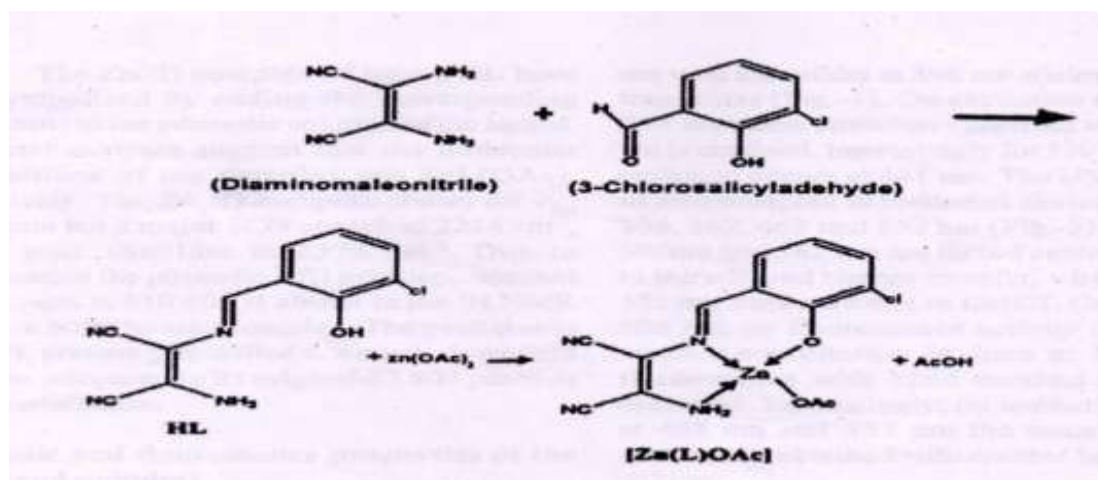


Experimenta

Materials and Methods:

All chemicals were obtained from commercial sources and used as received. Solvents were dried according to standard procedures and distilled prior to use. High purity 2, 3-diamino-cis-2-butenedinitrile (DAMN) and 3-chlorosalicylaldehyde were purchased from Aldrich Chemical Company inc. and used as received. All other chemicals were AR grade.

Elemental analyses (Carbon, hydrogen, nitrogen, chlorine and zinc) were performed using elemental analyzer. Infrared spectra (4000-400 cm^{-1}) were recorded in KBr at 300 K using a FTIR.



Electronic spectra (1500-300 nm) were obtained at 25°C using a spectrophotometer in methanol. Fluorescence spectra of the ligand and complex were recorded in solution using methanol as a solvent with a luminescence spectrometer. HNMR spectra (300 MHz) were recorded (CD₃SO) solvent on a NMR spectrometer using the solvent signal as the internal standard in a 5 mm probe.

Synthesis of the ligand (HL):

To an ethanolic solution (10 ml) of 3-chlorosalicylaldehyde (2 mmol), an ethanolic solution (5 ml) of DAMN (2 mmol) was added dropwise with constant stirring. The stirring was continued further overnight. The yellow monoamine which precipitated out, was filtered, washed with ethanol and dried under vacuum (Yield: 45%).

Preparation of Zn(II) complex:

An ethanolic solution (20 ml) of Zn(OAc)₂ (2.10 mmol) was added to an ethanolic solution of the ligand, HL (2 mmol) with constant stirring. The resulting mixture was then refluxed for 4 hrs. The intense red-purple solution deposited a deep purple solid, which was filtered off, washed with ethanol and dried under vacuum. Yield: 86%. Anal. (%): Calcd for [C₁₁H₈N₂O₂ClZn](1): C, 42.40; H, 2.44; N, 15.22. Cl, 9.58, Zn: 17.77 Found: C, 42.32; H, 2.46; N, 15.28. Cl, 9.58. Zn, 17.68

Results and Discussion

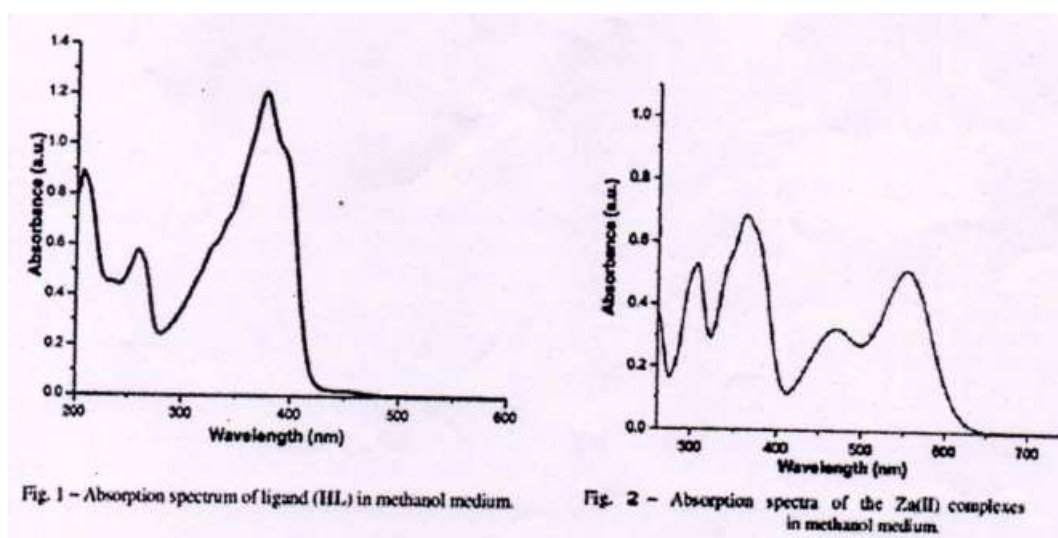
Synthesis and characterization

The Schiff base ligand HL has been synthesized by 1+1 condensation of DAMN and 3-chlorosalicylaldehyde in ethanol. It has been characterized by common physicochemical techniques. IR spectrum of the half-condensed ligand shows major NH stretches at 3416, 3307 and 3193 cm⁻¹ and a strong CN stretching band at 2203 cm⁻¹, with a sharp, weak shoulder at very high energy 2363 cm⁻¹. The bands at 1627 cm⁻¹ and 1566 cm⁻¹ are due to the imine (C=N) and skeletal vibrations, respectively. ¹H NMR spectrum of the ligand exhibits the peaks at & 10.400 (s, 1H; for phenolic -OH), 8.548 (s, 1H, for imine H), 8.996 (m, 1H, aromatic H), 8.803 (s, 2H, for -NH), 8.286 (m, 1H, aromatic H) and 5.876 (m, 1H, aromatic H), which corroborate well with the proposed structure of HL.

The Zn(II) complex of ligand HL have been synthesized by adding the corresponding acetate salts to the ethanolic solution of the ligand. Elemental analyses suggest that the molecular composition of the complex are Zn[LOAc]₂ respectively. The Zn(II) complex shows no absorption but a major CN stretch at 2214 cm⁻¹ with a peak shoulder at 2374 cm⁻¹. Due to complexation the phenolic -OH gets deprotonated and the peak at 10.400 is absent in the ¹H NMR spectra in both the zinc complex. The peak due to two NH protons gets shifted to a much downfield region as compared to its original 8.803 position due to metallation.

Electronic and fluorescence properties of the ligands and complex:

The ligand in methanol medium shows three absorption band maxima at 207, 259 and 379 nm with a shoulder at 396 nm arising due to transitions (Fig-1). On excitation at 207 nm and 259 nm emission spectrum with a peak at 294 nm is obtained. Interestingly for 379 nm excitation, emission occurs at 441 nm. The UV-vis spectrum of zinc complex in methanol shows four bands at 306, 362, 468 and 553 nm (Fig-2). The bands at 306 nm and 362 nm are ligand centred arising due to intra-ligand charge transfer, whereas, 468 and 553 nm bands are due to LMCT. On excitation at 306 nm, no fluorescence activity is noticed, but when the excitation is done at 362 nm, blue fluorescence with band maxima at 423 nm is observed. Interestingly, on excitation separately at 468 nm and 553 nm the same fluorescence spectrum is obtained with emitted band maxima at 632 nm.



Conclusion

A Schiff base ligand, HL, has been synthesized by 1 condensation of diaminomalconitrile and 3-chlorosalicylaldehyde. The solution phase structure of the ligand has been evaluated. They have a double bond. Our study proves that the ligand is highly fluorescent and the fluorescence is due to the transition Zn(II) complex of the ligand was prepared and characterized by routine physicochemical studies.

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