Two Unique Zn(II) Azide and Thiocyanate Bridged Complexes of A Tetradeptate Schiff Base Ligand (H₄L) Derived from N,N'-Bis-(2-Amino-Ethyl)-Ethane-1,2-Diamine and 1-(5-Chloro-2-Hydroxy-Phenyl)-Ethanone

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1. Introduction

Today Schiff base is one of the most important compound due its wide application in different fields of inorganic chemistry. Schiff base was first reported by Sir Hugo Joseph Schiff in 1864 year [1] and in the honour of inventor it was referred as 'Schiff base'. According to Hugo Schiff, it is a compound that contains azomethine functional group [2] connected to aryl/alkyl but no hydrogen. Commonly such kind of ligand synthesis has been achieved from an amine and aldehyde or ketone. Owing to its easily synthetic routes and product isolation it is also referred as 'privileged ligands' [3].

![Scheme 1](image1)

**Scheme 1 Synthetic procedure of Schiff base**

![Fig. 1](image2)

**Fig. 1 Different binding modes of SCN⁻¹**

The formation of Schiff base is a combination of elimination followed by addition Scheme 1[4].

Schiff bases are capable to form vast number of mono, di & polynuclear chelate complexes with nitrogen or oxygen donor atom [5-7]. Schiff base metal complexes have numerous applications, such as, in the treatment of cancer [8], as antibactericide agents [9-11], as antivirus agents [11-13], as fungicide agents [14-15], and in the field of biological [16-18]. Azomethine complexes of ChromiumSchiff base, Cobalt complexes are popularly used as dyes. Two important Schiff base Thiazole and benzothiazole exhibit effective antifungal activity. Apart from other well behaved applications are in chemical analysis [19], absorption and transport of oxygen, in pesticides [20-21], and homo and heterogeneous catalysis for oxidation and polymerization of organic compounds [22]. Versatility of Schiff base ligands complexes and their wide applications field like biological, chemical, industrial, researcher makes further investigations for recent time. In the present scenario, Schiff base complex formation have been extended in presence of pseudohadides, azide or thiocyanate linker owing to their ambidentate character [23-27]. Hence polymericallity can be introduced by thiocyanate or azide bridging between metal centers. The versatile linking character of azide & thiocyanate give rise to different characteristics and magnetic exchanges of Schiff base complexes Fig. 1 and Fig. 2.

![Fig. 2](image3)

**Fig. 2 Different binding modes of N₃⁻¹**

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Schiff base **H₄L** derived from 5-chloro-2-hydroxyacetophenone and triethylentetramine. Infrared, mass, and NMR spectroscopic characterization of respective Schiff base ligand and metal complexes.

### 2. Experimental Methods

#### 2.1 Materials

All chemicals were of reagent grade and used as received without further purification. Solvents like methanol, ethanol, and other reagents used in this work were obtained from commercial sources. 5-chloro-2-hydroxyacetophenone was purchased from Sigma Aldrich Company, USA. Triethylentetramine zinc acetate both are purchased from Merck Chemical Company. Sodium azide, potassium thiocyanate were purchased from SD Fine Chemicals, India. The synthetic reactions and work-up were done in open air.

*Caution!* The azide complexes are potentially explosive particularly in the presence of Schiff base. Even though no such accident occurred during the time of research work since only 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 ligand and the complexes were determined with a Perkin-Elmer CHB analyzer 2400. Mass spectra were done with a JEOJMS-AX 500 mass spectrometer. IR spectra (KBr pellet) were recorded on a Perkin-Elmer model 883 infrared spectrophotometer. The ¹H NMR spectra of novel Schiff base were recorded on Bruker 300 MHz FT-NMR spectrophotometer using trimethylsilane as internal standard in CDCl₃ solvent.

### 2.3 Synthesis

#### 2.3.1 Synthesis of Novel Schiff Base H₄L

To a purified dry methanol solution (50 mL) of 5-chloro-2-hydroxyacetophenone (1.024 g, 6 mmol) was added with triethylentetramine (0.439 g, 3 mmol) in the same methanol solvent (5 mL) with constant stirring for 1 hr. The colour of the overall solution turned to yellow and it was then allowed reflux for 7 hours. The solution was then heated on a steam bath to reduce the volume 15 mL and overall solution was cooled on an 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 CaCl₂ desiccator Scheme 2.

**Scheme 2 Synthetic procedure of H₄L**

For novel Schiff base **H₄L** (Yield: 85%), M.wt. (451.39). Exact Mass: 450.16, m/e: 451, Anal. Calc. for C₃₂H₂₀N₄O₂Cl₂: 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, 7.09 IR (KBr) νmax/cm⁻¹: ν(O-H) = 2800-2920; ν(C=N) = 1616.06; ν(C=O) = 1700-1800.

#### 2.3.2 Synthesis of Zn(II) Complexes

(a) To a (20 mL) methanolic solution of novel Schiff base **H₄L** (0.451 g, 1 mmol) was added to (10 mL) Zn(OOCCH₃)₂·H₂O (0.21949 g, 1 mmol) dropwise with constant stirring. After 20 minutes Na[N₃] (0.065 g, 1 mmol) in aq. methanol (v/v, 1:1) was added and reaction was stirred further 2 hr. A yellow ppt. appeared, filtered under suction and was dried in vacuum over fused CaCl₂ desiccator. For complex **a** (Yield: 80%), M.wt. (598.11). Exact Mass: 588.08, m/e: 588, Anal. Calc. for C₃₄H₂₈N₄O₄Zn: C, 49.38; H, 3.70; Cl, 11.80; N, 23.31; O, 5.33 Found: C, 43.7; H, 4.71; Cl, 11.7; N, 23.1; O, 5.31 IR (KBr) νmax/cm⁻¹: ν(N-N) = 2036.06; ν(C=N) = 1576.

(b) To synthesize complex **b** we have consider similar procedure using methanolic KSCN solution in place of sodium azide. For complex **b** (Yield: 78%), M.wt. (630.04). Exact Mass: 632.94, m/e: 632. Anal. Calc. for C₃₄H₂₈Cl₂N₄O₂Zn(NCS): C, 45.54; H, 4.46; Cl, 11.20; N, 13.28; O, 5.06; S, 10.13 Found: C, 45.6; H, 4.4; Cl, 11.0; N, 13.31; S, 10.11 IR (KBr) νmax/cm⁻¹: ν(NCS) = 2083.23; ν(C≡N) = 1755.

### 3. Result and Discussion

#### 3.1 Synthesis

Schiff base ligand (**H₄L**) and two Zn(II) azide/thiocyanate bridging complexes have been synthesized successfully in our laboratory. They are characterized by different physicochemical techniques like elemental analyses, IR, UV-Vis, mass (m/e), and ¹H NMR spectroscopic studies.

#### 3.2 Individual Characterization of Novel Schiff Base H₄L and Derived Two Zn(II) Complexes

**3.2.1 Characterization of Novel Schiff Base H₄L**

From infrared spectroscopy (Fig. 3), the presence of IR band near 1616.06 cm⁻¹ provides the evidence of for 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. ¹H NMR different spectroscopic data was further confirmed the formation of novel Schiff base Fig 4. The UV-Vis spectrum of novel Schiff base reflects three main peaks at 272 nm, 333 nm and 400 nm. The first two UV-Vis spectrum are assigned due to benzene π→π* and imino π→π* transitions. Additional peak 400 nm is due to n→π* transition Fig 5.

![Fig 3 IR spectra of Schiff base ligand H₄L, 20(s), 826.07(s), 1570.65(m), 1293.10(IR (KBr, νmax/cm⁻¹)): 1616.07(s), 1491(m), 1102.94(m), 1570.65(m), 2920.63(w), 2817.35(w)](image)

![Fig 4 ¹H NMR spectra of Schiff base ligand H₄L (1HNR, 300 MHz, CDCl₃) δ/ppm 2.292 (6H, -CH₃), 2.772 (4H, -CH₂ alpha to NH), 3.000 (4H, -CH₂ beta to N=C), 6.806- 7.449 (aromatic ring H)](image)

![Fig 5 UV-Vis spectra of Schiff base ligand (H₄L)](image)
3.2.2 Characterization of Two Unique Zn(II) Complexes

Two unique Zn(II) complexes show IR frequency near at 2036.06 cm⁻¹ and 2082.23 cm⁻¹ indicating the presence of azide and thiocyanate complex formation. In both complexes, the peak being bifurcated, hence azide and thiocyanate function as bridging moiety. The lowering frequency of C-N group indicates the coordination of C-N nitrogen to the Zn metal centre. The literature values of IR frequencies of SCN⁻ could be used for differentiation purpose between S-bonded (2110-2140 cm⁻¹) and N-bonded (less than 2110 cm⁻¹) complexes [30-31]. Hence here SCN⁻ can be coordinated with Zn metal as terminal fashion through N atom. Since Zn(II) d8-filled shell configuration, diamagnetic in nature both complexes does not exhibit d-d transition band. In both complexes shift of ligand π* and nπ transition takes place due to complexation with Zn(II) metal centre. The peak 337 nm in SCN⁻ bridged complex is due to nπ* transition. In Fig. 6.

![Fig. 6](image)

**Fig. 6** IR spectra of Zn-azole bridged complex IR (KBr, ν (cm⁻¹)): 2036.06(s), 2082.23(m), 1560.16(s), 1400.31(m), 1333.60(m)

4. Conclusion

We have successfully synthesized novel Schiff base HHL, two Zn(II) azide, thiocyanate bridged complexes. Both are characterized by elemental analyses, FT-IR, UV-Vis, mass and finally ¹H NMR spectroscopic study. In the present research work we have investigated the nature of azide or thiocyanate bridged Zn(II) complexes structure with the aid of microanalytical tools since pseudo halides are capable to form wide variety of complex structures. This is the prime objective of the present research work.

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