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Preparation and Characterization of a Mononuclear Cobalt Complex Containing a Water Soluble Triazole Ligand

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Abstract: Cobalt(II) perchlorate hexahydrate, ($Co(ClO_4)_2.6H_2O$) was reacted with a water soluble sulphonated pyridyl-triazole *N,N*-bidentate ligand (2-(1-((pyridine-2-yl)methyl)-1*H*-1,2,3-triazol-4-yl)ethyl sodium sulfate, `ligand 1.Na) in methanol to form [Co(ligand 1)$_2$(H_2O)$_2$].4H_2O as a microcrystalline solid. In this context, ligand 1.Na was first synthesized by the cycloaddition reaction of 2-(azidomethyl)pyridine and sodium 3-butyn-1-sulfate in 4:1 *tert*-BuOH/water solvents in presence of $Cu(AcO)_2 \times H_2O$ (10-15 mol %) as catalyst. The ligand 1.Na was white solid, absorbed moisture at open air, soluble in methanol and DMSO and characterized by elemental analysis, ESI-MS spectrum in the negative mode, ^{1}H NMR and ^{13}C NMR spectroscopy. In the ^{1}H NMR spectrum of ligand 1.Na in CD_3OD, a characteristic triazole strong singlet peak appeared at 7.97 ppm, a remarkable shift of δ value for CH_2 proton of 2-(azidomethyl)pyridine was observed. In the ^{13}C NMR spectrum, the triazole carbon resonates at 137.90 ppm. The prepared complex was characterized by physical data, FT-IR, ESI-MS and elemental analysis. The light pink crystals are fairly stable at open atmosphere even if they slowly loose the lattice solvent. The ESI-MS spectrum of [Co(ligand 1)$_2$(H_2O)$_2$].4H_2O indicates the species [Co(ligand 1.Na)(ligand 1)]$^+$ and [Co(ligand 1.Na)]$^+$ which corresponds to the *m/z* value at 648.6 and 402.6 respectively. Based on the observed data, octahedral geometry of the synthesized complex was suggested.

Keywords: Pyridyl Ligand, Octahedral Geometry, Cobalt(II) Perchlorate Hexahydrate, 3-butyn-1-sulfate

1. Introduction

Transition-metal-catalyzed reactions have become powerful tools in the production of pharmaceuticals and fine chemicals. Among the several synthetic methods, the copper(I)-catalyzed azide-alkyne cycloaddition reaction is one of the most emerging because of its modular properties, includes all the advantages of click reactions [1-3]. The important application of this type of chemistry is the synthesis of novel triazole ligands for coordination chemistry [4]. There are several studies which report the synthesis of 1,2,3-triazole ligands and their coordination behavior in the presence of transition metals. Urankar *et al.* synthesized a series of triazole ligands and studied their chelation to Pt(II), Pd(II), Cu(II), Ru(II), and Ag(I) [5]. Later on he reported the synthesis and anticancer activities of ruthenium-triazole complexes against human cancer cell mentioning the effects of aquation of the complexes [6]. Among transition metal complexes, palladium-triazole complexes are widely employed as catalysts in cross-coupling reaction, a very powerful and versatile tool for organic synthesis. R. J. Detz *et al.* synthesized a triazole-phosphine bidentate ligand for palladium catalyzed Suzuki-coupling reactions [7]. By taking the advantages of copper(I)-catalyzed azide-alkyne cycloaddition click reaction, our group has long been involved in the synthesis of triazole ligands and their application in homogeneous catalysis. For example, in 2011 our group reported the synthesis, characterization and catalytic activity of palladium-triazole complexes for Suzuki-Miyaura coupling. Amadio *et al.* reported the synthesized

triazole ligands for palladium catalyzed Suzuki-coupling reactions by azide-alkyne cycloadition reaction [8-9]. Afterward our group synthesized the highly active water soluble ligand for the same cross coupling reaction. The structure and properties of the ligands are not only effective in the preparation of active homogeneous catalyst but also plays an important role in catalyst separation catalysis. For example, a number of synthetic and commercially available water soluble ligands are successfully used by Paganelli *et al.* in the biphasic hydrogenation and hydrofomylation reaction [10-11].

Next we prepared a water-soluble 2-pyridyl-1,2,3-triazole ligand (Figure 1) and the *in-situ* catalyst preparation with a 1:1 mixture of ligand and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ which provides an efficient catalytic system for the Suzuki-Miyaura (S-M) coupling reactions. The S-M coupling reaction of phenylboronic acid with aryl bromide has been carried out in water phase. Water is used as an important alternative to organic solvents usually employed in coupling reaction because it is nontoxic and inexpensive. The use of water as the solvent in catalysis allows the additional advantages: Prompt catalyst separation and reuse in recycle experiments and easy recovery of the product by extraction or filtration with an appropriate organic solvent [12]. The success of this aqueous phase reaction encouraged us to prepare cobalt-triazole metal complex, their physical and spectroscopic characterizations.

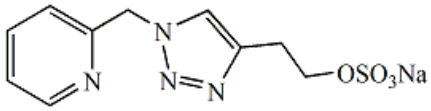
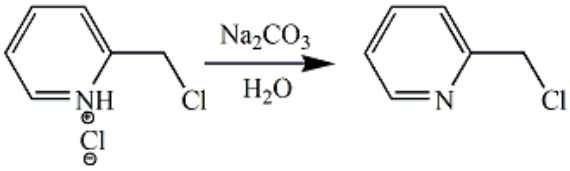


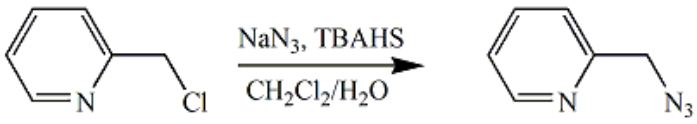
Figure 1. *Structure of water-soluble ligand.*

2. Results and Discussion

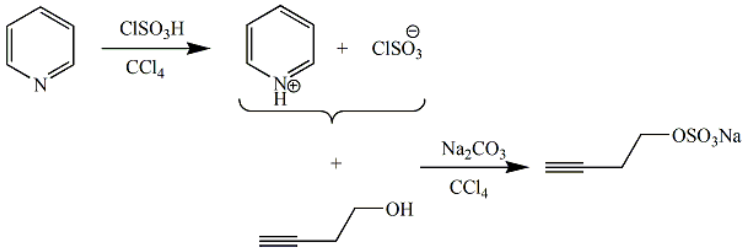
The synthesis of 2-(1-((pyridine-2-yl)methyl)-1*H*-1,2,3-triazol-4-yl)ethyl sodium sulfate (ligand 1.Na) consists of four distinct reactions (Figure 2). (a) deprotonation of 2-(chloromethyl)pyridine hydrochloride, (b) preparation of 2-(azidomethyl)pyridine, (c) preparation of sodium 3-butyn-1-sulfate, (d) synthesis of the ligand 1.Na.



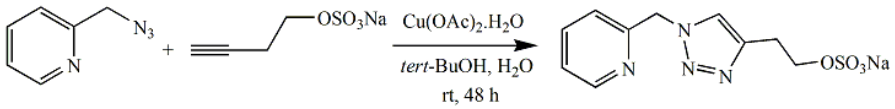
(a) Synthesis of 2-(chloromethyl)pyridine



(b) Synthesis of 2-(azidomethyl)pyridine



(c) Synthesis of sodium 3-butyne-1-sulfate



Ligand **1.Na**

(d) Synthesis of ligand **1.Na**

Figure 2. *Synthesis of 2-(1-((pyridine-2-yl)methyl)-1H-1,2,3-triazol-4-yl)ethyl sodium sulfate (ligand 1.Na).*

The deprotonation of 2-(chloromethyl)pyridine hydrochloride in the presence of Na_2CO_3 gives 2-(chloromethyl)pyridine. 2-(azidomethyl)pyridine was prepared by the reaction of 2-(chloromethyl)pyridine with NaN_3 in a biphasic system (dichloromethane/water) in the presence of a phase transfer agent tetrabutylammonium hydrogensulfate (TBAHS) [13]. Sodium azide (NaN_3) is dissolved in water while 2-(chloromethyl)pyridine in dichloromethane. TBAHS allows NaN_3 to transfer from aqueous phase into the organic phase containing 2-(chloromethyl) pyridine where the substitution of chloride (–Cl) by N_3 occurs. The preparation requires a large excess (slight excess of 2 equivalents) of azide and 48 hours to achieve complete substitution with azide. The yield is 89%. ^{1}H NMR spectrum is consistent with the structure of the prepared 2-(azidomethyl)pyridine.

The preparation of sodium 3-butyn-1-sulfate is carried out by the treatment of 3-butyn-1-ol in the presence of chlorosufonic acid ($ClSO_3H$) and pyridine [14]. The addition of chlorosufonic acid into carbontetrachloride and pyridine at 0º C produces a mixture of pyridinium and chlorosulfonate ion (Figure 2c). The observation is the formation of white smoke. Dropwise addition of 3-butyn-1-ol into the reaction vessel and overnight stirring at room temperature produces pyridine hydrocholoride and 3-butyn-1-hydrogensulfate. 3-butyn-1-hydrogensulfate is extracted with water. The combined aqueous phase is evaporated to almost half of the volume, the basification by saturated solution of Na_2CO_3 (until no CO_2 evolution, pH ≈ 9-10) gave the desired product, sodium 3-butyn-1-sulfate which is recrystallized from hot EtOH (84%). The white crystal is characterized by ^{1}H NMR and ^{13}C NMR spectra.

Finally, water-soluble 2-(1-((pyridine-2-yl)methyl)-1H-1,2,3-triazol-4-yl)ethyl sodium sulfate (ligand 1.Na) is obtained by [3+2] cycloaddition reaction (a class of click reaction) between the previously prepared 2-(azidomethyl) pyridine and sodium 3-butyn-1-sulfate in *tert*-BuOH/water (4/1) solvents. $Cu(AcO)_2{\times}H_2O$ (10-15 mol %) is used as catalyst. The azide acts as a diene while the terminal alkyne as a dienophile. In this synthetic protocol, a Glaser-type reaction produces copper(I) catalytic species which permit azide-alkyne cycloaddition reaction to give 1,4-disubstituted 1,2,3-triazole product. The *tert*-BuOH itself acts as a reducing agent to generate active copper(I) species [15]. After 48 hours of stirring at room temperature, the green solid obtained was purified by column chromatography (silica gel, dichloromethane / methanol = 8/2 or tetrahedronfurane/methanol = 8/2) to give a pure white solid (ligand 1.Na) in 79% yield. The bidentate nitrogen ligand 1.Na is soluble in water, methanol, and DMSO. The composition of ligand 1.Na was confirmed by elemental analysis, NMR spectra, and ESI-MS spectrum in the negative mode. In the ^{1}H NMR spectrum (Figure 3) of ligand 1.Na in CD_3OD, the evidence of the formation of triazole ring comes from the presence of a characteristic triazole-H(7) strong singlet at 7.97 ppm. A remarkable shift of δ value ($\Delta\delta$ = 1.21) for CH_2 (6) proton of 2-(azidomethyl) pyridine has been noticed upon the formation of ligand 1.Na.

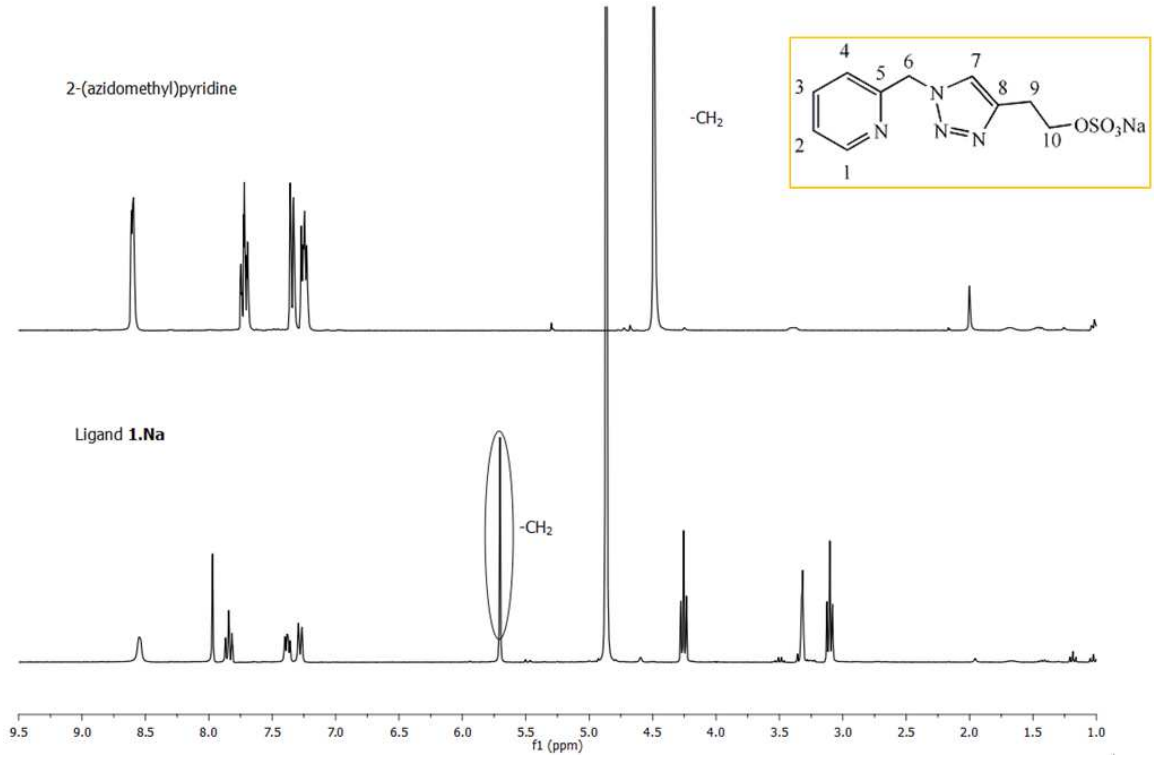


Figure 3. *Comparison between the ^{1}H NMR spectra of 2-(azidomethyl)pyridine and ligand 1.Na.*

In the ^{13}C NMR spectrum, the triazole carbon (C7) which resonates at 137.90 ppm indicates the formation of ligand 1.Na. These observations are consistent with the ^{13}C NMR spectrum of triazole ligand reported by Urankar *et al* [5].

Anal. cal. for $C_{10}H_{11}N_4O_4SNa$ (306.27): C, 39.22; H, 3.62. Found: C, 39.3; H, 3.5. In the ESI-MS spectrum, 283.0

($C_{10}H_{11}N_4O_4S^-$, 100%), 589 (ligand 1+$C_{10}H_{11}N_4O_4S^-$, 4%) are in good agreement with the formation of ligand 1.Na.

The prepartion of cobalt(II)-ligand 1 complex was carried out by simple mixing of the ligand 1.Na with $Co(OAc)_2.4H_2O$ in methanol solution [Figure 4] [16].

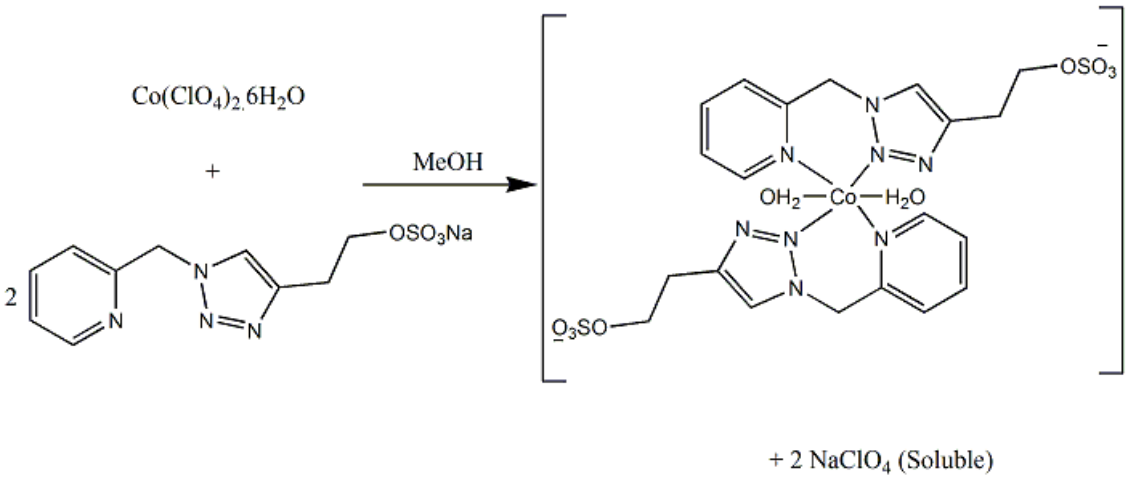


Figure 4. *Preparation of [Co(ligand 1)$_2$(H$_2$O)$_2$] complex.*

Before starting the synthetic reaction, the species present in the reaction solution were characterized by ESI-MS. We used three metal sources such as $Co(ClO_4)_2.6H_2O$, $CoCl_2.6H_2O$, and $Co(OAc)_2.4H_2O$ and obtained the same complex species identified as $[Co(\text{ligand 1.Na})(\text{ligand 1})]^+$ which corresponds to the *m/z* value at 648.6, $[Co(\text{ligand 1.Na})]^+$ at *m/z* 402.6 (Figure 5). Considering the solubility of the byproduct ($NaClO_4$/NaCl/$Na(OAc)_2$ in methanol, we decided to use $Co(ClO_4)_2.6H_2O$ as a metal source because $NaClO_4$ has higher solubility than NaCl or $Na(OAc)_2$.

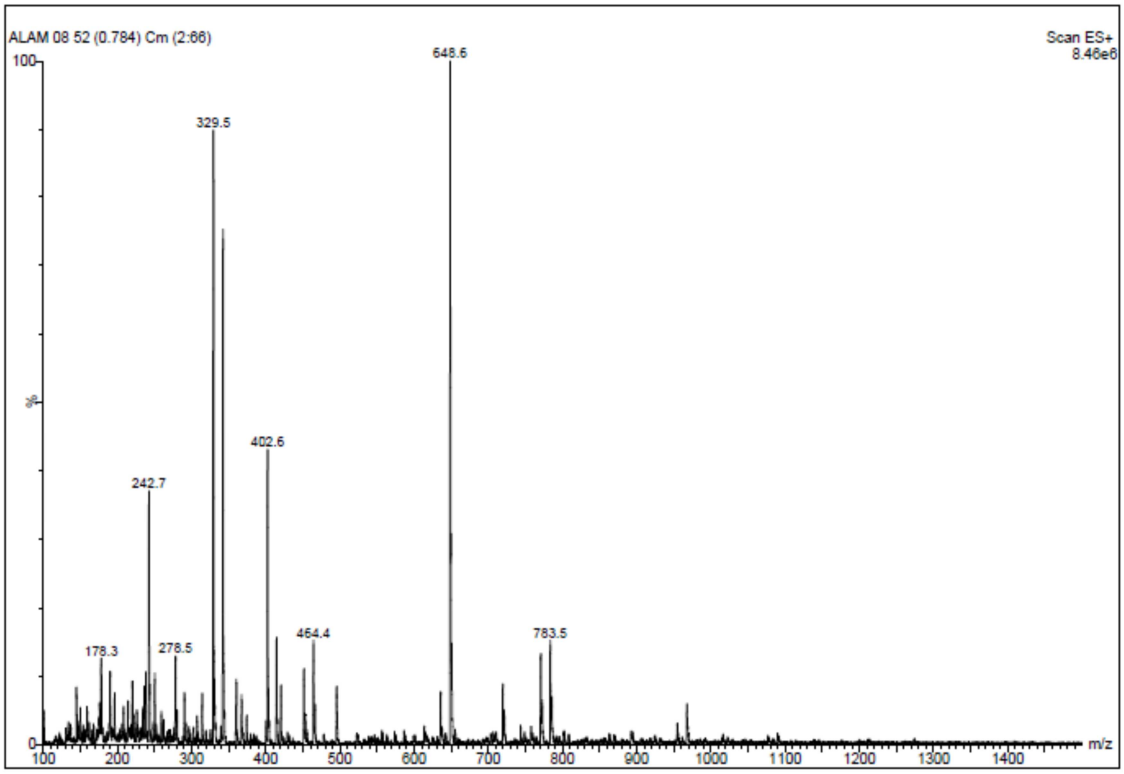


Figure 5. *ESI-MS spectrum of $[Co(\text{ligand 1.Na})(\text{ligand 1})]^+$ measured in MeOH.*

The complex was isolated as pure block like crystals $[Co(\text{ligand 1})_2(H_2O)_2].4H_2O$ which are soluble in dimethylformamide (DMF), light pink in color, fairly stable at open atmosphere and losses the lattice solvent slowly. The growth of crystals is largely depend on the concentration of the reaction mixture. From FT-IR spectrum, the absence of perchlorate as a counter ion indicates that the complex is neutral (Figure 6).

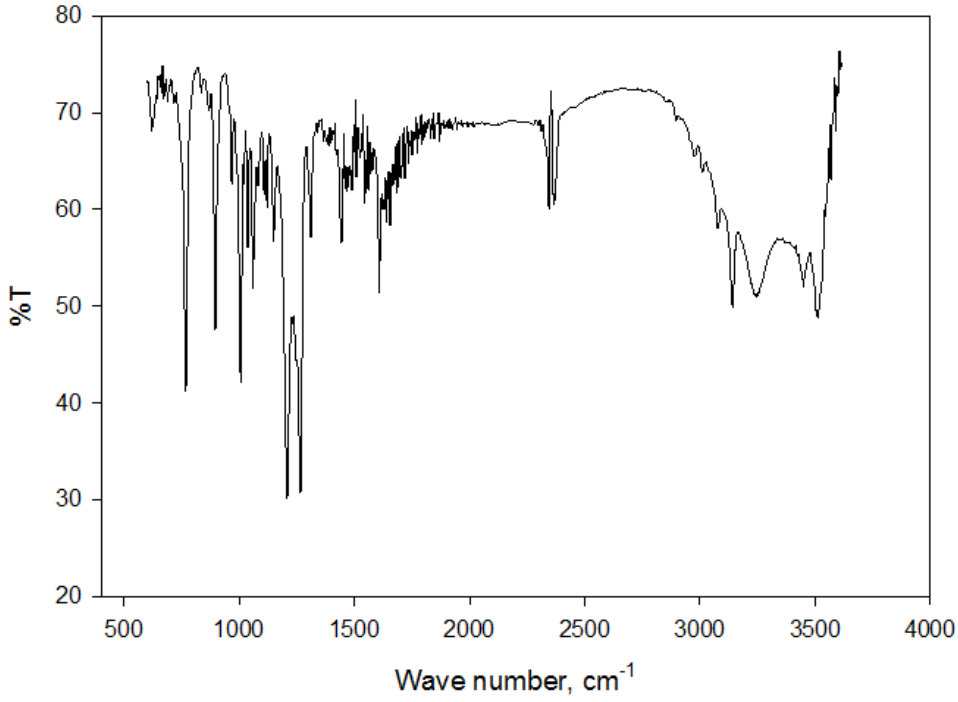


Figure 6. *IR spectrum of [Co(ligand 1)$_2$(H_2O)].4H_2O.*

The coordination number of the octahedral cobalt complex was satisfied by two water molecules. The CHN elemental analysis is in good agreement with four water molecules as lattice solvents.

3. Experimental

The reactions were carried out in an inert atmosphere. The reagents and solvents with high degree of purity were purchased directly from the market and used without further purification. In case where it is necessary to handle the reaction in absence of oxygen and water, solvents and reagents were distilled and dried according to the procedure reported in the literature [17]. ^{1}H NMR and ^{13}C NMR spectra were measured on Bruker Avance-300 spectrometer. Infrared spectra were recorded on a Perkin Elmer Spectrum One FT-IR in KBr pellet in the range of 4000-400 cm^{-1}. The conversion 2-(chloromethyl)pyridine into 2-(azidomethyl)pyridine was checked by gas chromatographic analysis on a Agilent Technologies 6850 gas chromatograph fitted with an HP-5 column (30m × 0.32 µm × 0.25 µm). The positive ion ESI-MS spectra of the complex were recorded with a Quattro micro API spectrometer made by Waters.

3.1. Synthesis of Ligand

3.1.1. Preparation of 2-(chloromethyl) Pyridine

In a 50.0 mL round bottom flask, 2-(chloromethyl)pyridine hydrochloride (1.30 g, 8.1 mmol) was dissolved in 8.0 mL of H_2O. A saturated solution of Na_2CO_3 was added until pH 10-11, under gentle stirring. The reaction mixture was extracted with CH_2Cl_2 (3 x 8 mL). The combined organic layers were dried with $MgSO_4$, filtered off, and the solvent evaporation under vacuum to give 0.80 g (77%) of a light yellow oil which was characterized by gaschromatography (t_r = 9.34 mins.) and ^{1}H NMR spectrum.

^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 8.52 (br d, 1H(1)), 7.64 (t, 1H(3), *J* = 7.0 Hz), 7.5-7.35 (m, 1H(4)), 7.25-7.1 (m, 1H(2)), 4.44 (br s, 2H(6)) ppm.

3.1.2. Synthesis of Ligand 1.Na

Ligand 1.Na = 2-(1-((pyridine-2-yl)methyl)-1*H*-1,2,3-triazol-4-yl)ethyl sodium sulfate

The synthesis of ligand 1.Na was carried out according to the procedure reported by Brotherton, W. S. *et al*. [15]. In a 50.0 mL two-neck round bottom flask, a *tert*-butanol solution (6.0 mL) of 2-(azidomethyl)pyridine (0.48 g, 3.57 mmol) was added to a *tert*-butanol solution (17.0 mL) of sodium 3-butyn-1-sulfate [13-14] (0.61 g, 3.57 mmol) under inert atmosphere. Additional 2.0 mL of water was added to dissolve all the reactants. The slow addition of 1.0 mL aqueous solution of cupric acetate monohydrate (0.036 g, 0.18 mmol) to the reaction vessel result in an immediate color change from light yellow to green. After 48 hours of stirring, the solution was evaporated to dryness under vacuum. The green solid obtained was purified by column chromatography (silica gel, dichloromethane/methanol = 8/2) to give the title compound as a white solid in 79% (0.86 g) yield which was characterized by ^{1}H NMR and ^{13}C NMR spectroscopy. ^{1}H NMR (300 MHz, CD_3OD, 298 K): δ 8.55 (br s, 1H(1)), 7.97 (s, 1H(7)), 7.84 (t, 1H(3), *J* = 7.7 Hz), 7.38 (br, m, 1H(2)), 7.28 (d, 1H(4), *J* = 7.9 Hz), 5.70 (s, 2H(6)), 4.26 (m, 2H(10)), 3.10 (t, 2H(9), *J* = 6.4 Hz) ppm. ^{13}C NMR (300 MHz, CD_3OD, 298 K): δ 154.62 (C1), 149.14 (C8), 144.55 (C5), 137.90 (C7), 123.73 (C2/4), 122.62 (C3), 66.39 (C10), 54.67 (C6), 25.58 (C9) ppm.

3.2. Preparation of [Co(ligand 1)$_2$(H$_2$O)$_2$] Complex

In a 25 mL one-neck round bottom flask, into a 3 mL of methanol solution of 133 mg (0.43 mmol) ligand 1.Na, 2 mL of methanol solution containing 79.4 mg (0.217 mmol) of Cobalt(II) perchlorate hexahydrate ($Co(ClO_4)_2.6H_2O$) was slowly added without stirring. The reaction mixture kept for several days to form a very good crystals of title compound. The complex was characterized by IR and elemental analysis. IR (KBr): ν 3511, 3449, 3247, 3141, 1608, 1444, 1265, 1208, 1059, 1006, 895, 768, 588 cm^{-1}. Anal. Calcd for $C_{20}H_{34}CoN_8O_{14}S_2$: C, 32.74; H, 4.67; N, 15.27. Found: C, 32.86, H, 4.26; N, 15.18.

4. Conclusions

In this paper, the water soluble sodium 2-(1-((pyridin-2-yl)methyl)-1*H*-1,2,3-triazol-4-yl)ethyl sulfate ligand (ligand 1.Na) was synthesized by the click reaction between 2-(azidomethyl)pyridine and but-3-ynyl sodium sulphate. The octahedral cobalt complex containing ligand 1.Na was prepared and characterized by FT-IR, ESI-MS and elemental analysis. Both elemental analysis and the ESI-MS data of $[Co(ligand\ 1.Na)(ligand\ 1)]^+$ corresponds to the *m/z* value at 648.6 confirms the formation of the complex.

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