $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (2 mmol and 0.732 g) was added dropwise to the ligand solution and stirred  
102 for another 12 hrs. The greenish-yellow coloured solution turned red with continuous stirring,  
103 then it was filtered and filtrate was kept for crystallization. Red coloured needle shaped  
104 crystals (Figure S1) suitable for X-ray diffraction were obtained after few days. Yield: 85%.  
105 Anal. Calc. for  $\text{C}_{15}\text{H}_{20}\text{Cl}_2\text{N}_4\text{NiO}_{11}$ : C, 32.05; H, 3.58; N, 9.97%. Found: C, 32.10; H, 3.6; N,  
106 9.90%.

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

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  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ . 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  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$  or  $1.5 U_{\text{eq}}(\text{O})$  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.

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

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> ·2(ClO <sub>4</sub> )
formula weight	561.96
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (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)
Z	4
ρ <sub>calc</sub> (g/cm <sup>3</sup> )	1.681
μ (Mo Kα) (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

138

139

#### 140 **Result and discussions:**

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

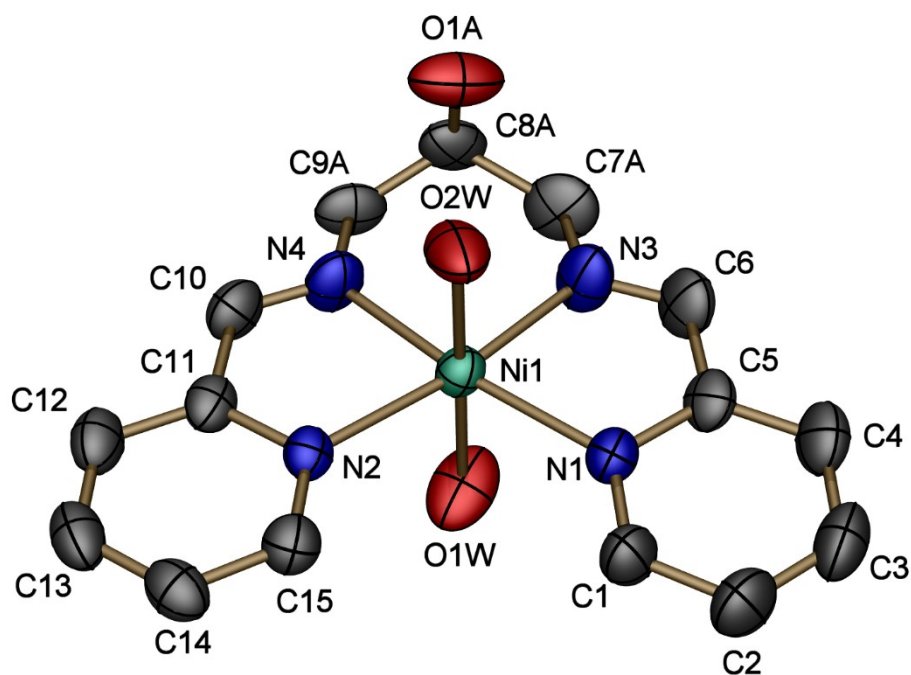
162 lower wavelength region as distortion from regular octahedral geometry increases to give a  
163 tetragonally elongated structure. The colour of the complex, therefore, shows a red shift from  
164 the greenish colour expected for regular octahedral structure. The isolated complex has a  
165 brownish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

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

182



183



184

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

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

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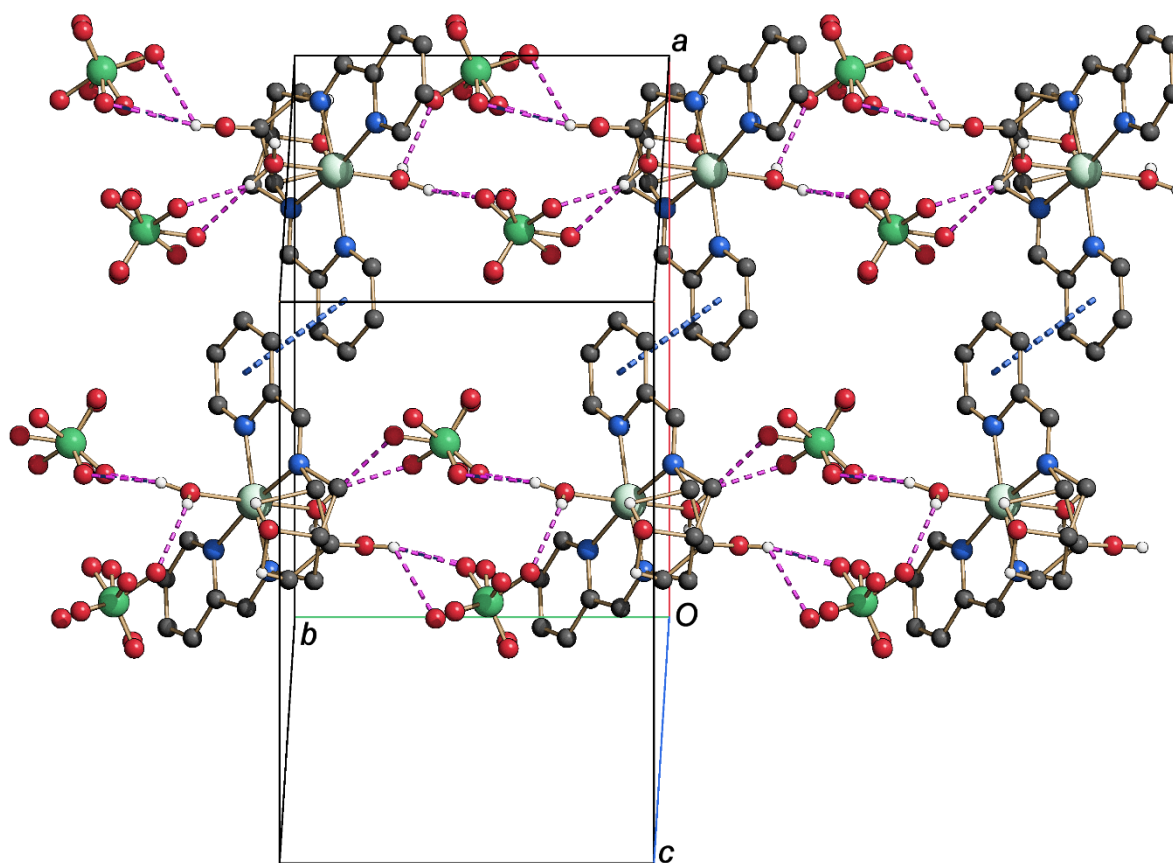
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202 **Figure 2:** Partial crystal packing of complex **1** showing the formation of chains through  
 203 O–H...Cl hydrogen bonds (purple dashed lines) and ribbons parallel to the *b* axis via weak  
 204  $\pi$ ... $\pi$  stacking interactions (blue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

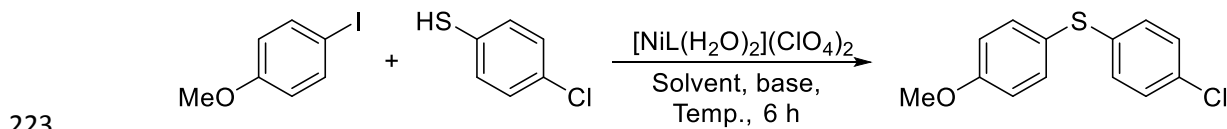
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207 **Catalysis:** To test the viability of the newly developed catalyst, we began our initial  
 208 optimizations using 4-iodoanisole and 4-chlorothiophenol as model substrates and the results  
 209 are presented in Table 2. At the beginning, we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

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

221

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



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 <sub>2</sub> CO <sub>3</sub>	80	73
3	H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	80	93
4	<b>H<sub>2</sub>O</b>	<b>K<sub>2</sub>CO<sub>3</sub></b>	<b>60</b>	<b>92</b>
5	H <sub>2</sub> O	Na <sub>2</sub> CO <sub>3</sub>	80	84
6	H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	r.t.	57
7	H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	60	39

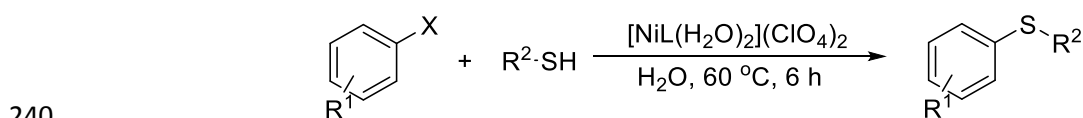
224 <sup>a</sup>Reaction conditions: 4-iodoanisole (1 mmol), 4-chlorothiophenol (1 mmol), catalyst (5 mg, 0.0089  
 225 mmol), solvent (2 mL) and base (2 mmol). For reaction in H<sub>2</sub>O as solvent, TBAB (10 mol%) have  
 226 been used.

227 <sup>b</sup>Isolated yield.

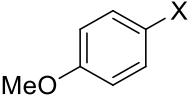
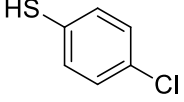
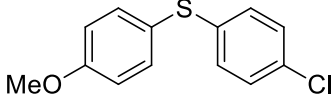
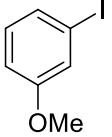
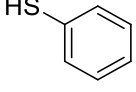
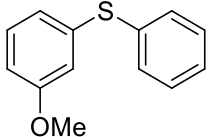
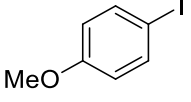
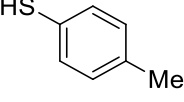
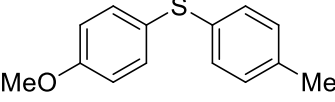
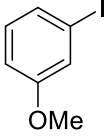
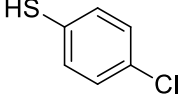
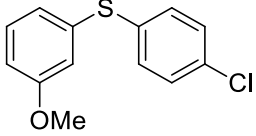
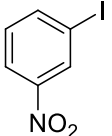
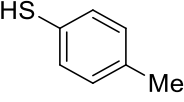
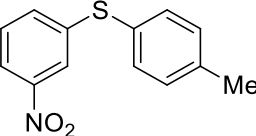
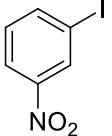
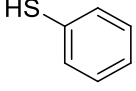
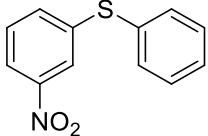
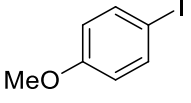
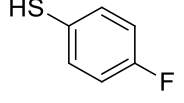
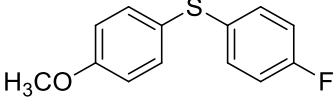
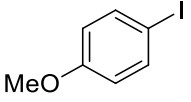
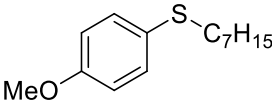
228

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

239 **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>



Entry	Aryl halide	Thiol	Thioether	Yield (%) <sup>b</sup>
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1	 X = I, Br, Cl			92 (X = I) 74 (X = Br) 0 (X = Cl)
2				84
3				87
4				81
5				88
6				86
7				90
8		$C_7H_{15}-SH$		79

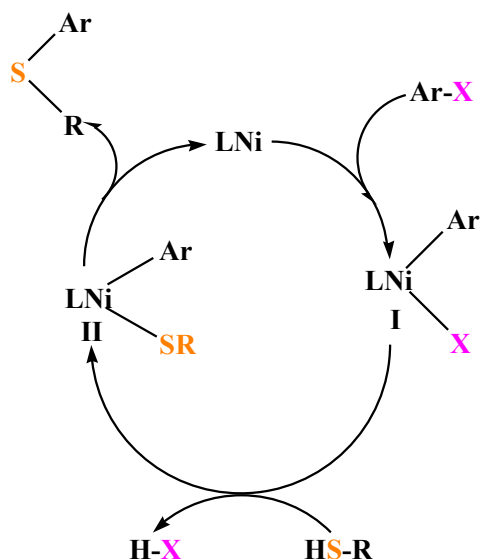
241 <sup>a</sup>Reaction conditions: aryl iodide (1 mmol), thiol (1 mmol), catalyst (5 mg, 0.0089 mmol),  $K_2CO_3$  (2  
242 mmol),  $H_2O$  (2 mL) and TBAB (10 mol%) were stirred at 60 °C for 6 h.

243 <sup>b</sup>Isolated yield.

244

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

251



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

252  
253  
254

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

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

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