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Two Novel Azido, Thiocyanato Bridged Co(II)/Cu(II) Complexes Derived from Potential Azo-Schiff Base Blocker Ligand (NN) of N,N'-bis-(2-amino-ethyl)-ethane-1,2-diamine and 1-(5-chloro-2-hydroxy-phenyl)-ethanone-synthesis, Characterization, and Magneto-structural Correlations

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ABSTRACT

The potential azo-linked tetradentate Schiff base (H_4L) blocker ligand was prepared from the 1:2 condensation of triethylenetetramine with 5-chloro-2-hydroxyacetophenone. The tetradentate nitrogen donor ligand was allowed to react with methanolic solutions of cobalt(II) nitrate hexahydrate and copper(II) nitrate trihydrate in the presence of sodium azide and ammonium thiocyanate afforded mainly complex(1) $[Co(H_4L)(N_3)]_2(NO_3)_2$ and complex(2) $[Cu(H_4L)(SCN)]NO_3$. Complex (1) and (2) were characterized by common elemental analysis(C, H and N), mass (m/e), molar conductivity, infrared, ^{1}nuclear magnetic resonance (H NMR), and ultraviolet-visible spectroscopy. The potential compartmental Schiff base (H_4L) ligand has been completely identified by ^1H NMR spectroscopic study. Molar conductivity studies confirmed that both complexes are electrolyte in nature. A brief magnetic moment data will be provided to find out the expected probable geometry of complex (1) and complex (2). All the experimental results unambiguously confirmed that in both complexes, Co(II) and Cu(II) bonded to the nitrogen donor center only along with EO modes of azide bridging and common thiocyanate (S) terminal linkage, thus fulfilling completely octahedral and square pyramidal geometry. Synthesized Co(II) and Cu(II) complexes also showed magnetic moment value within the range 4.75-4.79 and 1.76 BM, respectively.

Key words: *Schiff base (H_4L), SCN^{-1}/N_3^{-1} bridging, Ultraviolet-visible, Infrared, ^1H nuclear magnetic resonance spectra and Magnetic moment (μeff).*

1. INTRODUCTION

During 19th century, Professor Sir Hugo Schiff [1] opened a beautiful research gate for all inquisitive inorganic chemists after his successful novel discovery of Schiff base according to Scheme 1, but significant development was started from 1960's [2]. The indication of novel Schiff base formation is due to the azomethine linkage followed by C=N double bond formation.

Most of the Schiff base ligands are ubiquitous in coordination chemistry as they are potentially able to form vast number of complexes with transition or non-transition metal ions and hence modern inorganic chemists always have a target to synthesized well-active "privileged ligands"[3] due to their simple synthesis, good yield, high purity, and wide range of applications. Complexes with Co(II)/Cu(II) metal ions in presence of potential compartmental Schiff base ligand (H_4L) and pseudohalogens (SCN^{-1}/N_3^{-1}) have drawn extensive attention in the domain of polymeric complex formation chemistry due to their synthetic accessibility, fascinating structural diversities [4-14], and diverse range of applications covering organic synthesis, photochemistry [15], magnetic and elctrochromism [16-22], and catalysis [23,24]. Recently, Co(III)-Schiff base complexes find important applications in the biological field [25]. Pseudohalides (OCN^{-1}, SCN,N_3^{-1}) always shows diverse bridging modes (Scheme 2) with particular transition metal ions [26-33] and the indentified research field strongly influence the magnetic interaction between adjacent metal ions ranging from antiferro to ferromagnetic couplings [34-40]. Considering all these aspects, in the present research scenario, we communicate a facile synthesis of compartmental Schiff base (H_4L), azide/thiocyanate bridging Co(II)/Cu(II) complexes synthetic details. Azo-linked compartmental Schiff base (H_4L) and the respective two metal complexes 1 and 2 were further characterized by various spectroscopic techniques (infrared [IR], ultraviolet-visible (UV-VIS), ^{1}nuclear

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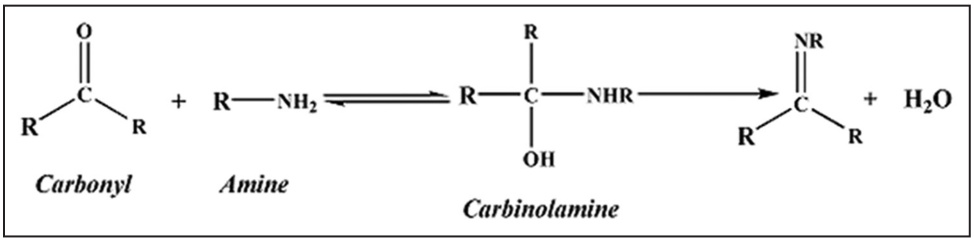
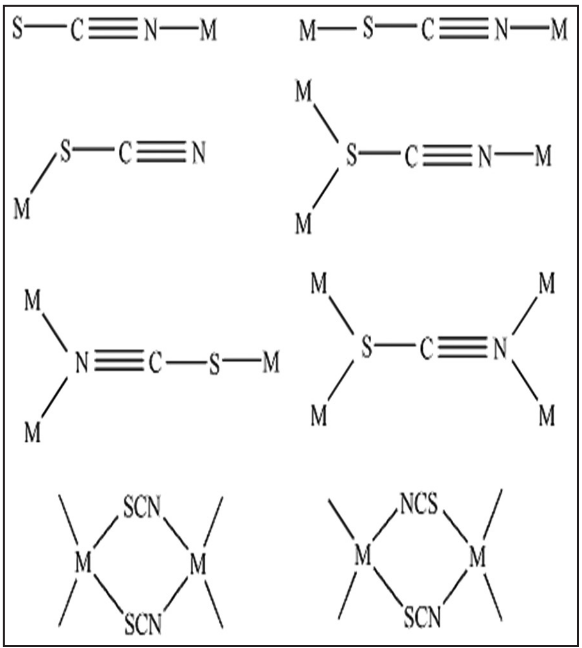


Scheme 1: Common synthetic path for all Schiff base.



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

magnetic resonance [H NMR]), and magnetic moment studies were also conducted.

2. EXPERIMENTAL

2.1. Materials

All chemicals were of reagent grade, purchased from commercial sources and used as received. 5-chloro-2-hydroxyacetophenone was purchased from Sigma Aldrich Company, USA. Triethylenetetramine (Trien), $Co(NO_3)_2.6H_2O$, and $Cu(NO_3)_2.3H_2O$ both are purchased from Sigma Aldrich Company, USA. Sodium azide and Ammonium thiocyanate were purchased from SDFCL, India. The total synthetic reactions and work-up were done in open air condition.

Caution! The azide complex preparations are highly explosive particularly in the presence of compartmental schiff base (H_4L). 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 compartmental Scihff base (H_4L) and Co(II)/Cu(II) metal 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, 400-4000 cm^{-1}) were recorded on a Perkin–Elmer model 883 infrared spectrophotometer. The electronic spectra of both complexes in methanol solvent were recorded on a Hitachi model U-3501 spectrophotometer. The ^1H NMR spectra of novel Schiff base (H_4L) were recorded on Bruker 300MHz FT-NMR spectrophotometer using trimethylsilane as internal standard in $CDCl_3$ solvent. The magnetic susceptibility values of two Co(II) and Cu(II) complexes were determined by Gouy method. Correction for diamagnetism of the constituent atoms was calculated, using common Pascal's constant. The effective magnetic moments values (μ_{eff}) of Co(II) and Cu(II) complexes were calculated using the given equation: μ_{eff}=2.83 $(\chi_M T)^{-1}$.

3. SYNTHESIS

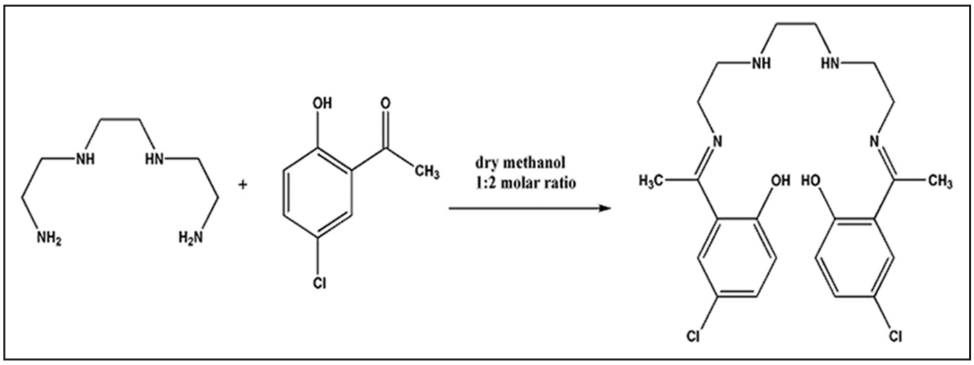
3.1. Synthesis of Schiff Base Blocker Ligand (H_4L)

To a purified dry methanol solution (50 mL) of 5-chloro-2-hydroxyacetophenone (1.024 g, 6 mmol) was added with triethylenetetramine (0.439 g, 3 mmol) in the same methanol solvent (5 mL) with constant stirring for 1 h. The color of the overall solution turned to deep yellow, and it was then additionally reflux for 7 h. The solution was then heated on a steam bath to reduce the volume 15 mL and overall solution was cooled on a ice bath. At this moment, a deep yellow product was separated out, collected by filtration under suction, washed with cold methanol. Then, the yellow solid was dried in vacuum over fused $CaCl_2$ desicator (Scheme 3).

For novel Schiff base (H_4L) (Yield: 85%), M.Wt. (451.39), Exact mass: 450.16, m/e: 451, Anal. Calc. for $C_{22}H_{28}N_4O_2Cl_2$: C: 58.54; H: 6.25; Cl: 15.71; N: 12.41; O: 7.09 Found: C: 58.6; H: 6.22; Cl: 15.7; N: 12.4; O: 7.00 IR (KBr, $v_{max/}cm^{-1}$): v(O-H) = 2800-2920; v(C=N) 1616.07; v(C=O) 1700-1800, UV-VIS spectrum, $\lambda_{max}(CH_3OH)$: 272 nm, 333 nm, and 400 nm.

4. SYNTHESIS OF CO(II)/CU(II) COMPLEXES (1) AND (2)

I. To a (25 mL) methanolic solution of compartmental Schiff base (H_4L) (0.451 g,



Scheme 3: Synthesis of Schiff base (H_4L).

1 mmol) was added to (15 mL) $Co(NO_3)_2.6H_2O$ (0.291 g, 1 mmol) drop wise with constant stirring. After 10 min, NaN_3 (0.065g, 1mmol) in aq. methanol (v/v, 1:1) was added drop wise and solution was stirred further 2.5 h. A brown ppt. was appeared immediately, filtered under suction and was dried in vacuum over fused $CaCl_2$ desicator. For (a) (Yield: 70%), M. Wt. (1228.70), Exact Mass: 1226.18, m/e: 1228.00, Anal. Calc. for $[Co(H_4L)(N_3)]_2(NO_3)_2$ C: 43.01; H: 4.59; Cl: 11.54; N: 18.24; O: 13.00, Co: 9.59 Found: C: 43.00; H: 4.60; Cl: 11.52; N: 18.20; O: 13.00; Co: 9.6 IR(KBr, $v_{max/}cm^{-1}$): v(N-N) =2073.17; 1308; v(C=N) 1596.23, λ_{max} (CH_3OH: 367 nm).

II. To a (30 mL) methanolic solution of compartmental Schiff base (H_4L) (0.451 g, 1 mmol) was added to (10 mL) $Cu(NO_3)_2.3H_2O$ (0.241 g, 1 mmol) drop wise with constant stirring. After 10 min, NH_4SCN (0.076 g, 1 mmol) in aq. methanol (v/v, 1:1) was added dropwise and solution was stirred further 2.5 h. A deep green ppt. was appeared immediately, filtered under suction, and was dried in vacuum over fused $CaCl_2$ desicator. For (b) (Yield: 75%), M. Wt. (635.02), Exact Mass: 633.06, m/e: 633, Anal. Calc. for $[Cu(H_4L)(SCN)]NO_3$ C: 43.50; H: 4.44; Cl: 11.11; N: 13.23; O: 12.60, Cu: 10.01 Found: C: 43.48; H: 4.45; Cl: 11.10; N: 13.22; O: 12.58, Cu: 10.00 IR(KBr, $v_{max/}cm^{-1}$): v(SCN^-) =2159.49; v(C=N) 1596.23, λ_{max}(CH_3OH): 360 nm, 555 nm, 672 nm.

4.1. Characterization of Azo-linked Schiff Base (H_4L) Blocker Ligand

From IR study, the presence of IR band near 1616.06 cm^{-1} provides the evidence for the formation of azomethine functional group (C=N) in the synthesized novel Schiff base. The absence of C=O at around 1700-1800 cm^{-1} confirmed the Schiff base formation according to (Scheme 1). The very week band near 2800-2920 cm^{-1} indicates the presence of intramolecular hydrogen bond –OH. ^{1}H NMR different spectroscopic data was further confirmed the formation of novel Schiff base. The free Schiff base shows the following signals including aromatic and aliphatic proton. ^{1}HNMR (300 MHz, $CDCl_3$) δ/ppm 2.292 (6H, $-CH_3$), 2.772 (4H, $-CH_2$ alpha to NH), 3.008 (4H, $-CH_2$ beta to N=C), 3.654 (4H, $-CH_2$ alpha to N=C), 6.806-7.449 (aromatic ring H). The UV-VIS spectrum of Schiff base reflects three main peaks at 272 nm, 333 nm, and 400nm. The first two UV-VIS spectrum are assigned due to benzene $\pi\rightarrow\pi^*$ and imino $\pi\rightarrow\pi^*$ transitions. Additional peak 400nm is due to $n\rightarrow\pi^*$ transition (Figures 1-3).

4.2. Characterization of Co(II)/Cu(II) Complexes (1) and (2)

For complex (1), spectral IR frequency 2073.17 indicates the asymmetric stretching vibration of azide bridged ligand. The bifurcated split of this band is indicative of the bridging function of azide. The IR frequency band near at 1308 cm^{-1} is indicative the symmetric vibration of the azido ligand, and from this guide line, we can conclude that azide shows EO coordination mode rather than EE active azide mode. The sharp medium peak 1596.23 cm^{-1} of compartmental Schiff base ligand (H_4L) indicate that azomethine nitrogen is well coordinated to Co(II) metal ion. Complex of Co(II) d^7 electronic system is high spin. The band near at 367 nm due to charge transfer involved in complex (1). The nature of spectral band reflects that in complex (1) no d-d transition observed (Figures 4 and 5). For Cu(II) complex, presence of IR band near 2159.49 cm^{-1} confirmed the SCN^{-1} linkage formation. IR peak value greater than 2100 cm^{-1} indicates the nature of S-bonded SCN^{-1} ligand [41]. The medium sharp peak of Cu(II) complex directly confirmed that SCN^{-1} coordinated to Cu(II) metal as terminal S-bonded fashion. Generally, Cu(II) d^9 system charge transfer band originate at 360 nm. In the given complex (2) band near at 554 nm is due to d-d transition. This kind of spectral feature is consistent for 5-coordinated Cu(II) complexes that may be associated with low or high energy shoulder. The low energy shoulder indicates the square pyramidal geometry but high energy shoulder where λ>800 nm belongs trigonal bipyramidal stereochemistry. Based on the above reason, the given spectral data for complex (2) is consistent only for square pyramidal geometry (Figures 6-9).

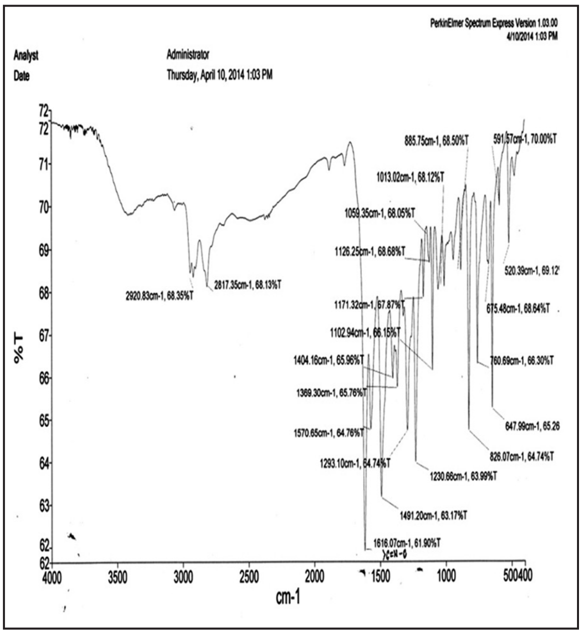


Figure 1: Infrared (KBr, ν_{max}/cm^{-1}): 1616.07(s), 1491.20(s), 1230.66(s), 826.07(s), 1570.65(m), 1293.10(m), 1102.94(m), 1570.65(m), 2920.83(w), 2817.35 (w).

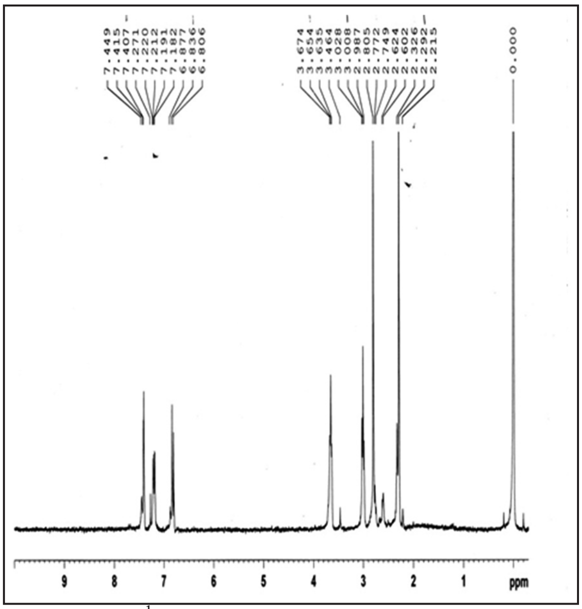


Figure 2: ^{1}HNMR (300 MHz, $CDCl_3$) δ/ppm 2.292 (6H, $-CH_3$), 2.772 (4H, $-CH_2$ alpha to NH), 3.008 (4H, $-CH_2$ beta to N=C), 3.654 (4H, $-CH_2$ alpha to N=C), 6.806- 7.449 (aromatic ring H).

4.3. Magnetic Moment Study of Complexes (1) and (2)

The Co(II) metal ion ($3d^7$) has three 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 spin orbit coupling and orbital contribution always higher values are expected. The magnetic moment values calculated for Co(II) azido bridged complex lies in the range of 3.88-4.88 BM For Co(II) complex μ=4.79 BM, is higher value than spin only value 3.87 BM corresponding three unpaired electrons. The magnetic moment data

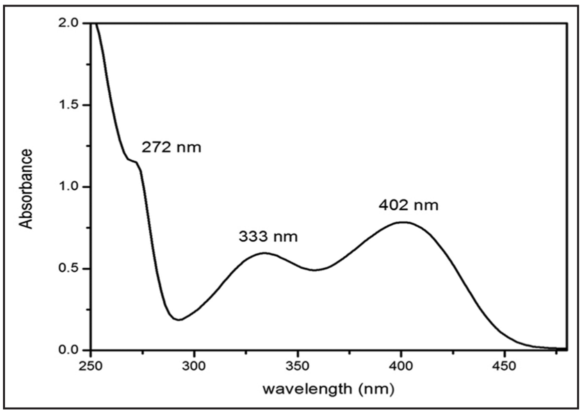


Figure 3: UV-Vis spectrum of Schiff base (H_4L) ligand.

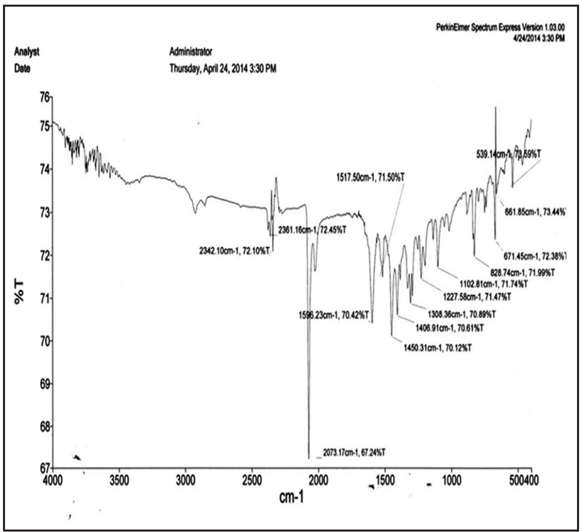


Figure 4: Infrared (KBr, ν_{max}/cm^{-1}): 2073.17(s), 1596.23(m), 1450.31(m), 1406.91(m), 1308.36(m), 1227.58(w), 1102.81(w), 2342.10(w).

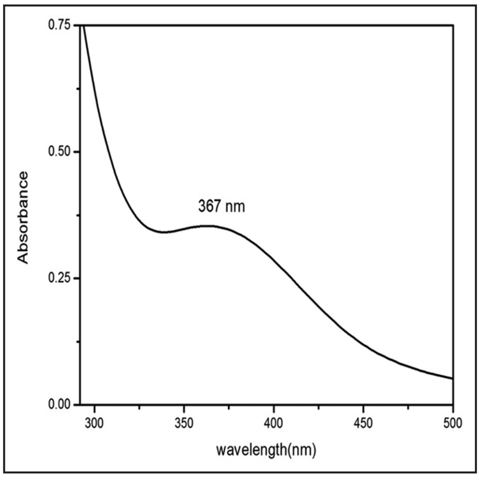


Figure 5: UV-Vis spectrum of Co(II) complex (1).

indicates substantial orbital contribution and this magnetic moment value suggest high spin Co(II) octahedral geometry. A detailed literature survey of high spin Co(II) octahedral geometry (μ_{eff}) values according to Table 1, further confirmed expected geometry of Co(II) complex is octahedral. The copper(II) metal ion ($3d^9$) has one unpaired electron in a 3d shell, therefore all Cu(II) complexes were considered to have magnetic moments close to the spin-only value, 1.73 μB but due to spin orbit coupling phenomenon, always higher values are expected. The magnetic moment calculated for Cu(II) lies in the range of 1.85-1.88 μB. Complexes having a square pyramidal configuration, the five-fold degenerate 3d level of Cu(II) is split by a ligand field of C4v symmetry into four components. The d_{x2-y2}, $d_{x2,}$ and d_{xy} levels are non-degenerate, while (dxz, dyz) levels are four-fold degenerate, including spin. The spin-orbit coupling interaction splits this level into two components, each of which is further split into two sublevels by the external magnetic field. Boudreaux calculated theoretically the magnetic moment of square-pyramidal Cu(II) complexes to be 2.11-2.21 μB at room temperature. These values are slightly higher than those obtained during the experimental measurements. The magnetic moment value of Cu(II) complex is 1.76 which almost agree with the spin only value 1.73 BM. We have extensive literature survey of Cu(II) square pyramidal geometry (μ_{eff}) values according to (Table 2). Since complex (2) (μ_{eff}) value very close to literature survey values complexes (Table 2), hence our synthesized Cu(II) complex geometrical environment is perfectly square pyramidal.

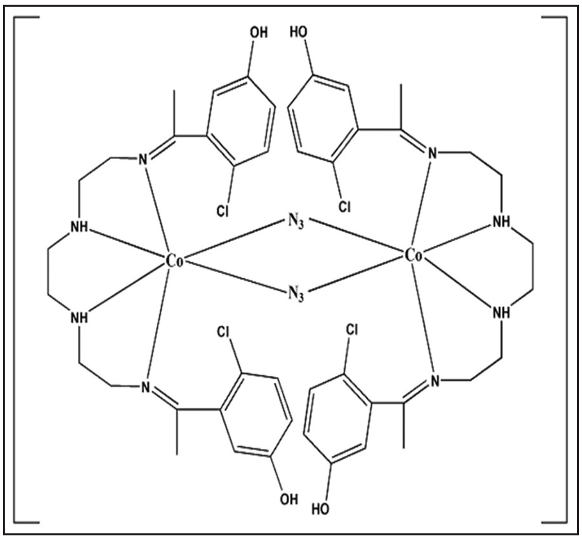


Figure 6: Complex (1) expected probable structure.

5. CONCLUSION

We have successfully synthesized potential azo-linked novel Schiff base (H_4L), two new Co(II) and Cu(II) azide/thiocyanate bridging complexes. Schiff base (H_4L) and Co(II)/Cu(II) complexes have been characterized by elemental analyses, FT-IR, UV-VIS, mass, and ^{1}H NMR spectroscopic study. Magnetic moment study will be provided to find out the probable expected geometry of synthesized complexes 1 and 2. The prime aim for current research work is to investigate the nature of binding modes of versatile azide/thiocyanate around Co(II) and Cu(II)

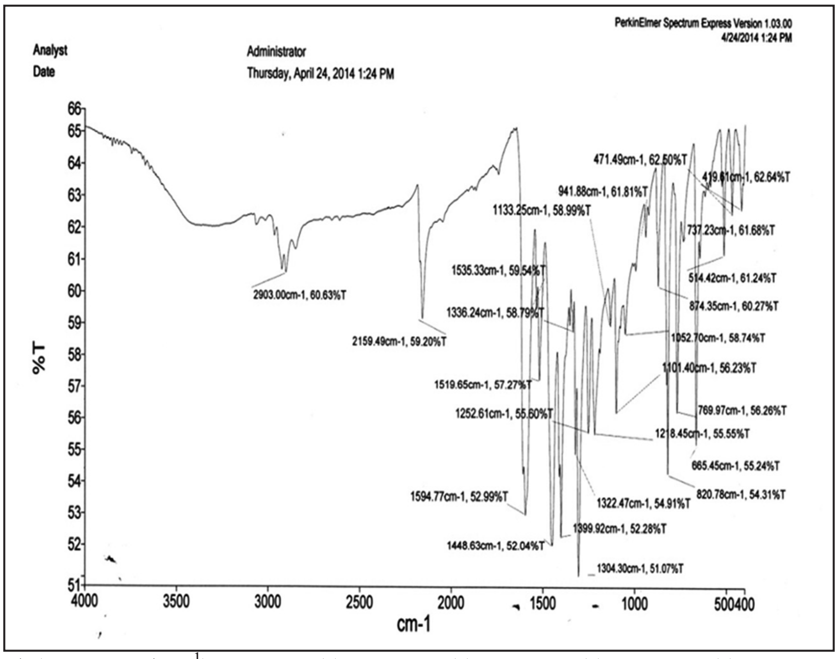


Figure 7: Infrared (KBr, ν_{max}/cm^{-1}): 2159.49(s), 1594.77(s), 1148.63(s), 1399.92(s), 1304.30(s), 1519.65(m), 1322.47(m), 1252.61(m), 1218.45(m), 1101.40(m). Complex (2) infrared spectra.

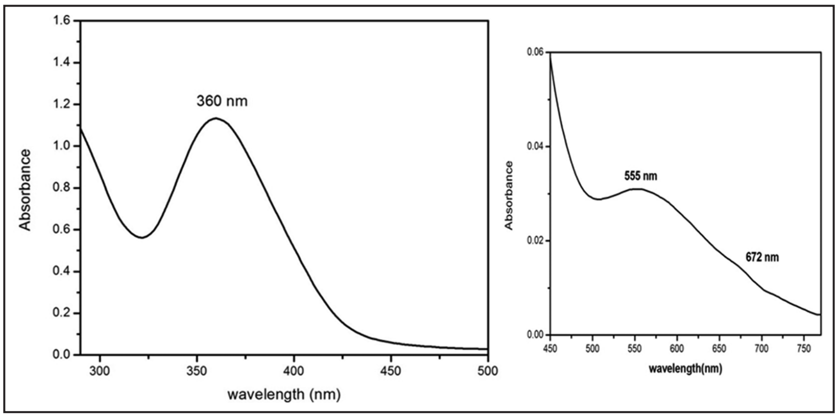


Figure 8: Complex (2) ultraviolet-visible spectra.

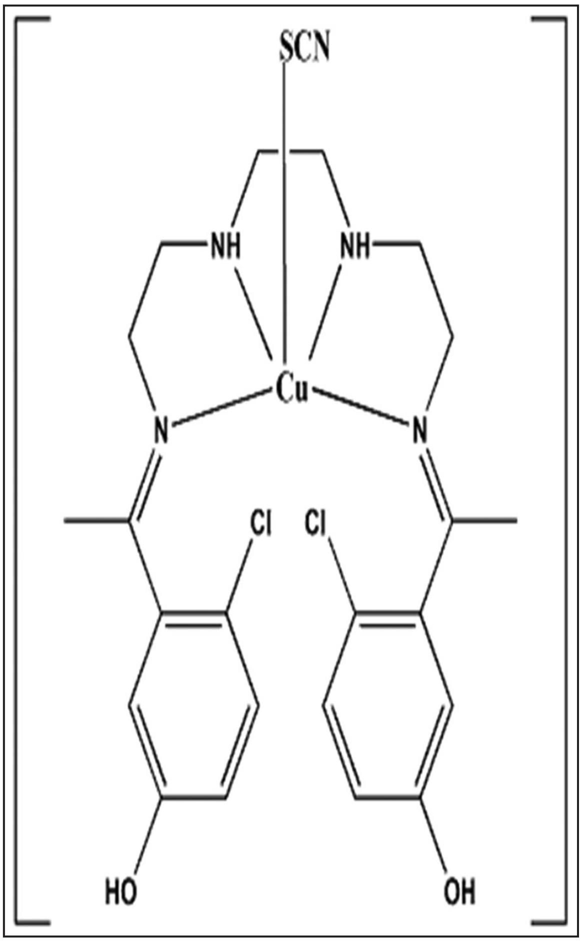


Figure 9: Complex (2) expected probable structure.

metal centers. Thus, we have carefully characterized complexes 1 and 2 with the aid of microanalytical tools as well as magnetic moment study that are comparable with literature survey values according to Tables 1 and 2.

Table 1: Literature of HS Co(II) octahedral complexes Magnetic moment values (μ_{eff}).

Complexes	μ_{eff} BM	References
[Co(α-naph.dtc) 2]	4.78 BM	[42]
$[Co(L)_2 2H_2O]$	4.75 BM	[43] (a+b)
Co (II) malonate, mandelate, tartarate complexes	4.79 BM	[44]
CoL_2	4.87 BM	[45]

Table 2: Literature of Cu(II) square pyramidal complexes Magnetic moment values (μ_{eff}).

Complexes	μ_{eff} BM	References
$[Cu(L^3)(H_2O)]$ $H_2L^3=C_{18}H_{18}Br_2N_2O_4$	1.85-1.8 BM	[46]
$[Cu(C_{18}H_{16}Br_2N_2O_4)(H_2O)]$	-	[47]

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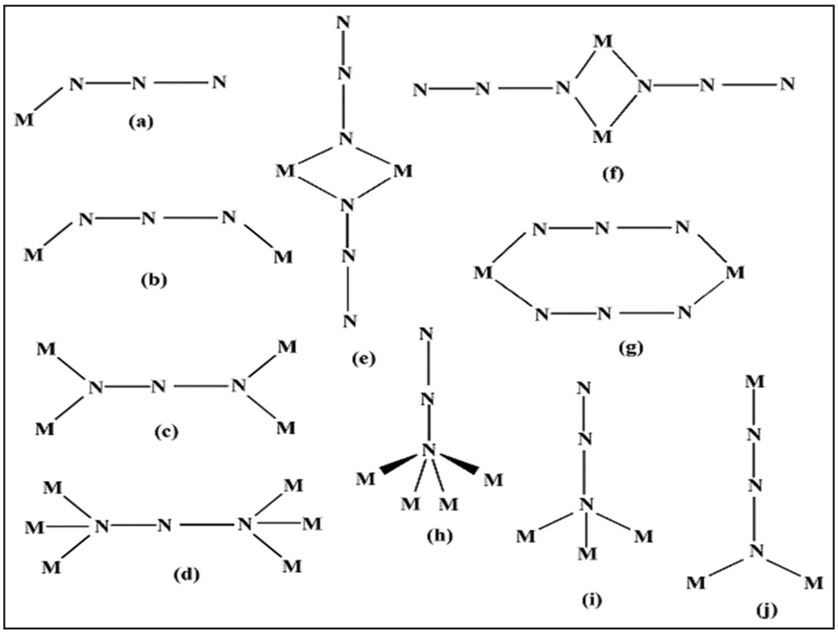
SUPPLEMENTARY



Versatile bridging modes of potential azido ion (N_3^{-1})