

One pot Synthesis of a Zinc complex of Schiff Base derived from Benzil and Cysteine: Characterization and Study of Fluorescence Activity

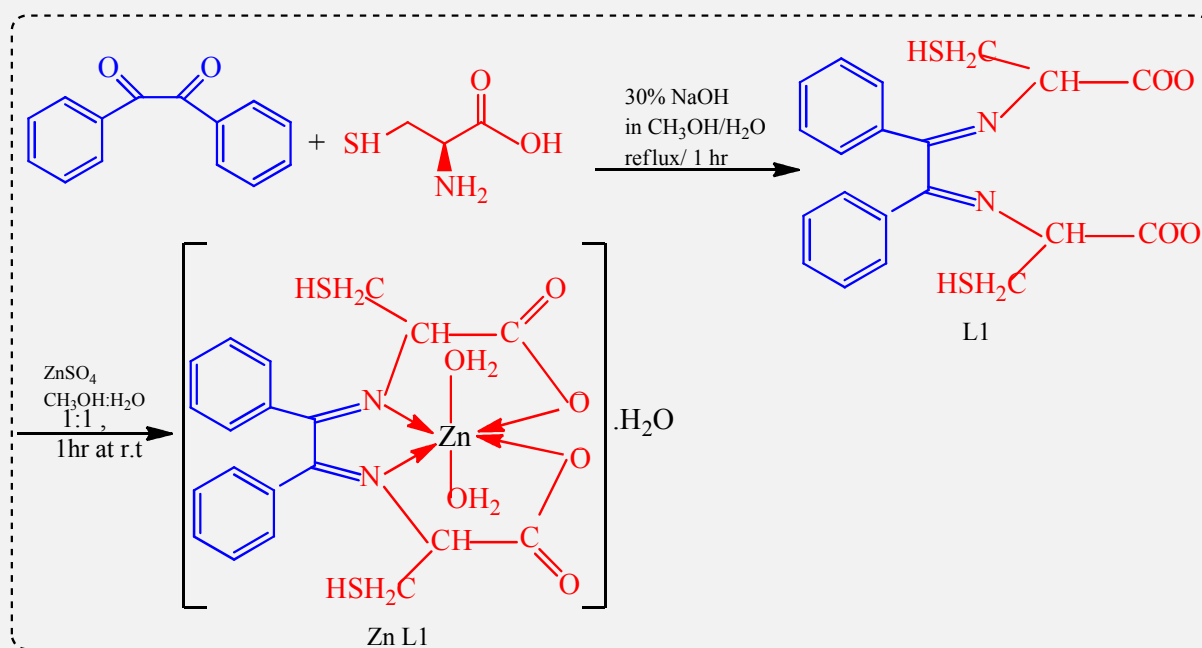
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Abstract: Synthesis of Schiff base and its metal complex is always gained interest among researchers due to its variety of applications such as in the field of medicine, as catalyst, as photoluminescent, as antioxidant. Researchers from all over the globe developed different methods for synthesis of Schiff base and their transition metal complexes. In this study synthesis of a Schiff base from benzil and cysteine have been carried out using one pot method and also zinc complex of the synthesized Schiff base have been prepared which is characterized by UV, IR, NMR, ESI-MS, TGA as well as fluorescence activity of the zinc complex have been reported.



Keywords: One pot, Schiff base, Benzil and Cysteine, Benzil and Cysteine, Fluorescence activity.

Introduction

Schiff base complexes of Zn (II) have gained recent interest because of different applications. Zn (II) complexes with functionalized Schiff bases have been reported to catalyze the transesterification of oil in mild conditions [1,2], antifungal and anti-bacterial activity [3], photo luminescent properties [4]. Anionic Schiff base surfactants have been used to synthesise Zn (II) complexes and applied as anticorrosion agent

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[5]. Nano structured Zn (II) complexes are also known with Schiff base ligands [6] Zn (II) complex with Schiff base bis-salicylaldiminato showed orange light emission when irradiated with UV light while the ligand emitted green light [7]. Zn (II) square planar complex with Schiff base has been recently reported to show anticancer activity [8]. Tridentate NNO coordinated Schiff base complex of Zn (II) is reported to show cytotoxic effects [9]. Condensation of isatin with 2-aminopyrimidine led to Schiff base and its Zn (II) complex was applied for DNA cleavage [10].

Investigation of biological role of Zn in cellular metabolism shows that about 10% of human protein binds to Zn, in addition to hundreds which carry Zn. More than 200 enzymes require it for its catalytic activity and it plays a role in immune function, wound healing, synthesis of protein, synthesis of DNA and in cell division [11,12]. Zn ions are bonded to the side chains of amino acid like aspartic acid, glutamic acid, cysteine and histidine [13]. The metal has a flexible three-dimensional geometry, which gives permission for proteins to change conformations to perform various biological function [13]. Zinc also performs catalytic, and structural roles in variety of chemical reactions [14].

■ Results and Discussion

In this study a benign zinc complex of Schiff base derived from benzil and cysteine has been developed in a simple condensation reaction. Characterization of the product reveals the formation of the Schiff base and the metal complex in good yield. IR spectra of the complex particularly at 1593.20 cm^{-1} suggest the formation of the Schiff base which is confirmed by ^{13}C peak at 172. The molecular mass at m/e value 417 agrees with the proposed structure as shown in scheme 1. TGA study shows the co-ordination of two water molecules with the metal. Fluorescence property of the complex has been studied and found active.

FT-IR

Figure 1 shows the FT-IR spectrum of L1 in KBr. Peaks were observed at 2927 cm^{-1} due to $\nu\text{ C-H}$, 2611 cm^{-1} due to $\nu\text{ S-H}$, 1396 cm^{-1} due to $\nu\text{ C=O sym}$, 1577.77 cm^{-1} due to $\nu\text{ C=N}$, frequency at 671 cm^{-1} for $\nu\text{ C-S}$.

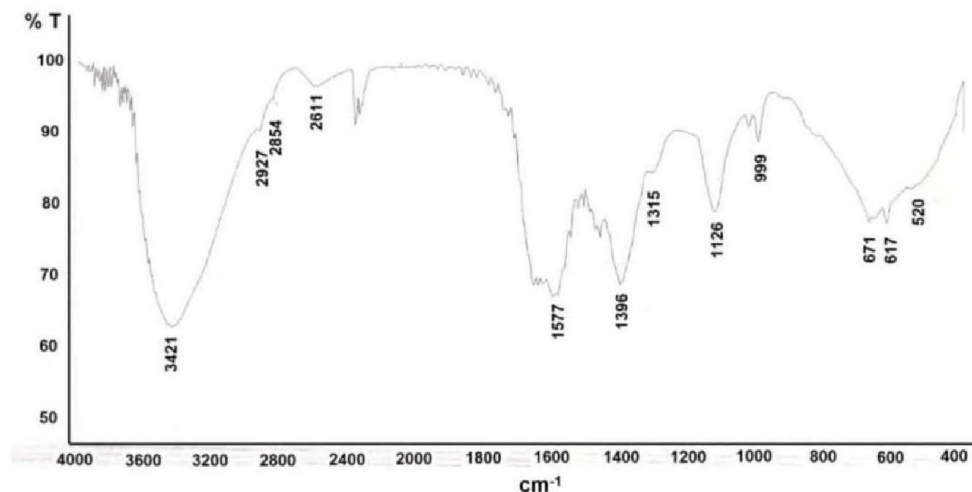


Figure 1. FT-IR spectrum of L1 in KBr.

ESI-MS analysis of L1

The ESI-MS spectrum of L1 has been reported in **Figure 2**. The molecular ion peak was observed at m/e value 417. The calculated value of mass of L1 according to Scheme 1 is 414. Thus, the structure of L1 has been confirmed as that shown in **Scheme 1**.

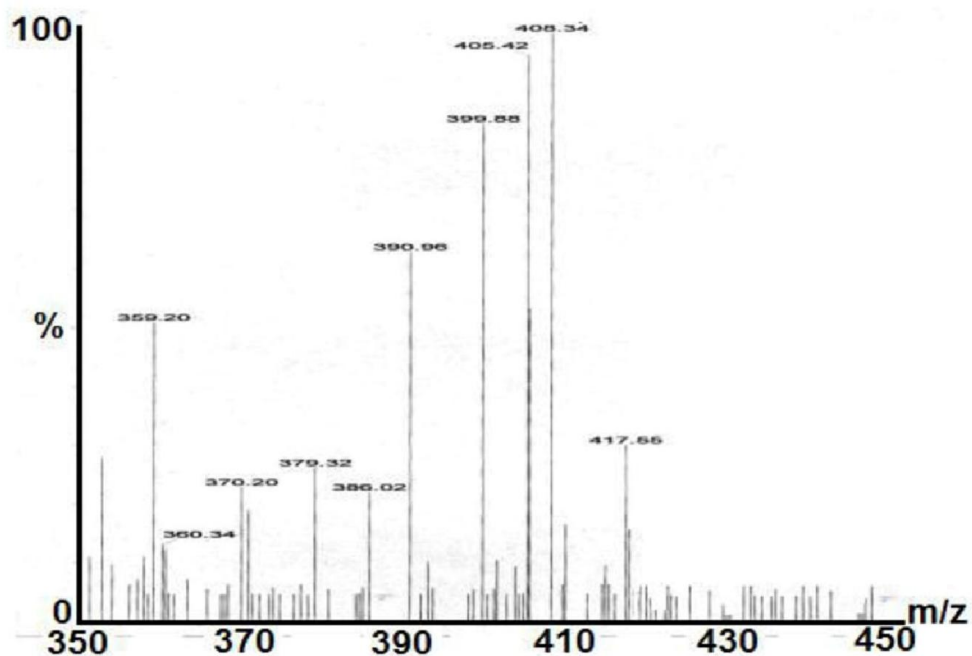
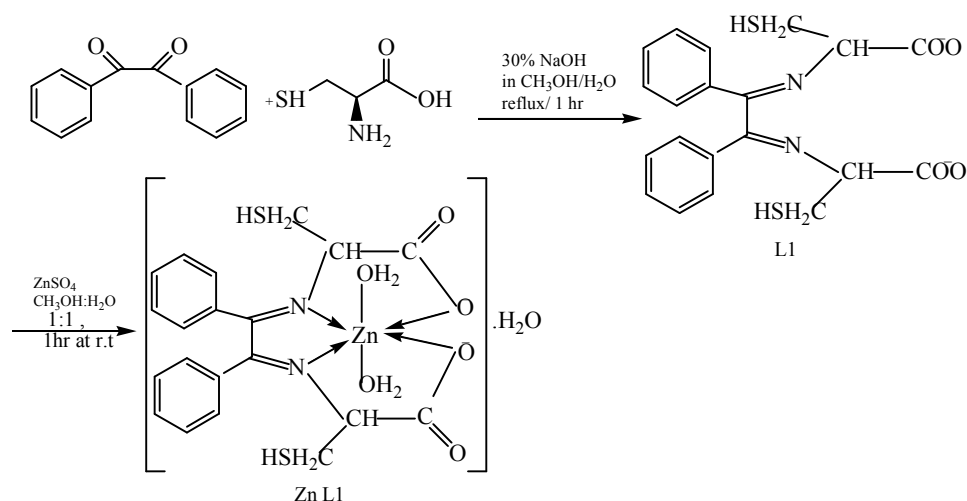


Figure 2. ESI-MS spectrum of L1 in MeOH.

Elemental analysis:

The elemental analysis of the Zn (II)L1 complex showed C=38,8% (39.0%), N=4.4% (4.64%), S=10.55% (10.61%), H=2.95% (2.98%), Zn=10.6% (10.65). The close proximity of the theoretically calculated values based on formula Zn (II)L1(H₂O)₂. H₂O with the experimental ones supports the structure as shown in

Scheme 1.**Scheme 1.** Zn complex structure.**FT-IR spectral analysis**

FTIR spectra was recorded for the Zn (II)L1(H₂O)₂.H₂O complex in KBr pallet. The FT-IR spectrum has been shown in **Figure 3**. Peaks were observed at 798.53 cm⁻¹, 852.54 cm⁻¹ due to ν_{C-H} out of plane vibration of phenyl ring; 1400.32 cm⁻¹ due to ν_{C-N} stretch which has been shifted from ligand ν_{C-N} showing coordination of zinc with N atom. Further the S-H band in free ligand at 2611 cm⁻¹ does not shift in the complex showing no zinc to S bonding.

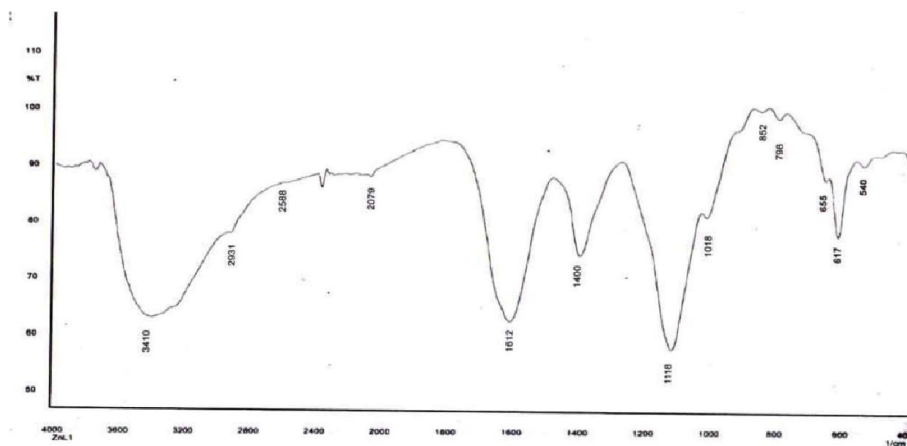


Figure 3. FT-IR spectrum of Zn (II)L1(H₂O)₂.H₂O complex in KBr.

ESIMS analysis

ESI-MS spectrum of Zn (II)L1(H₂O)₂. H₂O complex was recorded in CH₃OH. The spectrum has been shown in **Figure 4**. Molecular ion peak has been observed at *m/z* 524.99. The calculated molecular weight of the Zn (II)L1(H₂O)₂.H₂O complex as shown in Scheme II is 528.0 which confirms the proposed structure.

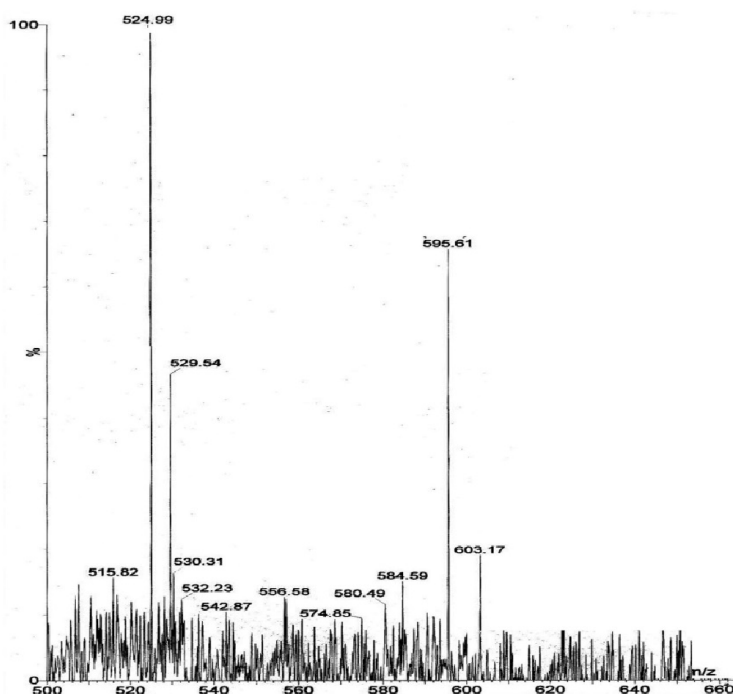
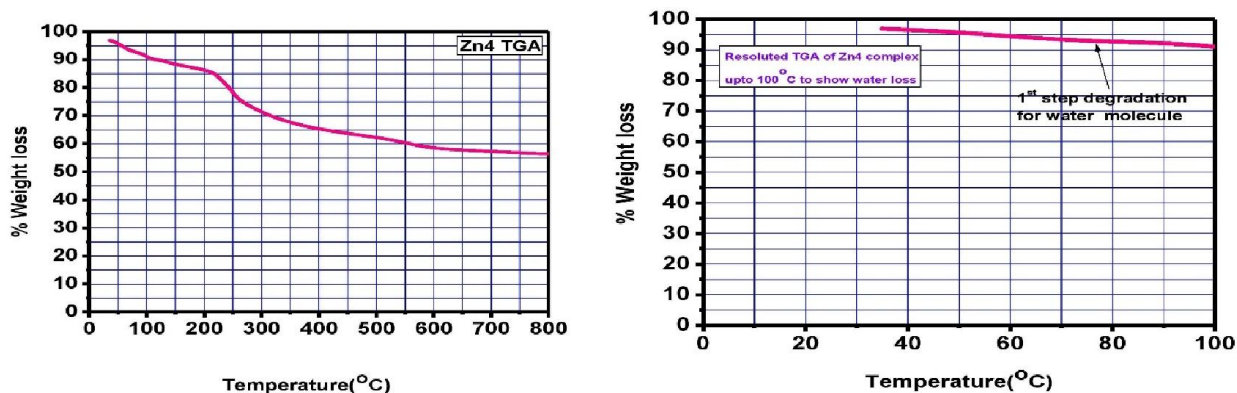


Figure 4. ESI-MS spectrum of Zn (II)L1(H₂O)₂. H₂O complex in CH₃OH.

TGA analysis of Zn (II)L1(H₂O)₂. H₂O

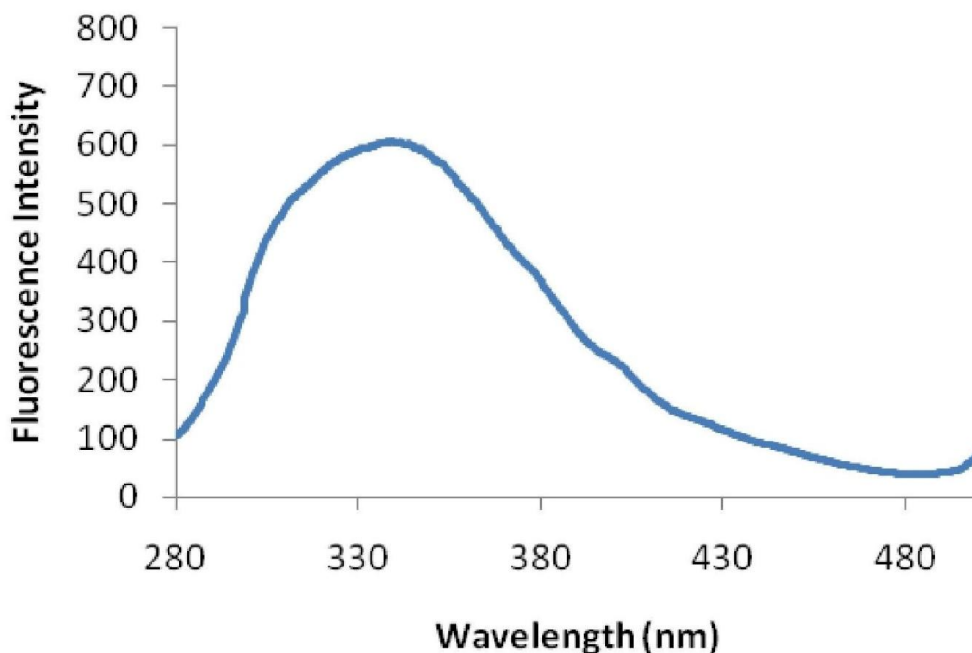
Figures 5 represent TGA thermograms of the ZnL1(H₂O)₂. H₂O complex and were recorded in non-oxidative nitrogen environment within the temperature range of 35°C to 800°C. The first 4% weight loss of the complex within the temperature range of 60°C – 100°C is due to the removal of the water molecule of crystallisation. Decomposition was observed from 100°C till 600°C with a total weight loss of 35%. This accounts for the loss of the two coordinated water molecules and decomposition of the ligand and formation of some Zn (II) compound with S of unknown composition.



Figures 5. TGA analysis of Zn (II)L1(H₂O)₂. H₂O complex.

Fluorescence property of ZnL1(H₂O)₂. H₂O

Fluorescence activity is widely applied in the field of imaging and diagnosing tumour and other disorders. The complex ZnL1(H₂O)₂. H₂O in CH₃OH when excited by 260 nm photon showed fluorescence emission peak at 338 nm. The ligand L1 did not show any fluorescence spectrum due to the presence of photoinduced electron transfer (PET) process but in ZnL1(H₂O)₂. H₂O binding of Zn (II) to L1 through $-COO^-$ snaps the PET process and hence the complex shows fluorescence property.



Figures 6. Fluorescence spectrum of $\text{ZnL1}(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}$ in CH_3OH when excited by 260 nm photon.

■ Conclusion

In this experimental work we have reported a new complex of Zn(II) with the ligand derived from condensation of benzil and cysteine. The complex has been characterized by Elemental, FT-IR, ESI-MS and TGA analysis. Zn(II) was coordinated by the ligand through a N_2O_2 coordination environment. Interestingly the S atoms present in the ligand did not bind to Zn(II). The complex was found to show fluorescence spectrum with very high intensity.

■ Experimental

Synthesis of the Ligand (L1)

L1 is a condensation product between benzil and cysteine. 2.1 g benzil (0.01 mol) and 2.42 g cysteine (0.02 mol) were taken in 1:2 (v/v) $\text{CH}_3\text{OH}:\text{H}_2\text{O}$. Few drops of 30% NaOH was added and stirred well to dissolve cysteine completely. The mixture was refluxed for 1 hour. Brown coloured product was obtained which was filtered, washed with water and dried. Yield: 60%, Melting point: 268°C- 270°C, Solubility: CH_3OH .

Synthesis of Zn (II)L1(H₂O)₂. H₂O complex

1.0 g (0.0029 mol) of L1 was dissolved in 1:1 (v/v) CH₃OH:H₂O. 0.39 g (0.0025 mol) of ZnSO₄ was added and stirred for 1 hour at room temperature. Yellow coloured precipitate was obtained which was filtered and washed with water and dried. Yield: 1.4 g. Solubility: CH₃OH.

¹H NMR analysis of L1

Aromatic H is between 7-8 ppm, 1.8 ppm due to S-H proton. In between these two peaks methylene proton peak was observed.

¹³C NMR analysis of L1

¹³C NMR of L1 was recorded in DMSO-d₆ and the spectrum has been shown in **Figure 7**. The peak around 172 is due to C=N.

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