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Original

A water soluble Ni-Schiff base complex for homogeneous green catalytic C S cross-coupling reactions / Biswas, Biplab; Choudhury, Prasun; Ghosh, Angshuman; Kumar Dubey, Soumen; Rizzoli, Corrado; Saha, Rajat; Bhattacharjee, Subham. - In: INORGANICA CHIMICA ACTA. - ISSN 0020-1693. - 532:(2022), p. 120755. [10.1016/j.ica.2021.120755]

Availability:

This version is available at: 11381/2906582 since: 2022-01-21T10:10:54Z

Publisher:

Published

DOI:10.1016/j.ica.2021.120755

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12 May 2025

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

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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 of a water soluble Ni-Schiff base complex as the green catalyst for the synthesis of thioethers. We have synthesized a Ni-Schiff base complex $[\text{NiL}(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ using N₄-donor Schiff 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 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 through coordinated water and perchlorate anions connect the monomeric units to form 3D 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 TBAB at 60 °C in aqueous media (yield 92%). At room temperature, an isolated yield of 57% can be achieved. This environmentally benign protocol is paramount in view of the environmental sustainability.

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

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[†] Both have equal contributions

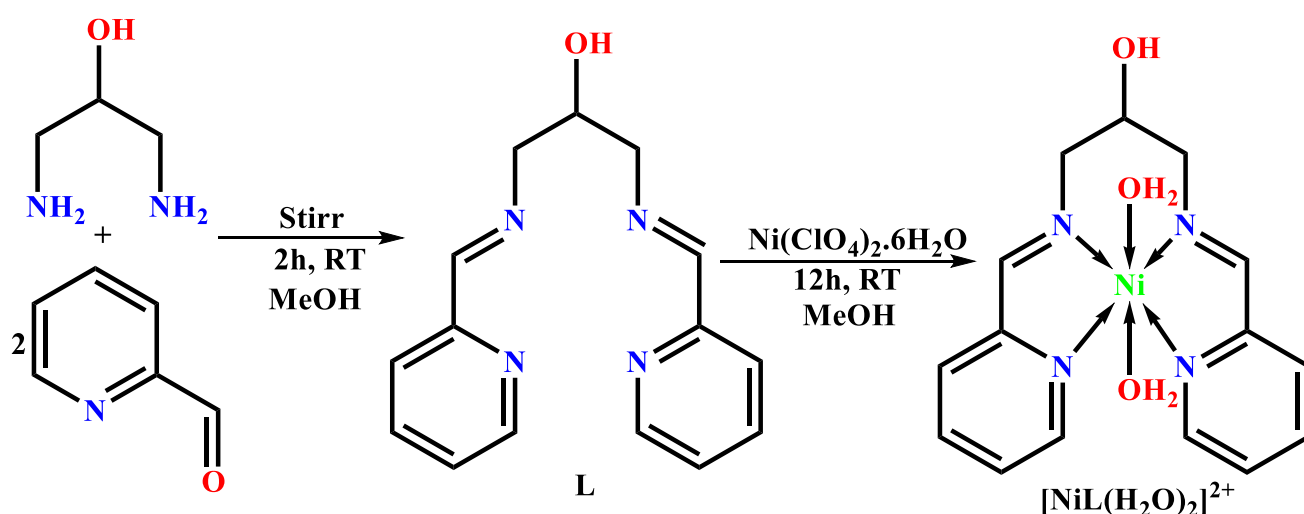
Introduction: Both the reaction kinetics and environmental sustainability are the two major parameters of an advanced catalysis reaction [1]. Easy availability of active sites and consequent pronounced interaction of substrates with the active sites boost the kinetics of homogenous catalytic reactions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

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

photoredox catalysis of Ni-complexes in C–S cross coupling has also been investigated [41-43]. 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 limitations, namely, use of environmentally harmful organic solvents [34, 44-45], reducing agents [34, 44], air sensitivity [46-47], requirement of inert atmosphere [48-49], high temperature [33, 50-51], high catalyst loading [43], longer time [41] and multi-step tedious synthetic process [24, 41] for catalyst synthesis etc. Thus, we are left with an absolute need of a catalytic system that minimizes the aforementioned limitations to some extent in green solvent so that sustainable environment prevails. Unlike petrochemical solvents, the uses of green solvents are highly beneficial in terms of their low cost, 100% biodegradability, non-toxic nature and non-ozone-depleting behaviours. The use of water as a solvent has been highly recommended because of its non-toxicity and wide availability.

In the present work, we have developed a Ni-based Schiff base complex $[\text{NiL}(\text{H}_2\text{O})_2]^{2+}$ (Scheme 1) and characterized by SCXRD analysis. The complex has been successfully employed as an efficient catalyst for C–S cross-coupling reactions between aryl 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 the catalyst provided more than satisfactory result by furnishing 57% yield at room temperature and 93% yield at 80 °C. To the best of our knowledge, this is the very first report for on-water C–S cross-coupling reactions by a Ni-Schiff base complex with a very simple and efficient protocol.



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 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 Mo-K_α ($\lambda = 0.71073 \text{ \AA}$) 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

Cl–O bond distances were restrained to be similar (SADI instruction). The water H atoms were located in a difference Fourier map and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. All other H atoms were placed geometrically and refined using a riding atom approximation, with 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 Figures were drawn by using PLATON, [55] and ORTEP, [56]. Data collection and structure 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 with the catalyst (5 mg, 0.0089 mmol) and H₂O (2 ml). After stirring the mixture for 10 minutes at r.t., alkyl halide (1 mmol), thiol (1 mmol), K₂CO₃ (2 mmol) and TBAB (10 mol%) 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 was cooled to r.t. and extracted with ethyl acetate (3 x 5 ml). The combined organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product obtained was purified by column chromatography using light petroleum ether as eluent. All products were characterized by ¹H NMR spectroscopy (see Supporting Information).

Table 1: Crystallographic data collection and refinement parameters of complex 1

Formula	C ₁₅ H ₂₀ N ₄ NiO ₃ ·2(ClO ₄)
formula weight	561.96
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ /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 ³)	2216.7(4)
Z	4
ρ _{calc} (g/cm ³)	1.681
μ (Mo Kα) (mm)	1.181
F(000)	1132
crystal size (mm ³)	0.08 x 0.12 x 0.16
Temperature, T (K)	300
θ _{min-max} (deg)	3.0, 25.2

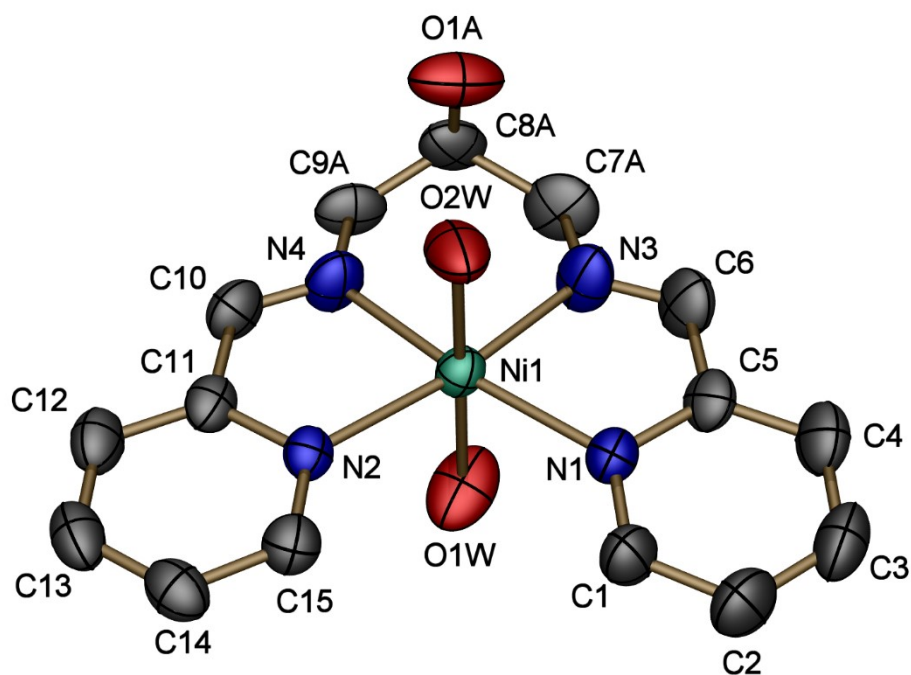
Total data	17560
Unique data	4008
R _{int}	0.023
Observed data [I>2.0 σ(I)]	3396
N _{ref}	4008
N _{par}	411
N _{restr}	152
R	0.0392
wR ₂	0.1120
S	1.041

Result and discussions:

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

lower wavelength region as distortion from regular octahedral geometry increases to give a tetragonally elongated structure. The colour of the complex, therefore, shows a red shift from 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 bands are obtained at 237 nm, 259 nm and 265 nm. The band at 237 nm may be attributed to high energy $\sigma \rightarrow \sigma^*$ transition whereas the band at 259 nm along with a wide band at 252 nm are probably due to $\pi \rightarrow \pi^*$ transitions and the coalescence of the band at 265 nm along with the band at 274 nm and 281 nm may be assigned to $n \rightarrow \pi^*$ transition.

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



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 $\pi\cdots\pi$ 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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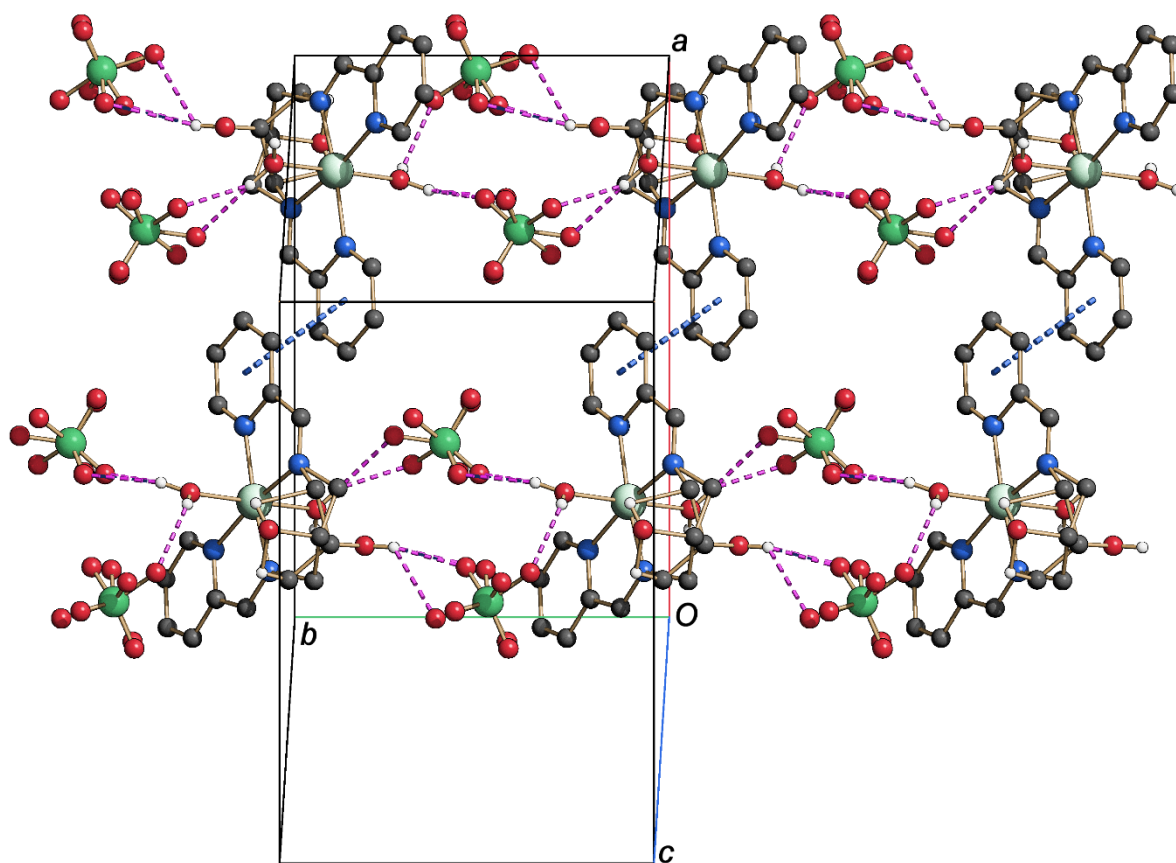
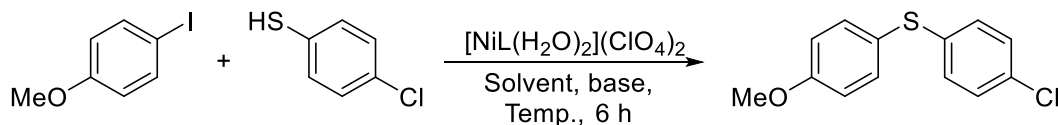


Figure 2: Partial crystal packing of complex **1** showing the formation of chains through O–H...Cl hydrogen bonds (purple dashed lines) and ribbons parallel to the *b* axis *via* weak π ... π stacking interactions (blue dashed lines). Hydrogen atoms not involved in hydrogen bonding are omitted.

Catalysis: To test the viability of the newly developed catalyst, we began our initial optimizations using 4-iodoanisole and 4-chlorothiophenol as model substrates and the results 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 presence of polar aprotic solvents like CH₃CN 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 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 to 60 °C and keeping all other parameters same resulted in almost similar conversion (entry 4, 92%). The use of Na₂CO₃ as base also formed the corresponding thioether in slightly lower 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

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

Table 2: Optimization of the reaction condition^a



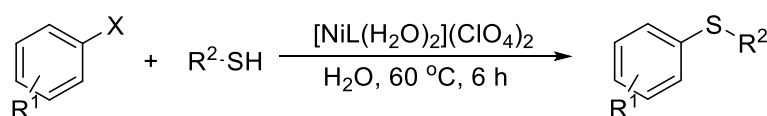
Entry	Solvent	Base	Temp (°C)	Yield (%) ^b
1	CH ₃ CN	K ₂ CO ₃	80	68
2	DMF	K ₂ CO ₃	80	73
3	H ₂ O	K ₂ CO ₃	80	93
4	H₂O	K₂CO₃	60	92
5	H ₂ O	Na ₂ CO ₃	80	84
6	H ₂ O	K ₂ CO ₃	r.t.	57
7	H ₂ O	K ₂ CO ₃	60	39

^aReaction 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 H₂O as solvent, TBAB (10 mol%) have been used.

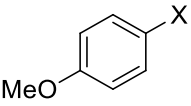
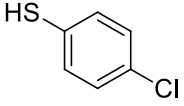
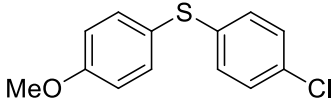
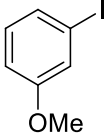
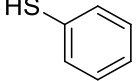
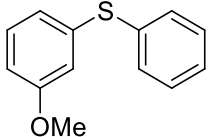
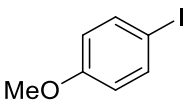
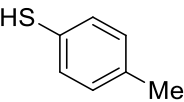
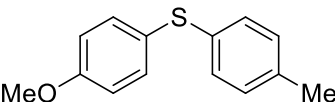
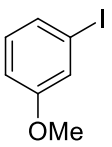
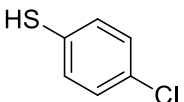
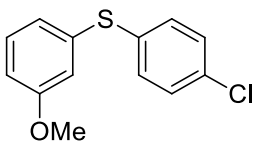
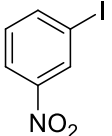
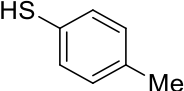
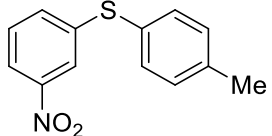
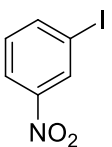
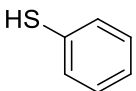
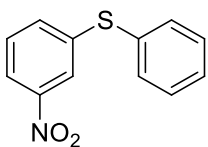
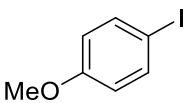
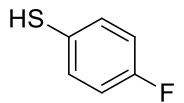
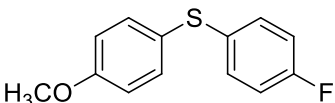
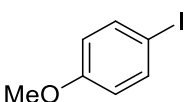
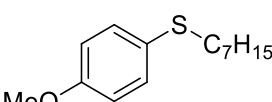
^bIsolated yield.

With the optimized reaction condition in hand we explored the scope of the reaction with different substrates (Table 3). Substitution pattern on both the reacting partners did not affect the course of the reaction and corresponding products were obtained in 92-74% yield (entries 1-8). We have tested the reactivity of aryl iodides, aryl bromide and aryl chloride under the standard reaction conditions (entry 1). Aryl iodides showed better results compared to other aryl halides in terms of product yield. Aryl chloride did not react at all during the course of the reaction. Electron donating groups (–OMe and –Me) as well as electron withdrawing groups (–NO₂ and –F) on the both the reacting partners were tolerated under the reaction conditions. Moreover, the reaction when carried out with aliphatic thiol (heptanethiol) also afforded the desired product in 79% yield (entry 8).

Table 3: $[\text{NiL}(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ catalysed C–S cross coupling reaction^a



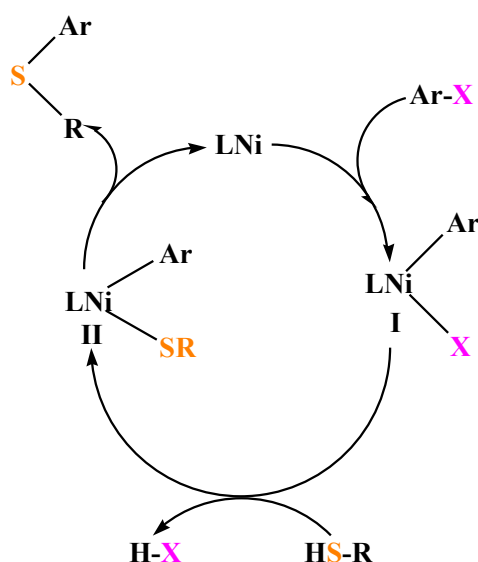
Entry	Aryl halide	Thiol	Thioether	Yield (%) ^b
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1	 X = I, Br, Cl			92 (X = I) 74 (X = Br) 0 (X = Cl)
2				84
3				87
4				81
5				88
6				86
7				90
8		$C_7H_{15}-SH$		79

^aReaction conditions: aryl iodide (1 mmol), thiol (1 mmol), catalyst (5 mg, 0.0089 mmol), K_2CO_3 (2 mmol), H_2O (2 mL) and TBAB (10 mol%) were stirred at 60 °C for 6 h.

^bIsolated 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.



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

Conclusion: In this contribution, we have shown the catalytic homogeneous C–S coupling in water by using Ni-Schiff base complex. A tetradentate N₄-Schiff base ligand based Ni-complex has been synthesized by one pot chemical reaction and characterized by SC-XRD analysis. The ready solubility of this mononuclear and cationic complex in water allows us to investigate the homogeneous C–S coupling reaction in water. Coupling reaction were successful for both alkyl and aryl thiols with their yields between 74 to 92%. To the best of our knowledge (Table S3), this is the first ever example of Ni(II)-Schiff base complex which is highly competent and productive green catalyst in catalysing C–S cross coupling from aryl iodide and alkyl or aryl thiols in aqueous medium. Our next goal is to find the condition to increase the yield (>90%) in room temperature using this catalyst in greener way.

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.

Acknowledgement: RS acknowledges and SB acknowledges. This work was supported by funding from TARE, SERB to R. S. (TAR/2018/000744) and DST Inspire Faculty Research Grant to S.B. (Faculty Registration No. : IFA18-CH304). PC thanks UGC, New Delhi, for Senior Research Fellowship under UGC-NET.

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