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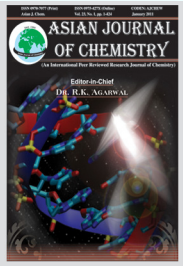

Synthesis, Spectral and Thermal Properties of Cu(II) Complex of Schiff Base Derived from Salicylaldehyde and 1,2,3,4-Thiatriazole-5-ylamine

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Schiff base ligand [2-(1,2,3,4-thiatriazole-5-yliminomethyl)-phenol] (L) was synthesized by condensation reaction of 1,2,3,4-thiatriazole-5-ylamine and salicylaldehyde. 1,2,3,4-Thiatriazole-5-ylamine is derived from thiosemicarbazide. The synthesized ligand was found to be potential ligand towards transition metal ions. The reaction of copper(II) salt with Schiff base ligand (L) resulted in the formation of a solid complex $[Cu(II)(L)_2]\cdot 2H_2O$. The ligand and the complex were characterized through elemental analysis, IR, UV-vis and ^1H NMR spectroscopies. The thermal property of the complex was studied by thermogravimetric analysis.

Key Words: Schiff base, Transition metal complex, Thiosemicarbazide, Salicylaldehyde, 1,2,3,4-Thiatriazole-5-ylamine.

INTRODUCTION

The Schiff bases have found wide applications in the field of coordination chemistry. Schiff base ligands containing strong donor sites like phenoxy oxygen atoms, imine nitrogen atoms and sulphur atoms are excellent for catalysis and biological replication for their special coordination ability with transition metal ions[1,2]. Transition metal complexes of Schiff base ligands have increased interest in the field of biological and magneto chemistry due to their key roles in many applications such as antibacterial, antiviral and antifungal agents[3-5]. Schiff bases are potential anticancer drugs and when administered as their metal complexes the anticancer activity of such complexes is enhanced in comparison to the free ligand[6,7]. Schiff base macrocyclic ligands based on thiosemicarbazone and their complexes have received considerable attention, because of their pharmacological properties[8-10]. They can yield mono or polynuclear complexes, some of which are biologically relevant[11-14]; *e.g.*, some Cu complexes can serve as models for enzymes such as galactose, oxidase and may be used as effective oxidant and redox catalysts[15,16]. Furthermore they allow selective complexation and extraction of metallic cations and anions of biochemical and environmental importance[17-20].

Thiadiazoles[21,22], triazoles[23,24] and their derivatives are also known for there biological activities[25,26]. Mesoionic oxatriazoles, thiatriazoles and tetrazoles, due to interesting structure, attract attention of chemists. The derivatives of mesoionic 1,2,3,4-thiatriazole imine have been investigated as multicentre ligands[27-29]. Compounds containing mesoionic 1,3-diphenyl-5-imino-1,2,3,4-tetrazole moiety were investigated as high energy molecules[30-32]. Recently, derivatives of mesoionic 5-phenylimino 1,2,3,4-oxatriazole imine have been examined as nitrogen oxide carrier agent in pharmacology[33,34].

However, the Cu(II) complex of Schiff base ligand (L) derived from salicylaldehyde and 1,2,3,4-thiatriazole-5-ylamine was not examined. In present communication, synthesis, spectral and thermal properties of ligand and Cu(II)complex are incorporated. The thermal decomposition products of the complex formed from nitrogen-sulphur containing ligand are apparently of significance in understanding the biochemistry of the compound[35].

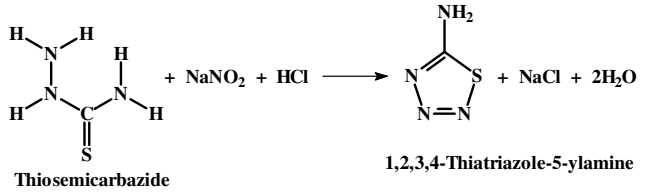
EXPERIMENTAL

Thiosemicarbazide, sodium nitrite, hydrochloric acid, salicyaldehyde, cupric chloride, N-methyl pyrrolidone (NMP), methanol, ethanol *etc*., analytical grade (Sigma Aldrich).

General procedure

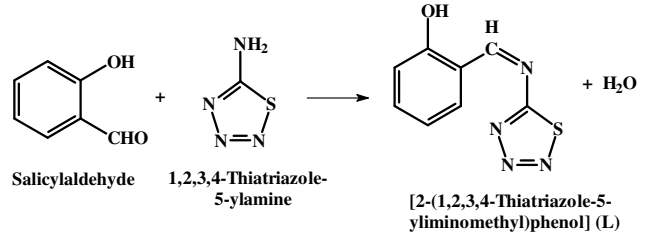
Synthesis of 1,2,3,4-thiatriazole-5-ylamine: Thiosemicarbazide (20 g) was dissolved in 95 mL of 2.2 (N) HCl in round bottom flask and sodium nitrite (14.7 g) was dissolved in 150 mL of distilled water separately. Both the solution was cooled in an ice bath for 1 h. Then sodium nitrite solution was added drop wise into the thiosemicarbazide solution with constant stirring in cold condition, off white product was

precipitated out. The product obtained was filtered and washed with ice cold water. The crude product was dried and recrystallized from methanol. Fine needle shaped, colourless product is obtained. The reaction is as shown in **Scheme-I**. Yield: 85 %, anal. calcd. (%) for CH_2N_4S: theo. C, 11.76; H, 1.97; N, 54.86; S, 31.40; expt. C, 12.02; H, 1.99; N, 56.84; S, 31.35; FT-IR (KBr, ν_{max}, cm^{-1}): (N-H stretching) 3418.2, 3263.7 and 3138.2; (>C=N and N=N stretching vibration) 1621.4, 1517.3; (>N-N=N- stretching in ring) 1337.4, 1112.9; (N-H wagging) 945.1; (C-S) 684.9. UV-vis (λ, nm): 260 ($n\rightarrow\pi^*$-NH_2 attached to thiatriazole ring). ^{1}H NMR (DMSO-d_6, ppm) δ: 3.36 (DMSO-d_6 in water), 8.2-8.5 (-NH_2, 2H, s).



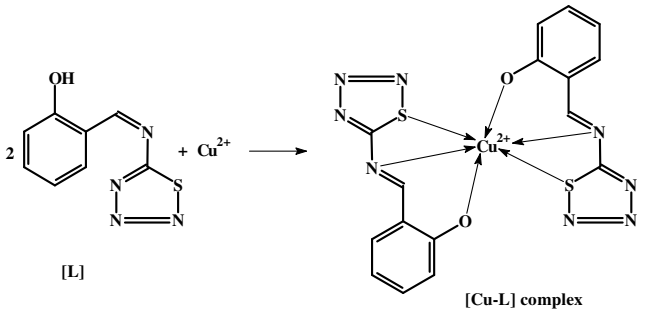
Scheme-I: Synthesis of 1,2,3,4-thiatriazole-5-ylamine

Synthesis of Schiff base ligand [2-(1,2,3,4-thiatriazole-5-yliminomethyl)-phenol] [L]: Schiff base ligand (L) was synthesized by condensation of salicyaldehyde and 1,2,3,4-thiatriazole-5-ylamine (1:1 molar ratio) in acidic medium by refluxing reaction mixture at 50-60 ºC with controlled temperature for 1 h. The yellow coloured product was precipitate out. The product obtained was filtered and vacuum dried. The reaction is as shown in **Scheme-II**. Yield: 80 %, anal. calcd. (%) for $C_8H_6N_4OS$: theo. C, 46.59; H, 2.93; N, 27.17; S, 15.55; expt. C, 46.52; H, 2.93; N, 27.22; S, 15.52; FT-IR (KBr, ν_{max}, cm^{-1}): (-OH intermolecular H-bonded) 3425.6; (=C-H stretching) 2937.8; (>C=N and -C=C- stretching vibration of ring) 1540-1620.9; [(C-N) + (N-S-C) + (N-N=N) stretching of ring of the ligand] 1458.2-1422.2; (C-O stretching) 1288.6; (C-S) 751.4. UV-vis (λ, nm): 248, 270 ($p\rightarrow\pi^*$ and $n\rightarrow\pi^*$ thiatriazole ring) ^{1}H NMR (DMSO-d_6, ppm) δ: 7.53 (1H, s, CH=N), 6.46-7.21(4H, m, Ar-H), 4.48 (1H, s,-OH).



Scheme-II: Synthesis of [2-(1,2,3,4-thiatriazole-5-yliminomethyl)-phenol] [L]

Synthesis of copper(II) complex with ligand [Cu-L]: Hydrated cupric chloride was dissolved in N-methyl pyrrolidone. The clear solution of copper(II) chloride and the ligand (L) were mixed in 1:2 molar ratios. The solution is acidified by adding 1-2 drop conc. HCl and refluxed on an oil bath. The dark green complex was precipitated out gradually. The product formed was washed with hot double distilled water to remove excess of metal present in the reaction and finally dried in vacuum oven at 60 ºC. The reactions occurred is as shown below in **Scheme-III**. Yield: 80 %, anal. calcd. (%) for $C_{16}H_{12}N_8S_2O_4Cu$: Theo. C, 40.37; H, 2.54; N, 23.54; %S, 13.47; Cu, 13.35 expt. C, 40.01; H, 2.59; N, 23.88; S, 13.42; Cu, 13.02. FT-IR (KBr, ν_{max}, cm^{-1}): (=C-H stretching) 2927.8; (aromatic C=C) 1650.9; (>C=N stretching in ring) 1454.2, (C-S) 668. UV-vis (λ, nm): 619 (conjugation increases of thiatriazole goes towards visible region), 365 (N=N), 260 (CH = N), 253 (C=C of benzene). ^{1}H NMR (DMSO-d_6, ppm) δ: 6.52-7.66 (4H, m, Ar-H), 7.84 (1H, s, CH=N).



Scheme-III: Synthesis of [Cu-L] complex

Microanalyses were carried out using VARIOEL elemental 'EL' CHNS/O elemental analyzer. The infrared spectra of the ligand and complex were recorded on a Perkin Elmer infrared spectrophotometer RX-I in KBr in the range of 4000-400 cm^{-1}. ^{1}H NMR spectra were recorded in DMSO-d_6 by Bruker-400 FT-NMR spectrophotometer. Electronic spectra were recorded on a Cary-5000 UV-visible NIR spectrophotometer. The thermal behaviour of the complex was investigated using Universal V4.2E, TGA 2950 TA Instrument USA in the range of 30-1000 ºC in nitrogen atmosphere at a heating rate of 10 ºC min^{-1}.

RESULTS AND DISCUSSION

The Schiff base ligand [2-(1,2,3,4-thiatriazole-5-yliminomethyl)-phenol] (L) has been synthesized by condensation reaction of salicylaldehyde and 1,2,3,4-thiatriazole-5-ylamine. 1,2,3,4-Thiatriazole-5-ylamine was derived from thiosemicarbazide. The reaction of cupric chloride with Schiff base ligand (L) yielded dark green complex compound. Elemental analysis indicates that [Cu-L] complex is formulated as $ML_2{\cdot}2H_2O$. The complexation of Cu(II) salt with the synthesized ligand (L) is further supported by spectral and thermal analysis.

FTIR spectra of the ligand [L] and its copper(II) complex [Cu-L]: The FTIR spectrum of the 1,2,3,4-thiatriazole-5-ylamine in KBr pallet shows bands at 3418, 3263 and 3138 cm^{-1} are due to NH_2- stretching attached to thiatriazole ring. The bands located at 1621 and 1517 cm^{-1} assigned to the >C=N and N=N stretching vibration, respectively. The FTIR band located at 1337 and 1113 cm^{-1} are due to >N-N=N- stretching in ring. The presence of band at 945 and 685 cm^{-1} are corresponding to N-H and C-S wagging. The FTIR spectrum of Schiff base ligand [2-(1,2,3,4-thiatriazole-5-yliminomethyl)-phenol] (L) shows a broad band with a medium intensity at 3425 cm^{-1}, assignable to hydrogen bonded -OH group. In case of Cu(II) complex, very weak intensity band in the region

3500-3300 cm^{-1} observed indicate that the -OH group of ligand involved in coordination with Cu(II) ion. In ligand (L) the band observed at 2938 cm^{-1} may be due to =C-H stretching of aromatic ring. In the spectra of complex [Cu-L], small shift of band of =C-H stretching from 2938 cm^{-1} to 2929 cm^{-1} shows that the OH-group of phenol of ligand (L) is involved in complexation. The band at 1621-1540 cm^{-1} attribute to -C=N- and -C=C- stretching vibration of thiatriazole ring. The FTIR spectra in the range of 1458-1422 cm^{-1} may be due to [ν(C-N), ν(N-S-C), ν(N-N=N)] stretching of thiatriazole ring of the ligand (L)[36], which is shifted to higher frequency region in the IR spectra of [Cu-L] complex between 1710-1643 cm^{-1} which indicates that the coordination of ligand occurred through S-atom of thiatriazole and N-atom of imine group of the ligand (L)[37,38]. The band at 1289 cm^{-1} of ligand (L) correspond to C-O stretching vibration is also shifted to higher frequency region due to complexation with Cu(II) ion. The band at 751.4 cm^{-1} is due to bending vibration of -C-S in a ring of ligand (L) shifted towards the lower frequency region 668 cm^{-1} and intensity of band is also reduced in the FTIR spectra of [Cu-L] complex.

UV-Visible study of the ligand and its Cu(II) complex: The electronic spectra of ligand and complex compound are also supported towards formation of ligand (L) and [Cu-L] complex. Absorption spectrums of the compounds were recorded using DMF as a solvent in the range of 270-900 nm. The absorption band near 260 nm was observed in the absorption spectra of 1,2,3,4-thiatriazole-5-ylamine may be assigned due to $n\rightarrow\pi^*$ transitions of $-NH_2$ group attached to thiatriazole ring. The band absorbed at 265 and 278 nm in case of [2-(1,2,3,4-thiatriazole-5-yliminomethyl)-phenol] may be due to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transition which is characteristic of >C=N- and absorption band at 320-340 nm may be due to *o*-substituted phenol ring, which causes an increase in conjugation in the 1,2,3,4-thiatriazole-5-ylamine molecule and thus lowers the $\pi\rightarrow\pi^*$ transition. Whereas in case of complex compound of Cu(II) ion the band at 260-270, 335-365 and 580-620 nm with broad envelop and low extinction most likely due to $\pi\rightarrow\pi^*$, $n\rightarrow\pi^*$ and d-d transition or charge transfer of complex compound, originate from metallization enforced by the chealated Cu(II) ion which can readily increase conjugation and delocalization of the whole electronic system and result in the observed energy level change of the $n\rightarrow\pi^*$ transition of the conjugated chromophore[39-41].

^{1}H NMR spectral study of the ligand and its copper(II) complex: The ^{1}H NMR spectrum of 1,2,3,4-thiatriazole-5-ylamine using DMSO-d_6 as solvent shows only one proton signal as a singlet at 8.2-8.5 ppm ($-NH_2$, 2H) of amino proton resonance. In case of NMR spectra of ligand [2-(1,2,3,4-thiatriazole-5-yliminomethyl)-phenol] (L) (Fig. 3b) three well resolved proton signals as a singlet at 7.53 ppm (CH=N, 1H), a multiplets at 6.46-7.21 ppm (Ar-H, 4H) and a singlet at 4.48 ppm (-OH, 1H) have been observed. Where as ^{1}H NMR spectra of [Cu-L] complex shows a multiplets at 6.52-7.66 ppm for aromatic protons and a singlet at 7.84 ppm for -CH=N proton as observed in case of ligand (L). The shifting of -CH=N- protonic peak towards low field and disappearance of -OH peak of ligand in the ^{1}H NMR spectrum Cu(II) complex indicates that coordination of complex occurs through imine and -OH group of ligand.

Thermoanalysis

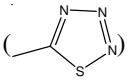
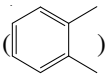
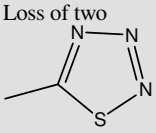
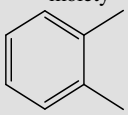
Thermogravimetric analysis of [Cu-L] complex: The thermogravimetric (TG) curves, which characterize the thermal decomposition of the complex $[Cu(II)(L)_2]\cdot 2H_2O$ in nitrogen atmosphere at a heating rate of 10 ºC min^{-1}. Examination of the TG curves reveals that the decomposition of Cu(II) complex occurred in four steps. In first step, there is mass loss from 100-120 ºC (obsd.: 17.27 %; calcd.: 17.66 %), which may be due to elimination of water molecule ($2H_2O$) and two -CH=N- moiety. In second step weight loss from 180-240 ºC (obsd.: 51.17 %; calcd.: 51.47 %). It may be due to loss of two () moiety. At third step gradual mass loss from 300-700 ºC (obsd.: 81.01 %; calcd.: 81.86 %) may be due to mass loss of two () moiety. The residue obtained corresponds to Cu_2O (obsd.: 28 %; calcd.: 28 %). It can be seen clearly (Table-1) that the mass losses obtained from the TG curves and that calculated for the corresponding molecules are in good agreement.

TABLE-1
THERMAL DEGRADATION PATTERN OF COMPLEX (Cu-L)

Temperature range (ºC)	Species degraded	Weight loss (%)	
		Found	Calcd. (%)
100-120	Loss of 2 H_2O molecule and two -CH=N- moiety	17.27	17.66
180-240	Loss of two  moiety	51.17	51.47
300-700	 Loss of two moiety	81.01	80.86
Above 750	Cu_2O formation (residue)	28.00	28.00

Conclusion

Schiff base ligand [2-(1,2,3,4-thiatriazole-5-yliminomethyl)-phenol] (L), obtained from the condensation reaction of 1,2,3,4-thiatriazole-5-ylamine (derived from thiosemicarbazide) and salicylaldehyde. Cu(II) complex has been synthesized using the Schiff base ligand (L). Based on spectral and analytical data the molecular formula of the Cu(II) complex is found to be $[Cu(II)(L)_2]\cdot 2H_2O$, which is also supported by thermal decomposition of the [Cu-L] complex through thermogravimetric analysis.

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