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Two Unique Zn(II) Azide and Thiocyanate Bridged Complexes of A Tetradentate Schiff Base Ligand (H_4L) Derived from N,N'-Bis-(2-Amino-Ethyl)-Ethane-1,2-Diamine and 1-(5-Chloro-2-Hydroxy-Phenyl)-Ethanone

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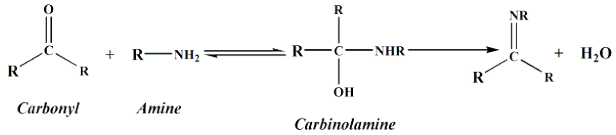
ABSTRACT

Tetradentate Schiff base **(H_4L)** on account of its beauteousness and endearing popularity and versatility towards wide range of complex formations, many inquisitive chemists got interested to their complex formation after inclusion of suitable bridging or linking agents like SCN^{-1}/N_3^{-1}. In the present research work, **H_4L** novel Schiff base has been obtained by the 1:2 molar condensation of triethylenetetramine with 5-chloro-2-hydroxyacetophenone. Using the reference ligand two Zn(II) azide & thiocyanate bridging complexes were synthesized and characterized by common elemental analysis, IR and ^1H NMR spectral data. Respective ligand and two Zn(II) complexes were further identified with the aid of UV spectral transition bands. The results confirmed that in both complexes Zn(II) bonded to the ligand through imine or amine nitrogen along with azide bridging or N-bonded thiocyanate as linker.

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



Scheme1 Synthetic procedure of Schiff base

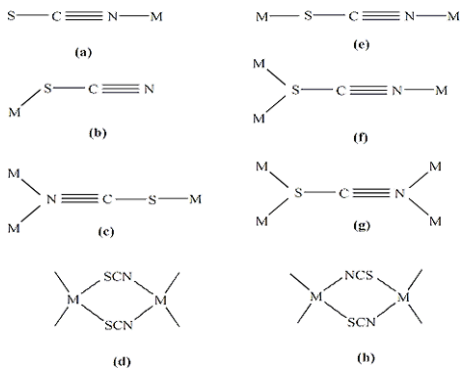


Fig. 1 Different binding modes of SCN^{-1}

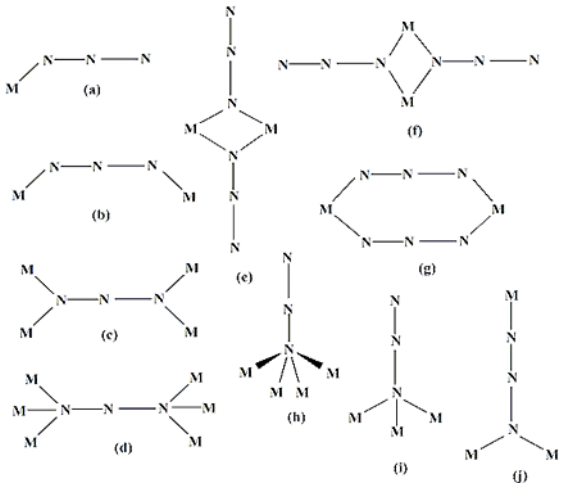


Fig. 2 Different binding modes of N_3^{-1}

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 [9-10], as antivirus agents [11-13], as fungicide agents [14-15], and in the field of biological [16-18]. Azomethine complexes of Chromium,Schiff 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 polynuclarity 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. In the present communication, we report a novel synthesis of new

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Schiff base **H_4L** derived from 5-chloro-2-hydroxyacetophenone and triethylenetetramine, azide and thiocyanate bridged two Zn(II) Schiff base complex synthetic details, UV, IR and ^{1}H 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. All 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. Triethylenetetramine zinc acetate both are purchased from Merck chemical Company. Sodium azide, potassium thiocyanate were purchased from SDFCL, 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.

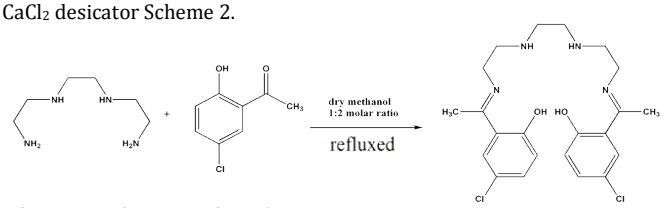
2.2 Physical Measurement

Elemental analyses (carbon, hydrogen and nitrogen) of the ligand and the 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 the complexes in organic solvent were recorded on a Hitachi model U-3501 spectrophometer. The ^{1}H NMR spectra of novel Schiff base were recorded on Bruker 300 MHz FT-NMR spectrophotometer using trimethylsilane as internal standard in $CDCl_3$ solvent.

2.3 Synthesis

2.3.1 Synthesis of Novel Schiff Base 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 hr. The colour of the overall solution turned to yellow and it was then additionally 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 $CaCl_2$ desicator Scheme 2.



Scheme 2 Synthetic procedure of H_4L

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,ν_{max}/cm^{-1}): ν(O-H) =2800-2920; ν(C=N) 1616.07; ν(C=O) 1700-1800.

2.3.2 Synthesis of Zn(II) Complexes

(a) To a (20 mL) methanolic solution of novel Schiff base **H_4L** (0.451 g, 1mmol) was added to (10 mL) $Zn(OCOCH_3)_2.2H_2O$ (0.21949 g, 1 mmol) dropwise with constant stirring. After 20 minutes NaN_3 (0.065 g, 1mmol) in aq. methanol (v/v, 1:1) was added dropwise and solution was stirred further 2 h. A yellow ppt. appeared, filtered under suction and was dried in vacuum over fused $CaCl_2$ desicator. For complex **(a)** (Yield: 80%), M.wt. (598.11), Exact Mass: 600.8, m/e: 600, Anal. Calc. for $C_{22}H_{28}N_4O_2Cl_2Zn(N_3)_2$: C, 43.98; H, 4.70; 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,ν_{max}/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 $C_{22}H_{28}N_4O_2Cl_2Zn(NCS)_2$: 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, 11.00; N, 13.31; S, 10.1 IR(KBr,ν_{max}/cm^{-1}): ν(NCS) =2083.23; ν(C=N) 1575.

3. Result and Discussion

3.1 Synthesis

Schiff base ligand **(H_4L)** 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 ^{1}H NMR spectroscopic studies.

3.2 Individual Characterization of Novel Schiff Base H_4L and Derived Two Zn(II) Complexes

*3.2.1 Characterization of Novel Schiff Base **H_4L***

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. ^{1}H 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.

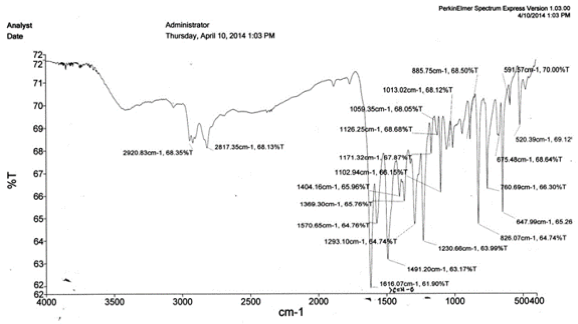


Fig. 3 IR spectra of Schiff base ligand H_4L .20(s), 1230.66(s), 826.07(s), 1570.65(m), 1293.10(IR (KBr, ν_{max}/cm^{-1}): 1616.07(s), 1491m), 1102.94(m), 1570.65(m), 2920.83(w), 2817.35 (w)

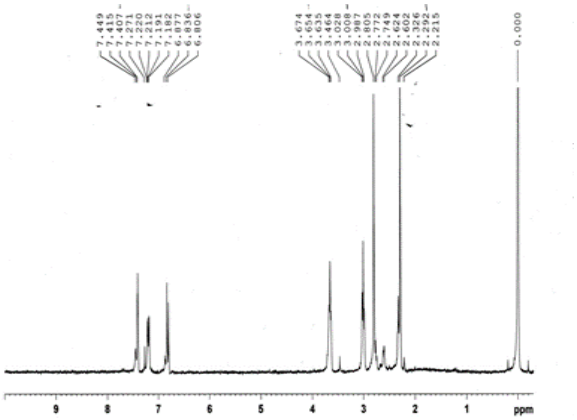


Fig. 4 1H NMR spectra of Schiff base ligand 1HNMR (300 MHz, CDCl3) δ/ppm 2.292 (6H, -CH3), 2.772 (4H, -CH2 alpha to NH), 3.008 (4H, -CH2 beta to N=C), 3.654 (4H, -CH2 alpha to N=C), 6.806- 7.449 (aromatic ring H)

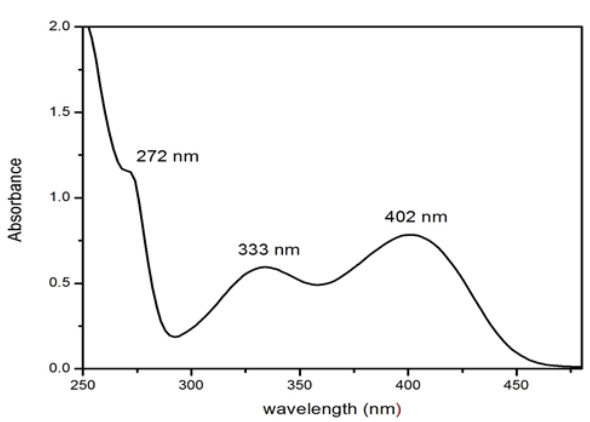


Fig. 5 UV-Vis spectra of Schiff base ligand(H4L)

3.2.2 Characterization of Two Unique Zn(II) Complexes

Two unique Zn(II) complexes shows 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 ν(C==N) frequencies of SCN^{-1} 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^{-1} can be coordinated with Zn metal as terminal fashion through N atom**.** Since Zn(II) d^{10} filled shell configuration, diamagnetic in nature both complexes does not exhibit d-d transition band. In both complexes shift of ligand π-π* and n-π* transition takes place due to complexation with Zn(II) metal centre. The peak 337 nm in SCN^{-1} bridged complex is due to π-π* transition Fig. 6-9.

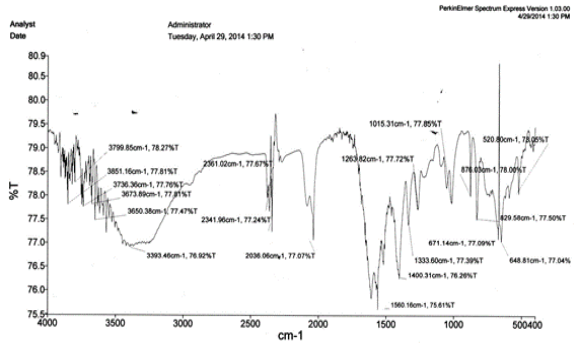


Fig. 6 IR spectra of Zn-azide bridged complex IR (KBr, ν_{max}/cm^{-1}): 2036.06(s), 2341.96(s), 1560.16(s), 1400.31(s), 1333.60(m)

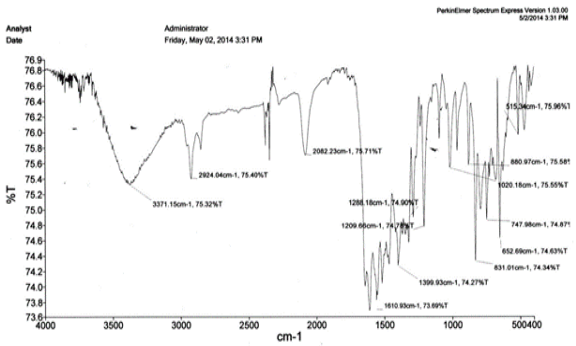


Fig. 7 IR spectra of Zn-SCN bridged complex IR (KBr, ν_{max}/cm^{-1}): 747.98(m), 2082.23(m), 831.01(s), 2924.04(m), 2082.23(m)

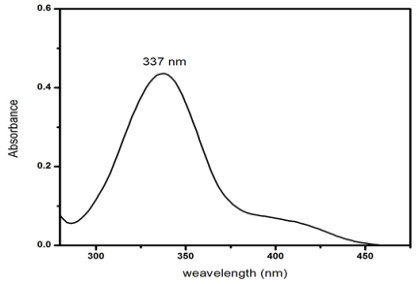


Fig. 8 UV-Vis spectra of Zn-azide bridged complex

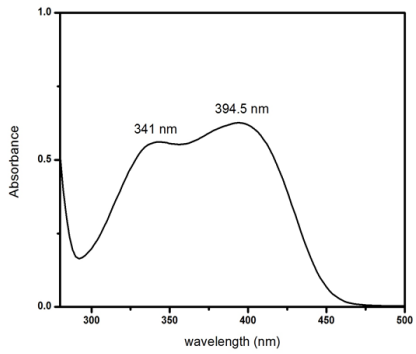


Fig. 9 UV-Vis spectra of Zn-SCN bridged complex

4. Conclusion

We have successfully synthesized novel Schiff base **H_4L,** 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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