



## Three New Azido/thiocyanato Bridged Complexes of Co(II)/Ni(II) Derived from Potential Schiff Base Blocker Ligand(H<sub>2</sub>L) of 1-(5-chloro-2-hydroxy-phenyl)-Ethanone and Propane-1,3-diamine---synthesis, Characterization and Magneto-structural Relationship

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### ABSTRACT

The 2:1 condensation of 1-(5-Chloro-2-hydroxy-phenyl)-ethanone and propane-1,3-diamine gives the tetradentate azo-linked Schiff base blocker ligand (H<sub>2</sub>L). The reference Schiff base was allowed to react with methanolic solution of Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O and Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O separately in the presence of sodium azide/ammonium thiocyanate yielding formulated complexes (1A), (1B) [Co<sub>2</sub>(L)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>, [Co<sub>2</sub>(L)<sub>2</sub>(SCN)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> and (2) [Ni<sub>2</sub>(H<sub>2</sub>L)<sub>2</sub>(SCN)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>], respectively. Co(II)/Ni(II) azide/thiocyanate series complexes were systematically characterized by elemental analysis (C, H and N), molar conductivity study, mass (m/e) and infrared and ultraviolet-visible (UV-VIS) spectroscopic study. Molar conductivity study unambiguously confirmed that Co(II) series complexes are completely electrolyte in nature, while Ni(II) complex is nonelectrolyte. The potential Schiff base blocker ligand (H<sub>2</sub>L) was further confirmed by <sup>1</sup>H Nuclear magnetic resonance (NMR) study. Additional magnetic moment data were provided to establish the expected probable geometry of Co(II), Ni(II) azido/thiocyanato bridging complexes. All the experimental results suggest that Co(II) bonded to the respective Schiff base blocker ligand (H<sub>2</sub>L) through both imino nitrogen and phenolate oxygen along with incorporated azide or thiocyanate bridging but distinctly imino nitrogen only takes part for Ni(II) complex formation. The electronic spectra and additional magnetic moment data further confirmed that the environment of Co(II) and Ni(II) metal ions in both complexes is octahedral or distorted octahedral. Co(II) and Ni(II) series complexes showed magnetic moment value within the range 4.82-5.08 BM and 2.79 BM, respectively. Literature survey magnetic moment values of some selected Co(II)/Ni(II) octahedral complexes are good agreement with our synthesized complexes confirming octahedral geometrical environment around the respective metal ions.

**Key words:** Schiff base (H<sub>2</sub>L), SCN<sup>-1</sup>, N<sub>3</sub><sup>-1</sup> bridging, Ultraviolet-visible, <sup>1</sup>H nuclear magnetic resonance, Spectra and magnetic moment.

### 1. INTRODUCTION

The name Prof. Sir Hugo Schiff is the pioneer behind the discovery of novel Schiff base during the 19<sup>th</sup> century [1]. After his novel discovery, many inorganic inquisitive chemists got interested to the same field but significant development was started from the 1960's [2]. Several naming of Schiff bases will be followed after the discovery of Prof. Sir Hugo Schiff such as anils, imine and azomethine [3]. Most commonly and popularly Schiff was prepared by the azomethine linkage formation by the reaction between an aldehyde/ketone with a particular primary amine where C=N double bond formation is the end path of synthesis (Scheme 1).

The above synthetic path implies that all novel Schiff base formations proceed through the initial beautiful carbinolamine intermediate formation followed by dehydration. The same reaction takes place in the presence of acid, alkali, or mild heating. Inorganic chemists got interested to still prepare different kinds of Schiff bases may which may be bi, tri or tetradentate and nowadays active and well-designed Schiff base ligands are considered as "privileged ligands" [4] because of their preparational accessibilities, structural varieties, varied denticities, and mobility of donor center [5-15]. Today, the endearing popularity of Schiff base is due to its beauteousness and bemusing versatility of a wide range of complex formation with different types of metal ions. Tetradentate potential

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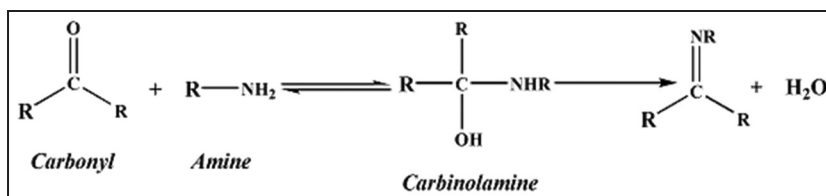
Schiff base having  $N_2O_2$  donor set are always well coordinated with metal ions, and this line of research has much attracted the puzzling interest of many inorganic chemists. The Schiff base complexes have wide applications in the field of dioxygen intake [16], oxidative catalysis [17] including bioinorganic chemistry, material science and magnetism, separation and encapsulation, hydrometallurgy, metal clusters, transport and activation of small molecules [18-25]. Recently, Co(II) Schiff base complexes with versatile catalytic activities and biological significance have been reported [26]. Transition metal polynuclear complexes with pseudohalide bridges ( $OCN^{-1}$ ,  $SCN^{-1}$ ,  $N_3^{-1}$ , dicyanamide) are a well interesting area of research field to the current researcher, from the structural point of view because of different modes of coordination to the metal ions (Scheme 2). In recent years, a great attention has also been devoted to the magneto-structural studies of such kind of complexes since the pseudohalogen bridges act as a superexchange pathway and the same line becomes prominent when azide/thiocyanate pseudohalides act as distinct bridging modes [27-34]. Plenty of research

work in the identical field has already completed by several inorganic chemists, hence in the current research scenario, we communicate a novel synthesis of Schiff base blocker ligand ( $H_2L$ ), two Co(II) azide/thiocyanate and one Ni(II) thiocyanate bridged complexes synthetic details. Further the novel Schiff base ( $H_2L$ ) and respective three metal complexes were characterized by various spectroscopic techniques (infrared [IR], mass, ultraviolet-visible [UV-VIS],  $^1H$  Nuclear magnetic resonance [ $^1H$  NMR]). Magnetic moment studies were also conducted to the respective three complexes.

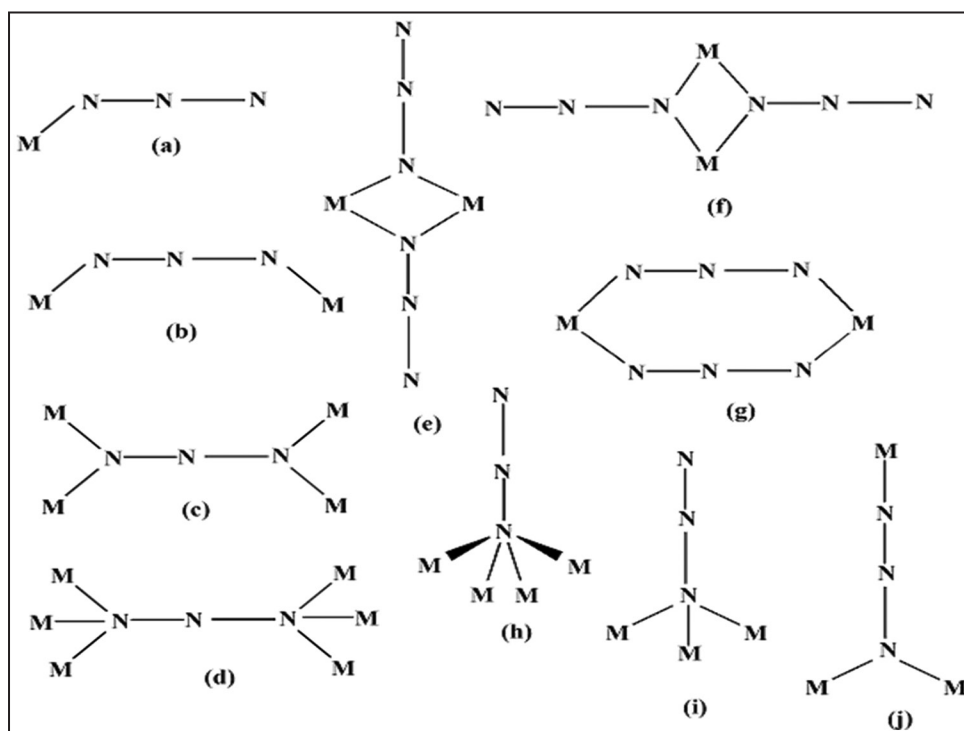
2. EXPERIMENTAL

2.1. Materials

All chemicals were of reagent grade, purchased from commercial sources, and used as received without further purification. 5-chloro-2-hydroxyacetophenone was purchased from Sigma-Aldrich Company, USA. 1,3-diaminopropane,  $Co(NO_3)_2 \cdot 6H_2O$  and  $Ni(NO_3)_2 \cdot 6H_2O$  both are purchased from Sigma-Aldrich Company, USA. Sodium azide and ammonium thiocyanate were purchased from SDFCL, India. The



Scheme 1: Common synthetic path of all Schiff base.



Scheme 2: Different bridging modes of  $SCN^{-1}$  and  $N_3^{-1}$ .

total synthetic reactions and work up were done in open atmospheric condition.

Caution! The azide complexes are highly explosive particularly in the presence of our synthesized Schiff base ( $H_2L$ ) ligand. Even though no such accident occurred during the course of my research work, since only a small amount of materials should be prepared, and must be handled with utmost care.

## 2.2. Physical Measurement

Elemental analyses (carbon, hydrogen, and nitrogen) of the novel Schiff base ( $H_2L$ ) and metal Co(II), Ni(II) complexes were determined with a Perkin–Elmer CHN analyzer 2400. Mass spectra were done with a JEOLJMS-AX 500 mass spectrometer. IR spectra (KBr pellet,  $400\text{--}4000\text{ cm}^{-1}$ ) were recorded on a Perkin–Elmer model 883 infrared spectrophotometer. The electronic spectra of three complexes in methanol solvent were recorded on a Hitachi model U-3501 spectrophotometer. The  $^1\text{H}$  NMR spectra of novel Schiff base ( $H_2L$ ) were recorded on Bruker 300MHz FT-NMR spectrophotometer using trimethylsilane as an internal standard in  $\text{CDCl}_3$  solvent. The magnetic susceptibility values of Co(II) and Ni(II) complexes were determined by Gouy method. Correction for diamagnetism of the constituent atoms was calculated using common Pascal's constant. The effective magnetic moment's values ( $\mu_{\text{eff}}$ ) of Co(II) and Ni(II) complexes were calculated using the given equation:  $\mu_{\text{eff}} = 2.83 (\chi_{\text{M}}T)^{-1}$

## 3. SYNTHESIS

### 3.1 Synthesis of Schiff Base ( $H_2L$ )

To a methanolic solution (30 mL) of 5-chloro-2-hydroxy acetophenone (0.171 g, 1 mmol), propylene diamine (0.0371 g, 0.5 mmol) in methanol (5 ml) was added with constant stirring. At this moment color of the solution turned deep yellow and it was refluxed continuously for 3 h. A yellow solid was immediately separated and collected by filtration after cooling the solution up to room temperature. Then, the yellow solid was dried and preserved in a desiccator (Scheme 3).

For novel Schiff base ( $H_2L$ ) (Yield: 75%), M.Wt. (379.28), exact mass: 378.09, m/e: 379.00, analytical calculated for  $\text{C}_{19}\text{H}_{20}\text{N}_2\text{O}_2\text{Cl}_2$ : C:

60.17; H: 5.32; Cl: 18.69; N: 7.39; O: 8.44 Found; C: 60.1; H: 5.31; Cl: 18.62; N: 7.35; O: 8.42 IR (KBr:  $\text{vcm}^{-1}$ ): 1611( $\nu\text{C}=\text{Ns}$ ), 1491.03(s), 1290.02(m), 1228.78(m); H NMR (in DMSO), UV-VIS spectrum,  $\lambda_{\text{max}}(\text{CH}_3\text{OH})$ : 272.89 nm, 334.10 nm and 400.08 nm.

### 3.2. Synthesis of Complexes (1A), (1B) and (2)

#### 3.2.1. For complex (1A)

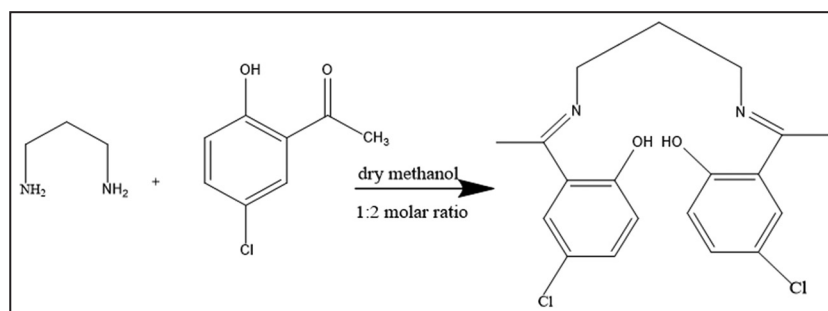
To a methanolic (30 mL) solution of the ligand (0.379 g, 1 mmol), Co ( $\text{NO}_3$ ),  $6\text{H}_2\text{O}$  (0.291 g, 1 mmol) taken in the same solvent was added dropwise with constant stirring. After 15 min  $\text{NaN}_3$  (0.065 g, 1 mmol) dissolved in 10 drops of water-methanol (1:1) mixture was added and stirred for 3.5 h. A brown colored complex was immediately precipitated out and this was filtered under suction, washed with methanol, dried and preserved in a desiccator properly.

For Complex (1A) (Yield: 69%), M.Wt.(1080.45), exact mass: 1078.01, m/e: 1080, analytical calculated for Complex (1A)  $[\text{Co}_2(\text{L})_2(\text{N}_3)_2](\text{NO}_3)_2$ ; C: 42.24; H: 3.36; Cl: 13.13; N: 15.56; O: 14.81; Co: 10.91. Found; C: 42.22; H: 13.30; Cl: 13.10; N: 15.54; O: 14.80; Co: 10.90 IR (KBr,  $\text{v}_{\text{max}}/\text{cm}^{-1}$ ):  $\nu(\text{N-N}) = 2029.36$ ;  $\nu(\text{C}=\text{N})$  1610.00, 1384, UV-VIS spectrum,  $\lambda_{\text{max}}(\text{CH}_3\text{OH})$ : 272.113 nm and 279.77 nm.

#### 3.2.2. For complex (1B)

This compound was prepared in a similar procedure to that mentioned above for complex (1A) using  $\text{Co}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.291 g, 1 mmol) and  $\text{NH}_4\text{SCN}$  (0.076 g, 1 mmol) in methanol was added after 10 min and stirred for 2.5 h. A black colored complex was immediately precipitated out and this was filtered under suction, washed with methanol, dried and preserved in a desiccator properly.

For Complex (1B) (Yield: 70%), M.Wt.(1112.57), Exact mass: 1109.94, m/e: 1111.0, analytical calculated for Complex (1B)  $[\text{Co}_2(\text{L})_2(\text{SCN})_2](\text{NO}_3)_2$ ; C: 43.18; H: 3.26; Cl: 12.75; N: 10.07; Co: 10.59. Found; C: 43.10; H: 3.25; Cl: 12.74; N: 10.00; Co: 10.60 IR (KBr,  $\text{v}_{\text{max}}/\text{cm}^{-1}$ ):  $\nu(\text{NCS}) = 2067.32$ ;  $\nu(\text{C}=\text{N})$  1610.00, UV-VIS spectrum,  $\lambda_{\text{max}}(\text{CH}_3\text{OH})$ : 376.343 nm.



Scheme 3: Synthesis of Schiff base ( $H_2L$ ).

### 3.2.3. For Complex (2)

To a methanolic (30 mL) solution of the ligand (0.379 g, 1 mmol), Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.290 g, 1 mmol) taken in the same solvent was added dropwise with constant stirring. After 15 min NH<sub>4</sub>SCN (0.076 g, 1 mmol) dissolved in methanol was added and stirred for 3.5 h. A deep green colored complex was immediately precipitated out, and this was filtered under suction, washed with methanol, dried and preserved in a desiccator properly.

For Complex (2) (Yield: 70%), M. Wt. (1116.12), Exact mass: 1111.98, m/e: 1113.9, analytical calculated for complex (2)[Ni<sub>2</sub>(H<sub>2</sub>L)<sub>2</sub>(SCN)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>]: C: 43.04; H: 3.61; Cl: 12.71; N: 10.04; O: 14.33; Ni: 10.52 Found; C: 43.00; H: 3.60; Cl: 12.70; N: 10.00; Ni: 10.50 IR(KBr, ν<sub>max</sub>/cm<sup>-1</sup>): ν(NCS) = 2347.63; ν(C=N) 1602.49, UV-VIS spectrum, λ<sub>max</sub>(CH<sub>3</sub>OH): 340.07 nm and 396.64 nm.

## 4. RESULTS AND DISCUSSION

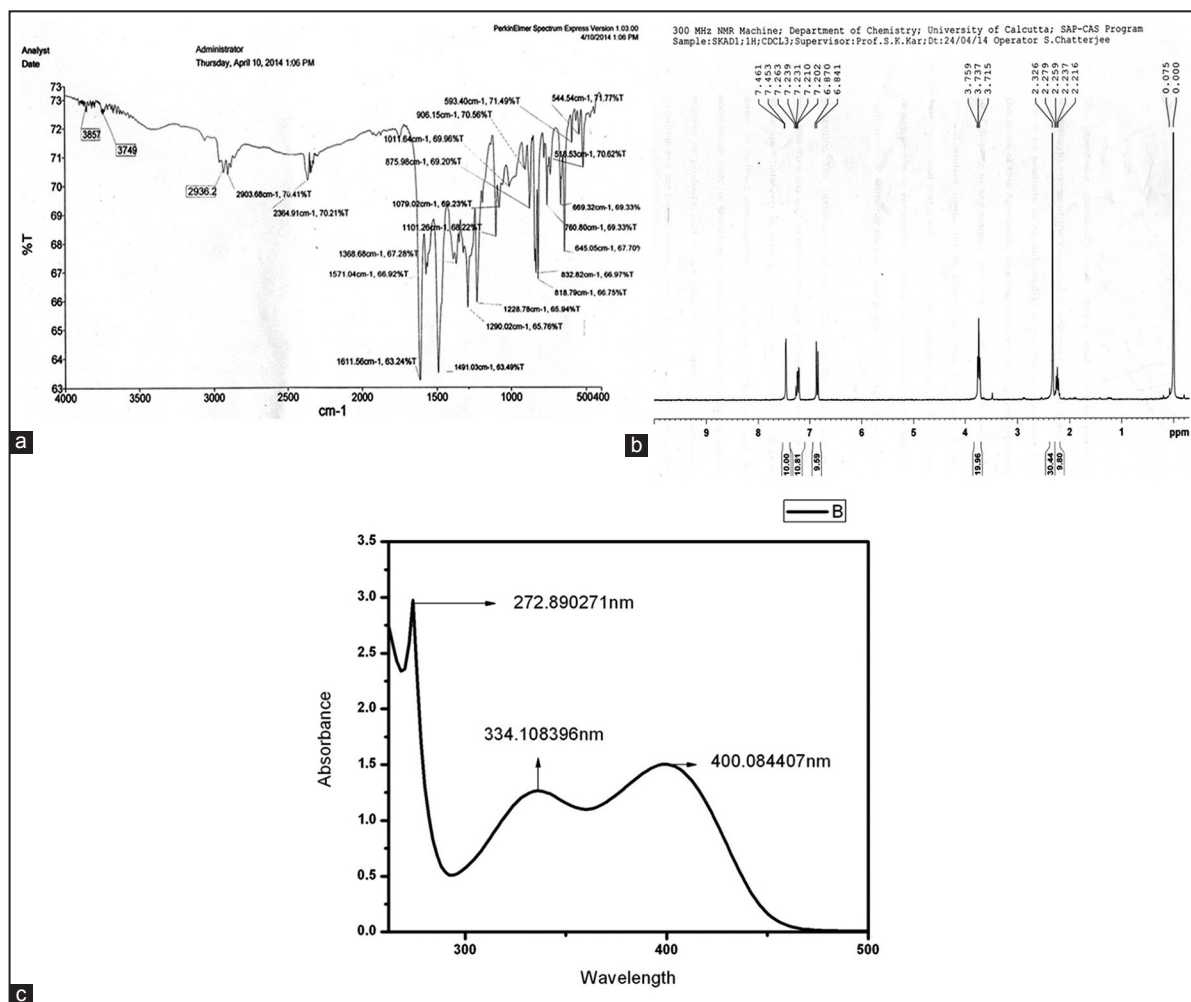
### 4.1. Synthesis

The azo-linked potential Schiff base blocker ligand (H<sub>2</sub>L) and three new Co(II)/Ni(II) azido/thiocyanato

bridged complexes have been synthesized very carefully in our laboratory. They are lucidly characterized by different physicochemical techniques such as elemental analyses, IR, UV-VIS, mass (m/e), and <sup>1</sup>H NMR spectroscopic studies. Additional magnetic moment data will be provided to establish expected probable geometry of the synthesized three respective series complexes.

### 4.2. Characterization of Schiff Base Blocker Ligand(H<sub>2</sub>L)

The presence of IR band near at 1611 cm<sup>-1</sup> provides the evidence for the formation of azomethine group (C=N) in the novel Schiff base. Again the absence of C=O group, IR band around 1700-1800 cm<sup>-1</sup> confirmed the Schiff base formation according to (Scheme 1). <sup>1</sup>H NMR spectroscopic data were further confirmed the formation of novel Schiff base. The Schiff base exhibits distinct <sup>1</sup>H NMR peaks with respect to aliphatic and aromatic protons. The UV-VIS spectrum in methanol of novel symmetrical Schiff base (H<sub>2</sub>L) reflects three main peaks at 272.89 nm, 334.10 nm, and 400.08 nm. The first two UV-VIS spectrum are assigned due to benzene π→π\* and



**Figure 1:** (a-c) infrared, <sup>1</sup>H nuclear magnetic resonance and ultraviolet-visible spectra presentation of Schiff base (H<sub>2</sub>L).



imino  $\pi \rightarrow \pi^*$  transitions. Additional peak 400.08 nm is due to  $n \rightarrow \pi^*$  transition (Figure 1).

#### 4.4. Characterization of Azido/Thiocyanato Bridged Complexes (1A, 1B and 2)

Co(II) complexes show IR frequency band near at  $2029.36 \text{ cm}^{-1}$  and  $2367.32 \text{ cm}^{-1}$  positively confirmed the presence of versatile azido and thiocyanato bridging. In both Co(II) complexes, the IR peak being bifurcated. This further supports azido or thiocyanato ligand function as a bridging moiety. The lowering frequency of C=N group indicates the coordination of C=N nitrogen to the Co(II) metal center. The literature [35]  $\nu(\text{C}=\text{N})$  frequencies of  $\text{SCN}^{-1}$  values could be used for differentiation purpose between S-bonded ( $2110\text{-}2140 \text{ cm}^{-1}$ ) and N-bonded ( $<2110 \text{ cm}^{-1}$ ) complexes. Hence, here  $\text{NCS}^{-1}$  can be coordinated with Co(II) metal as bridging fashion through S Atom. Since Co(II)  $d^7$  configuration, paramagnetic nature, both azido/thiocyanato bridged complexes exhibit broad d-d transition band. In both complexes, shift of ligand  $\pi\text{-}\pi^*$  and  $n\text{-}\pi^*$  transition takes place due to complexation with Co(II) metal center. The broadband peak near at 376.343 nm in  $\text{SCN}^{-1}$  bridged complex is due to  $\pi\text{-}\pi^*$  transition.

The Co(II) azide bridging complex exhibit a sharp peak at 272.113 nm again confirmed  $\pi\text{-}\pi^*$  transition. A shoulder peak near at 279.77 nm is due to Co(II)  $d^7$  (HS) configuration d-d transition (Figures 2 and 3). For Ni(II) thiocyanate bridged complex peak at 340.07 nm is due to  $\pi\text{-}\pi^*$  transition. A very broad band near 396.64 nm is due to Ni(II)  $d^8$  configuration d-d transition (Figure 4).

#### 4.5. Magnetic Moment Study

The Co(II) metal ion ( $3d^7$ ) (HS) state has four unpaired electron in the 3d shell, therefore all Co(II) complexes were considered to have magnetic moments close to the spin-only value but due to strong spin orbit coupling phenomenon, higher values are always expected. For octahedral Co(II) complexes, the ground state is  ${}^4T_{1g}$  and a large orbital contribution to the singlet state lowers the magnetic moment values for the values of Co(II) complexes which lie in the range 4.70-5.20 BM. The magnetic moment values calculated for complex (1A) are in the range of 4.80-4.88 BM. Hence, the environment around the cobalt metal in complex (1A) is octahedral. For complex (1B) the calculated magnetic moment values was found to be 5.08 BM.

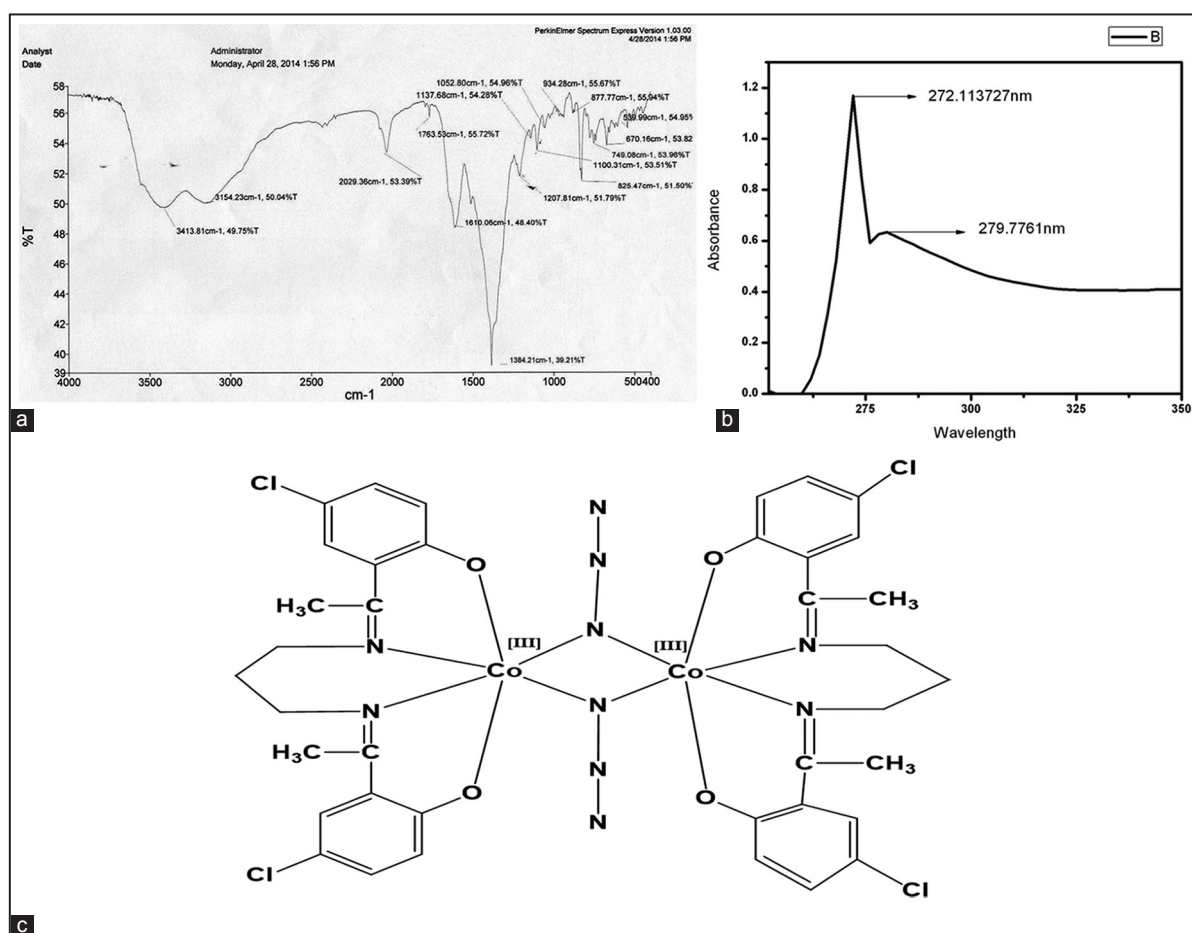
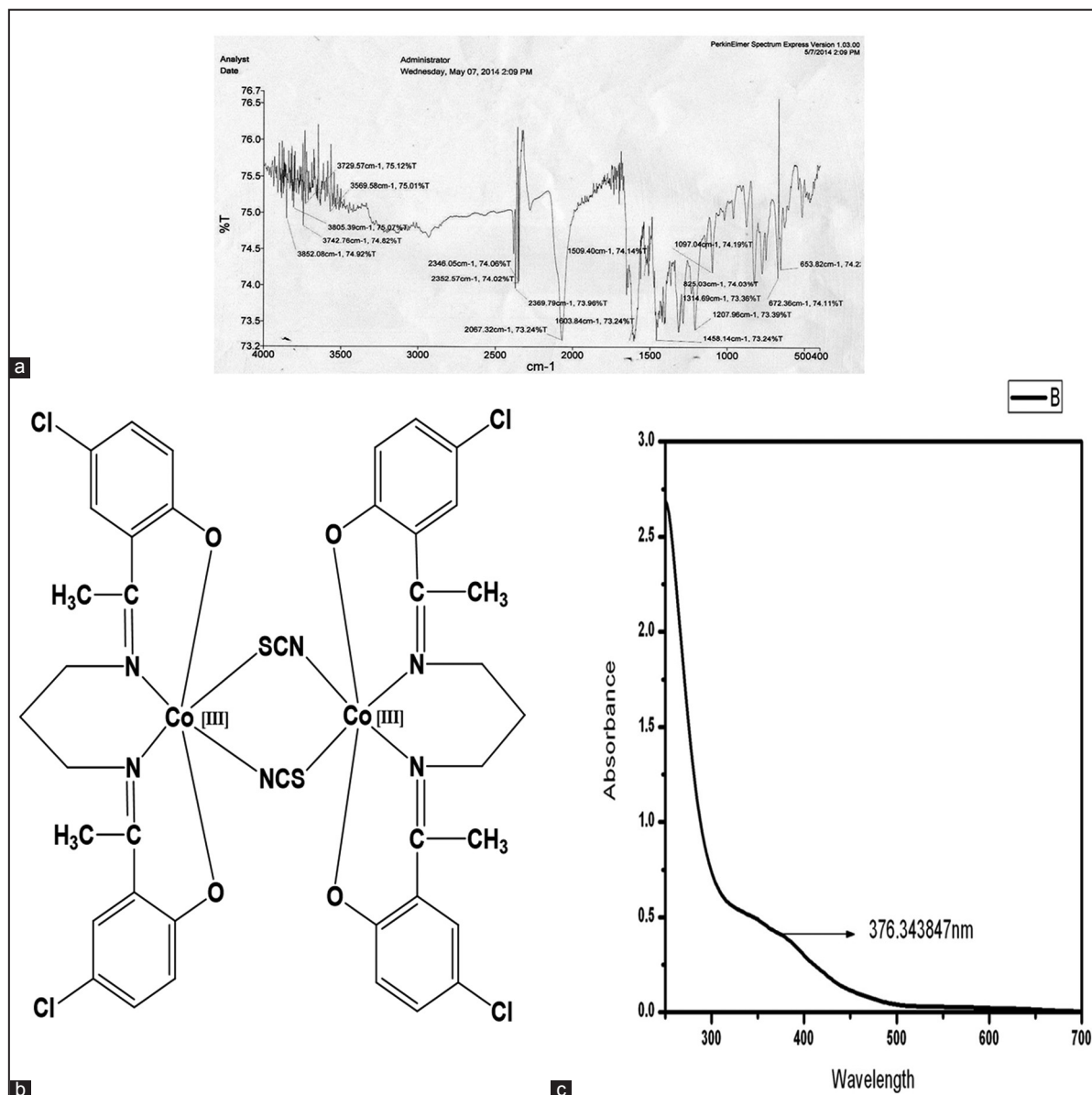


Figure 2: (a-c) Complex (1A) infrared, ultraviolet-visible spectra and probable structure. (c) Complex (1A) probable structure.



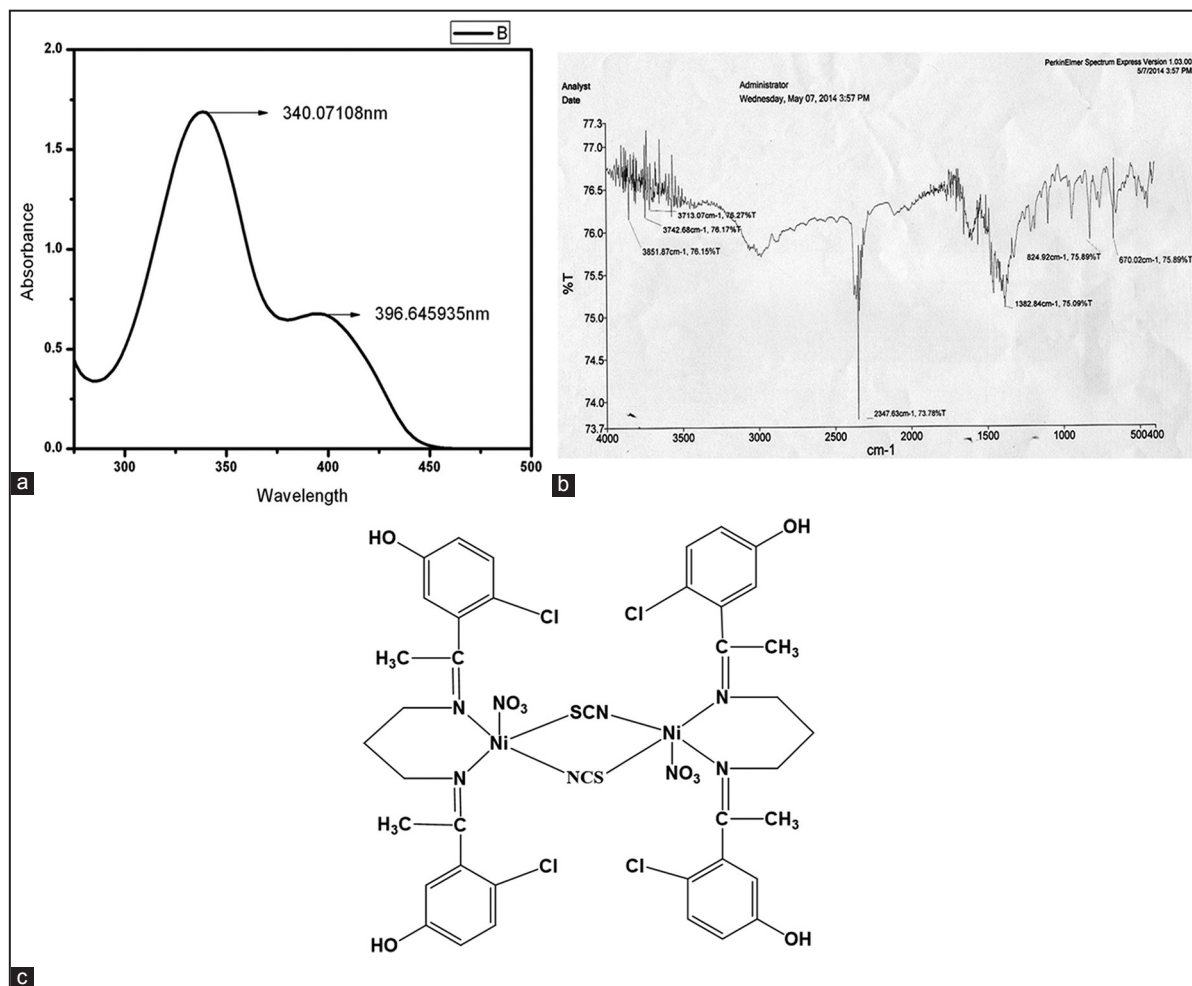
**Figure 3:** (a-c) Complex (1B) infrared, ultraviolet-visible spectra and probable structure. (b) Complex (1B) probable structure.

suggesting here Co(II) metal center environment is normal octahedral. Theoretically calculated magnetic moment data of all Co(II) octahedral complexes are within the range 4.80-5.08 BM at room temperature. These values are slightly higher than those obtained during the experimental measurements. Again Ni(II) octahedral complexes magnetic moment values are always higher than spin only value. This is mainly due to both orbital and spin-orbit coupling effects. Reference Ni(II) complex magnetic moment value was found to be 2.79 BM, slightly deviated from spin only moment. Since this value is a range of six coordinated complexes, complex geometrical environment must be distorted octahedral. The color of the complex was completely green further confirmed Ni(II) environment roughly octahedral.

During our research work, we have critically literature survey of some selected Co(II)/Ni(II) octahedral complexes magnetic moment (BM) values according to (Tables 1 and 2). Tables 1 and 2 values are nearly good agreement with our synthesized three series of complexes confirming octahedral geometrical arrangement around Co(II)/Ni(II) metal ions.

## 5. CONCLUSION

We have successfully synthesized symmetrical azo-linked novel Schiff base ( $H_2L$ ) blocker ligand, two new Co(II) azido/thiocyanato and one Ni(II) thiocyanato bridged complexes. Schiff base ( $H_2L$ ), and the respective three metal complexes have been characterized by elemental analyses, Fourier transform IR (FT-IR), UV-VIS, mass, and  $^1H$  NMR



**Figure 4:** (a-c) Complex Ni(II) infrared, ultraviolet-visible spectra and probable structure. (c) Ni(II) complex probable structure.

**Table 1:** Literature survey Co (II) octahedral complexes  $\mu_{\text{eff}}$  values (BM).

Complex	$\mu_{\text{eff}}$ value (BM)	Reference
[CoHg (SCN) 4(HPz) <sub>2</sub> ]	4.92	[36]
[CoHg (SCN) 4(lim) <sub>2</sub> ]	4.93	[36]
CoCl <sub>2</sub> .2(INH-DCB)	5.1	[37]
CoBr <sub>2</sub> .2(INH-DCB)	4.9	[37]
CoL <sub>2</sub>	4.70-5.20	[38]
Co (MeQd) <sub>2</sub> (NCS) <sub>2</sub>	4.48	[39]
Co (ETQd) <sub>2</sub> (NCS) <sub>2</sub>	4.52	[39]

**Table 2:** Literature survey Ni (II) octahedral complexes  $\mu_{\text{eff}}$  values (BM).

Complex	$\mu_{\text{eff}}$ value (BM)	Reference
Ni (NCS) <sub>2</sub> 2(INH-DCB)	2.6	[37]
Ni (OAC) <sub>2</sub> 2(INH-DCB)	2.8	[37]
NiL <sub>2</sub>	2.90	[38]
[Ni (HSalpn)(NCS)(H <sub>2</sub> O)].H <sub>2</sub> O	3.00	[40]
[Ni (Salpen) Ni (NCS) <sub>2</sub> ]	3.3	[40]

spectroscopic study. Additional magnetic moment data will be provided to confirm the expected probable structure of synthesized three complexes. Our prime aim for current research work is to investigate properly the nature of bridging modes of versatile azido or thiocyanato ligand around Co(II) and Ni(II) metal ions. Hence, we have to carry out research work very carefully by using different microanalytical techniques for characterization of Schiff base (H<sub>2</sub>L), Co(II)/Ni(II) azido/thiocyanato bridged complexes. Finally, magnetic moment study will be conducted and calculated magnetic moment data's have been compared theoretically with some selected Co(II)/Ni(II) octahedral complexes and results are a good agreement.

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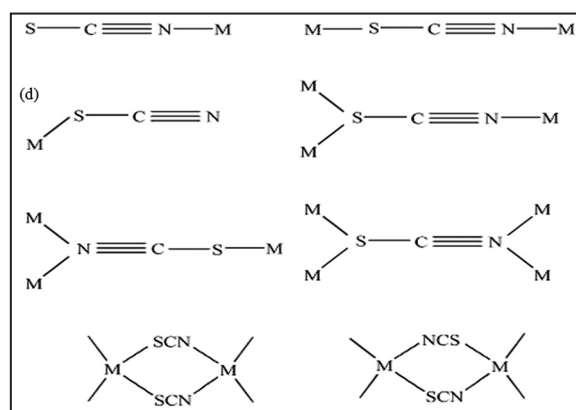
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**SUPPLEMENTARY**



Versatile bridging modes of potential SCN<sup>-</sup> ligand