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Synthesis, Characterization and SEM Analysis of 5-methyl-4-[(E)-(phenylmethylidene) amino]-4H-1,2,4-triazole-3-thiol and Its Metal Complexes with Cd(II) and Hg(II)

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ABSTRACT

The Schiff base containing triazole moiety and their derived metal complexes are widely studied due to their structural features and biological activities. In present work, the aldimine ligating molecule, 5-methyl-4-[(E)-(phenylmethylidene) amino]-4H-1,2,4-triazole-3-thiol (HL) and their complexes with bivalent cadmium and mercury ions have been synthesized. The structure of the compounds has been elucidated by conductivity data, microanalytical analysis and spectral techniques. The composition of complex is found to be $[M(L)_2]$ where M = Cd(II) & Hg(II) and L = deprotonated ligand. The proton NMR and vibrational spectra of the compounds indicates that HL is bidentate and metal binds to ligand utilizing aldimine N-atom and deprotonated sulfhydryl (SH) group. The surface morphology, grain size and texture of compounds as well as evidence of complex formation have been obtained by Scanning Electron Microscopy (SEM) analysis. The surface morphology of ligand is smooth and homogeneous with cuboidal grains while complexes have heterogeneous rough morphology. The grains in complexes are agglomerated. The compounds prepared are microcrystalline.

Keywords: Synthesis, Schiff base, Ligand, Metal Complex, 1,2,4-triazole, IR, SEM.

INTRODUCTION

Schiff bases and their metal derivatives are quite proficient compounds which are easy to prepare and have various applications as biologically active materials, homogeneous & heterogeneous catalyst and optical sensors[1-11]. Schiff bases containing triazole moieties are central point in research due to their utility in pharmaceutical sector, polymer, sensors, corrosion inhibitor, metal-organic frameworks, functional and energetic materials[12]. Triazole derived aldimine ligands and their coordination complexes are widely studied due to their easeness of preparation, stability, structural diversity and bonding beauties[13-19]. Amino and mercapto substituted 1,2,4-triazoles and their metal derivatives provides exciting field of research in coordination chemistry due to their biochemical applications and diversified structural aspect[20-25].

This paper deals with synthetic route and structural investigation of Cd(II) and Hg(II) complex with 4-(benzylideneamino)-5-methyl-4H-1,2,4-triazole-3-thiol. The surface features have been studied by SEM.

MATERIALS AND METHOD

The chemicals and solvents used in the experiment were AR or ACS grade reagents. The conductivity was measured on Systronic Digital Conductivity meter 304 in DMF making M/1000 solution at 30°C. ^{1}H-NMR of the compounds were taken on 500 MHz NMR Spectrometer: JEOL ECZ500R/S1 in DMSO D6 solvent. The microanalytical analysis was performed by ELEMENTAR Vario EL III. The metal was estimated by standard procedure[26]. The FT-IR spectra of compounds in the range 4000 cm^{-1} to 400 cm^{-1} was taken using KBr pellets on FT-IR spectrometer: Thermo Nicolet iS50. SEM images taken by JEOL 6390LA/OXFORD XMXN up to magnification value of 3000X and optimum energy 20kV were used for analysis.

EXPERIMENTAL

Synthesis of 4-(benzylideneamino)-5-methyl-4H-1,2,4-triazole-3-thiol (HL)

The ligand HL was prepared by slight modification of reported method[27]. 4.7 g (0.045 mol) benzaldehyde and 5.8 g (0.045 mol) 4-amino-5-methyl-3-mercapto-4H-1,2,4-triazole was refluxed in 100 mL ethanol containing catalytic amount of acetic acid for 3 hours. On cooling, yellow crystals of desired product was obtained, filtered on suction, washed with cold ethanol thrice and dried in desiccator over $CaCl_2$. The crude product was recrystallized using hot ethanol. The schematic diagram of synthesis of ligand HL shown in Figure 1.

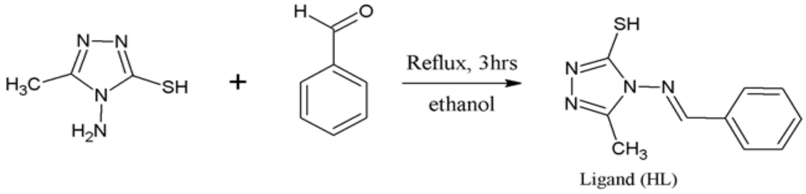

Fig. 1. Schematic diagram of synthesis of ligand HL

Synthesis of $[Cd(L)_2]$

Methanolic solution of 0.616 g, 2 mmol $Cd(NO_3)_2.4H_2O$ was dropwise added to hot methanolic solution of 0.872 g, 4 mmol ligand HL with constant stirring. The desired compound precipitated on raising the pH by adding ammonia, filtered, washed with methyl alcohol thoroughly and dried.

Synthesis of $[Hg(L)_2]$

Methanolic solution of 0.542 g, 2 mmol $HgCl_2$ was treated with 0.872 g, 4 mmol ligand dissolved in hot methyl alcohol. The desired compound obtained on making the solution alkaline by adding sodium acetate, collected on filter, washed with methyl alcohol thrice and dried.

RESULTS AND DISCUSSION

The synthesized products were non-hygroscopic and stable in oxygenated environment. The conductivity of compounds in DMF is in the range of non-electrolytes indicating that complexes are neutral compounds[28]. The microanalytical analysis is quite consistent with the composition proposed to metal complex. Table 1 presents the elemental analysis data and physicochemical properties.

Table 1: Elemental analysis and physicochemical data

Composition	Colour	Melting point(°C)	Found (Calculated) %					Conductivity
			C	H	N	S	Metal	(Ω^{-1}cm^{2}mol^{-1})
HL	Pale yellow	197	55.00(55.03)	04.95(04.62)	25.79(25.67)	14.58(14.69)	-	-
$[Cd(L)_2]$	Cream	250 d	43.85(43.92)	3.51(3.32)	20.61(20.49)	11.65(11.72)	20.30(20.55)	9
$[Hg(L)_2]$	Dull white	224 d	37.93(37.82)	2.90(2.86)	17.60(17.54)	10.16(10.10)	31.97(31.58)	8

d = decompose

Proton NMR spectra

The ^{1}H-NMR of HL and $[Hg(L)_2]$ in DMSO-D6 solvent are provided in Fig. 2 and 3 respectively.

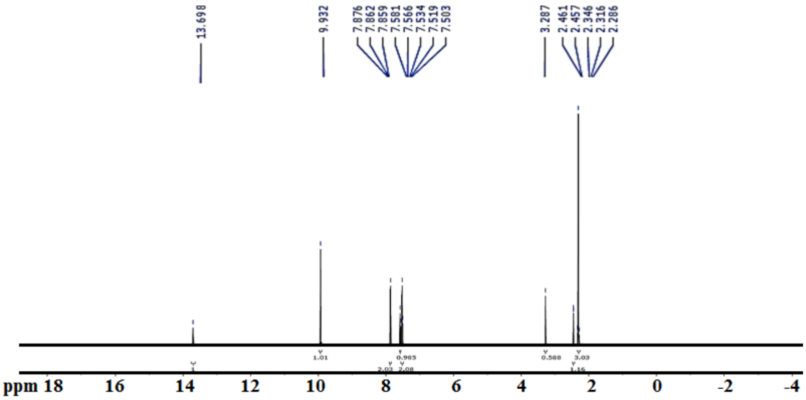

Fig. 2. ^{1}H-NMR of 4-(benzylideneamino)-5-methyl-4H-1,2,4-triazole-3-thiol (HL)

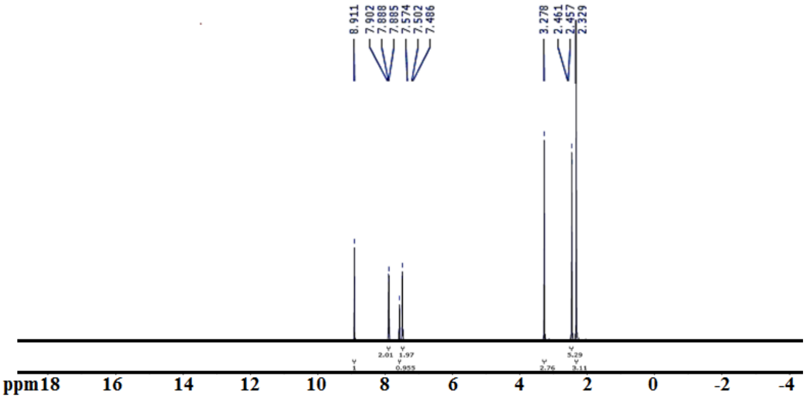

Fig. 3. ^{1}H-NMR of [Hg(L)$_2$]

The structure of ligand HL was accomplished by proton NMR. In the spectra, peak at 2.316 ppm is assigned to methyl group of triazole ring[29]. The multiplet observed at 7.503-7.876 ppm corresponds to aromatic protons on phenyl ring[30]. A singlet at, 9.932 ppm is associated with azomethine H-atom and small singlet at, 13.698 ppm is assigned to thiol H-atom[31]. The multiplets presents around 2.461 ppm and 3.287 ppm corresponds to DMSO-D5 1H and moisture present in DMSO-D6 respectively[32].

The complexation of Hg(II) ion with ligand HL was investigated through ^{1}H-NMR spectroscopy. In the spectra of complex, the singlet due to thiol proton disappeared which clearly indicates deprotonation of ligand and coordination via S-atom. All other peaks are present in complex with slight shift in position. The azomethine H-atom gives a singlet at 8.911 ppm in the spectra which shifts towards upfield due to coordination via N-atom which changes electronic environment which in turns changes the magnetic environment of proton[33]. The multiplet at, 7.486-7.902 ppm is assigned to aromatic-H of phenyl. The singlet observed at 2.329 ppm corresponds to CH_3 group proton of triazole ring[29]. The peaks at 2.461 ppm and 3.278 ppm is due to solvent impurity[32]. On the basis of NMR it can be clearly inferred that ligand HL coordinates to Hg(II) ion in [Hg(L)$_2$] as bidentate molecule through aldimine Nitrogen atom and deprotonated sulfhydryl group. The chemical shift values are provided in the Table 2.

Table 2: ^{1}H-NMR interpretation table

Chemical Shift (δ) in ppm	Assignments
Ligand (HL)	
2.316	3H, Singlet, CH_3
2.461	Solvent peak, DMSO-D^5 ^{1}H
3.287	Moisture in DMSO-D^6
7.503-7.876	5H, Multiplet, Aromatic-H
9.932	1H, Singlet, Azomethine-H
13.698	1H, Singlet, Thiol-H
[Hg(L)$_2$]	
2.329	3H, Singlet, CH_3
2.461	Solvent peak, DMSO-D^5 ^{1}H
3.278	Moisture in DMSO-D^6
7.486-7.902	5H, Multiplet, Aromatic-H
8.911	1H, Singlet, Aldimine-H

Infrared spectra

The mode of coordination of ligand HL in [Cd(L)$_2$] and [Hg(L)$_2$] has been studied through infrared spectroscopy. The tentative bands assignments have been tabulated in Table 3.

Table 3: IR frequencies and band assignment

Band assignments	IR frequencies (cm^{-1})		
	HL	[Cd(L)$_2$]	[Hg(L)$_2$]
O-H stretch (H_2O)	-	-	-
C-H stretch	3063.61 sb	2927.34 sb	3059.42 m
	2930.42 sb	2855.00 sb	2927.46 w
	2870.54 m		
S-H stretch	2749.79 m	-	-
-HC=N- stretch	1616.31 m	1613.56 m	1611.12 m
CH_3 bending	1444.92 s	1448.87 s	1448.09 s
C-S stretch	-	720 w	715 w
C-H out of	758.48 s	757.18 s	757.18 s
Plane bending	687.63 s	689.40 s	688.12 s
M-N stretch	-	480.81 w	474.07 w
M-S stretch	-	431.90 w	425 w

sb=strong & broad, s=strong, m=medium, w=weak

The synthesis of ligand HL was confirmed by a medium band at 1616.31 cm^{-1} which is assigned to azomethine (-HC=N-) stretching[34]. In complexes, this peak shifts towards lower frequency indicating formation of coordinate bonds via azomethine N-atom[35]. The medium intensity absorption peak at 2749.79 cm^{-1} in ligand spectra is assigned to S-H stretching. This peak is absent in the complexes revealing the deprotonation of ligand in complexes[36]. The various strong to medium bands present at 3063.61 cm^{-1}, 2930.42 cm^{-1} & 2870.54 cm^{-1} belongs to C-H vibrations. These peaks are present in complexes with slight shift in position and intensities[37]. The new bands present at 720 cm^{-1} and 715 cm^{-1} in Cd(II) & Hg(II) complexes corresponds to C-S stretching bands[38]. The appearance of new bands around 481-474 cm^{-1} in complexes is assigned to M-N stretch while bands around 425-432 cm^{-1} corresponds to M-S stretching band[39].

Scanning Electron Microscopy analysis

The SEM images of ligand HL and its complexes with Cd(II) and Hg(II) has been provided in Figure 4a, 4b & 4c.

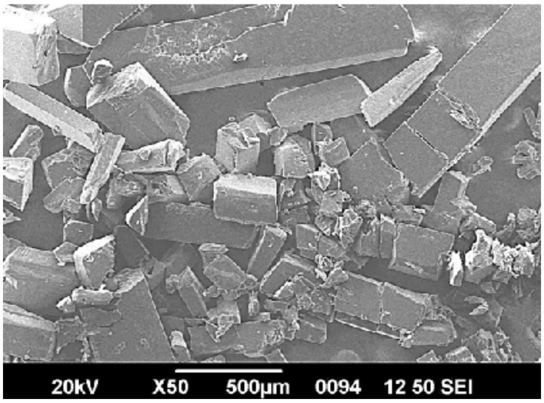

Fig. 4(a). SEM image of Ligand HL

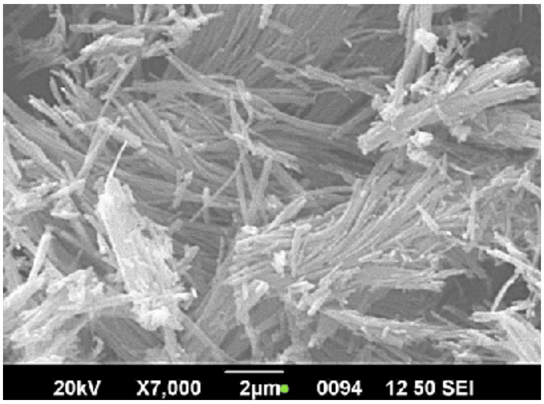

Fig. 4(b). SEM image of [Cd(L)$_2$]

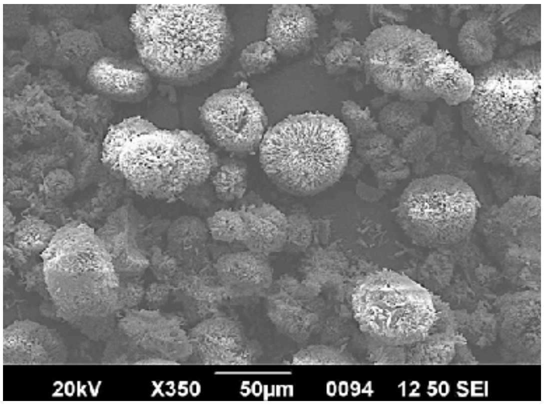

Fig. 4(c). SEM image of [Hg(L)$_2$]

The SEM images were studied to investigate the surface morphology, grain size & texture, composition and formation of complexes. The ligand HL has a smooth surface morphology with cuboidal shaped crystals. The crystals are of different sizes and have sharp edges[40].

The surface morphology of $[Cd(L)_2]$ and $[Hg(L)_2]$ is quite heterogeneous containing rough surface. The grains of Cd(II) complex are fibrous while Hg(II) is rod shaped. In both complexes grains are agglomerated[41-42]. The change in surface morphology and particle size of the complexes in comparison to ligand is providing evidence of complex formation[43]. The phase material present in the compound is homogeneous[44].

CONCLUSION

The ligating compound HL and its metal derivatives were obtained in solid state. The molar conductivity data, elemental analysis and spectral studies revealed the composition of complex is $[Cd(L)_2]$ and $[Hg(L)_2]$. The structure of ligand is established by NMR spectroscopy. The spectral analysis indicates that ligand HL is bidentate and coordinates to metal ions through azomethine N-atom and deprotonated thiol (SH) group. The confirmation of complex formation has been achieved by SEM analysis. The surface morphology, grain size and texture has been elucidated. The expected structure of complex is shown in Figure 5.

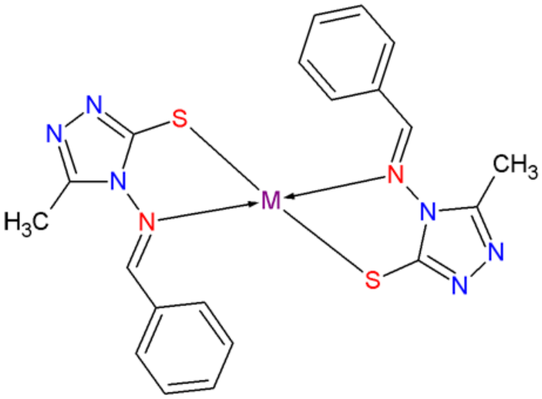

Fig. 5. Expected structure of the complex $[M(L)_2]$ where M=Cd (II) & Hg (II)

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Conflict of interest

The author declare that we have no conflict of interest.

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