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# Metal Complexes of Schiff Base: Synthesis, Characterization and Antibacterial Activity

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**ABSTRACT: A new metal complex derivatives of 2,4-diiodo-6-(((5-mercapto-1,3,4-thiadiazol-2-yl)imino)methyl)phenol, HL with the metal ions Cu(II), Zn(II) and Cd (II) have been successfully prepared in alcoholic medium. The complexes obtained are characterized quantitatively and qualitatively by using elemental analysis, FT-IR , UV–Vis spectroscopy, mass spectroscopy, $^{1}$H & $^{13}$C-NMR, magnetic susceptibility and molar conductance measurements. From the spectral study, all the complexes obtained as dimeric structure and the metals center moieties are six-coordinated with octahedral geometry. The preliminary *in vitro* antibacterial and antifungal screening activity revealed that some metal complexes showed moderate activity against tested bacterial *S. aureus* and *B. subtilis* and fungal strains *A. Niger* and *F. Oxysporum* slightly higher compared to the ligand, HL using Kirby-Bauer disc diffusion method.**

**Keywords:** Antibacterial activity; Antifungal activity; Metal Complexes; Magnetic Susceptibility; 1,3,4 Thiadiazole.

**INTRODUCTION:** Schiff bases derived from an amino (-$NH_2$) and carbonyl (>C=O) groups are an important class of ligands that coordinate to metal ions through azomethine nitrogen and have been studied largely. In azomethine derivatives, the C=N linkage is important for the biological activity, several azomethine has been noted that remarkable antibacterial, antifungal, antimalarial and anticancer activities[1]. 1,3,4-Thiadiazole derivatives having interesting and beneficial biological activity probably due to the strong aromaticity of this ring system , which leads to better in vivo stability and a lack of toxicity for higher vertebrates, including humans beings. When distinct functional groups that interact with biological receptors that are attached to this Thiadiazole ring, compounds possessing magnificent properties are obtained. Except for some antibacterial sulfonamides,no longer used clinically, but that possessed historical importance, the most interesting examples are given by 5-amino-l,3,4-thiadiazole-derivatives[2]. Further addition, the chemistry and the applications of these novel Schiff bases thiadiazoles containing moieties derivatives could be extensively study by coordinating to various metal ions. As a result, the structural activity relationship study of 1,3,4-thiadiazoles could be enlarge in the future[3-9].

Present study the synthesis and characterization of new complexes Cu (II), Zn (II) and Cd (II) of 2,4-diiodo-6-(((5-mercapto-1,3,4-thiadiazol-2-yl)imino) methyl)phenol. Moreover,the preliminary *in vitro* antibacterial and antifungal screening activities of the metal complexes obtained are carried out and the results are reported herein.

## MATERIALS AND METHODS:

**Experimental:** All chemical of analytical grade. All salts are metal nitrates i.e. Cd $(NO_3)_2.4H_2O$ $Cu(NO_3)_2.3H_2O$,$Zn(NO_3)_2.6H_2O$ were purchased from Sigma-Aldrich. 2-hydroxy-3,5-diiodobenzaldehyde and 5-amino-1,3,4-thiadiazole-2-thiol from Sigma-Aldrich and Alfa Aesar used without further purification. Dist. Ethanol used for synthesis of metal complexes and ligand diethyl ether (Sigma-Aldrich). IR Spectra recorded on Perkin Elmer Spectrometer in range 4000-400 $cm^{-1}$ KBr pellets. $^{1}$H and $^{13}$CNMR Spectra were recorded on BRUKER AVANCE III HD NMR 500 MHz spectrophotometer. Room Temperature magnetic moments by Guoy's method in B.M.

Electronic Spectra using DMSO on Varian Carry 5000 Spectrometer. Molar Conductance measurements in dry DMSO having $1\times10^{-3}$ concentration on Systronics conductivity bridge at room temperature. Elemental analysis (C,H,N) were carried out by using perkin Elmer 2400 elemental analyser.Mass Spectra were recorded on Bruker IMPACT HD.

**Biological Activity:** Schiff Base and their metal complexes evaluated in vitro their antibacterial activity against two bacteria,viz, *B. Subtilis*; *S. aureus*,Two fungal strains *A. niger and F. oxysporum* by Kirby-Bauer method[10].The fungal and bacterial strains sub-cultured on PDA and Nutrient Agar as a media. The stock solution was prepared in DMSO(1 mg $mL^{-1}$) solution. The stock solution again diluted by using sterilized water to dilute to 500 ppm. The bacteria were subculture in agar medium and disc were kept incubated for 37°C at 30 hrs. The standard antibacterial drug Miconazole and Ciprofloxacin was also screen under same condition for comparison of bioactivity. Activity was measure and calculated by zone of inhibition (mm) surrounding the discs. The experimental value compare with standard drug value Miconazole for the Antifungal activity and Ciprofloxacin for the antibacterial activity of ligand and its metal complexes.

**Synthesis of Schiff base Ligand:** The mixture of 1:1 2-hydroxy-3,5-diiodobenzaldehyde (3.73 g,0.01mol) with 5-amino-1,3,4-thiadiazole-2-thiol (1.33 g, 0.01 mol) dissolved in ethanol. Then add Few drops of glacial acetic acid was added .The resultant mixture stirred for 4-5 hrs the colored precipitate of Ligands was obtained. Wash with Ethanol recrystalised with Ethanol and Ether then dried. The purity of compound was checked by TLC using Silica Gel method (Fig.1).

**Synthesis of Metal Complexes:** The metal complexes were prepared by mixing of $Cd(NO_3)_2.4H_2O$ ,$Cu(NO_3)_2.3H_2O$,$Zn(NO_3)_2.6H_2O$, with (40 ml) ethanolic solution of Ligand in (metal: ligand) 1:2 stoichiometric ratio. the resulting mixture refluxed on water bath for 4-5 hrs. Colored product obtain washed with ethanol, filtered, and recrystalised with ethanol (Fig.2) name of the metal complexes is bis(2,4-diiodo-6-(-((5-mercapto-1,3,4-thiadiazol-2-yl)imino)methyl) phenoxy) cadmium dehydrate, bis(2,4-diiodo-6-(-((5-mercapto-1,3,4-thiadiazol-2-yl)imino)methyl) phenoxy) copper dehydrate, bis(2,4-diiodo-6-(-((5-mercapto-1,3,4-thiadiazol-2-yl)imino)methyl) phenoxy)zinc dihydrate.

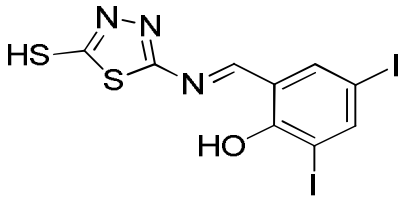


**Figure 1: Structure of Schiff base Ligands.**

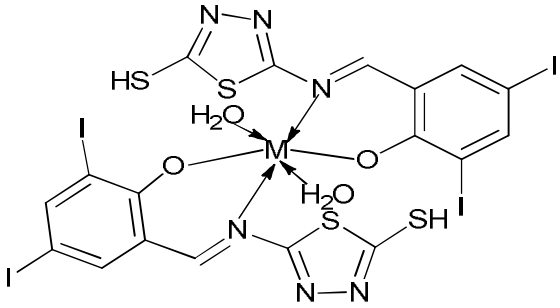


**Figure 2: Proposed Structures of metal complexes M: Cd(II),Zn(II) and Cu(II).**

**RESULTS AND DISCUSSION:** The ligand (Fig.1) 2,4-diiodo-6-(((5-mercapto-1,3,4-thiadiazol-2-yl) imino)methyl)phenol and its transition metal Cu(II),Zn(II) and Cd(II) complexes are stable at room temperature in solid state. The ligand is soluble in organic solvent DMSO, DMF and metal complexes are soluble in DMSO. The synthesized complexes having 1:2 metal to ligand stoichiometric ratio. The physical and analytical data shown in Table 1.Spectral analysis shows formation of ligand and its metal complexes**.**

**IR Spetra**: The IR spectra of 2,4-diiodo-6-(((5-mercapto-1,3,4-thiadiazol-2-yl)imino)methyl)phenol (HL) Schiff base ligand and its complexes are listed in Table 2.The IR data of ligand and complexes are compared to know the coordination site of ligand to metal to form chelate ring. (HL) Schiff base ligand Schiff base ligands having the most characteristic bands at 3310-3325 $cm^{-1}$ ν(O-H), 1620-1670 cm-1 ν(C=N, azomethine) and 1230-1290 $cm^{-1}$ν(C-O). The ligand showed bands at 3312-3322 and 1336-1348 $cm^{-1}$ due to the stretching and deformation of the phenolic –OH[11] these are absent in the spectra of the metal complexes indicates that deprotonation of the hydroxyl group (-OH) and co-ordination through phenolic oxygen of Aromatic ring. The band 1,641–1,650 $cm^{-1}$ due to the azomethine group of the Schiff bases have shifted to lower frequency (1,610–1,634 $cm^{-1}$) after complexes formation, indicating that donation of electron from nitrogen of the azomethine group to the empty vacant d-orbital metal ion[12,13] .The phenolic λ(C–O) stretching vibration at1,259–1265 $cm^{-1}$ in

Schiff bases shift to higher frequencies (18–32 $cm^{-1}$) in the metal complexes. This shift proved that participation of oxygen in the C–O–M bond in metal complexes. The occurrence of broad bands around at (3,372–3,450 $cm^{-1}$) in the spectra of complexes may be due to water molecules[14].Two new bands appearing in the low frequency range 518–580 $cm^{-1}$ and 458–490 $cm^{-1}$ are due to ν(M–O) and ν(M–N), respectively. The ν (C–S–C) at 750–754 $cm^{-1}$ of the Thiadiazole ring remain intact Thiadiazole ring directly does not take part in the donation of electron to the metal in metal complexes[15].

**$^{1}$H NMR and $^{13}$C NMR Spectra :** The spectra of ligands singlet at δ 7.18-8.10 ppm due to aromatic proton while azomethine (>C=N-) proton resonate at singlet δ 8.92 ppm the phenolic -OH has singlet at δ 11.50 ppm and Thiadiazole containing –SH group singlet at δ 13.21 ppm [16,17].

$^{13}$C NMR of Ligand, peak at δ159-165 ppm imine peak 183 ppm Due to C-SH bonding in Thiadiazole.123.96-141.75 ppm due to aromatic carbon,155-170 ppm peak due to Ar-OH group[18] shown in Table 3.

**Mass Spectra**: ligand peak at m/z 489 is M+H peak at 100% intensity this peak support to the structure formation of ligand.

**Magnetic Susceptibility and molar conductance:** The magnetic susceptibility measure at room temperature. Metal complexes of Zinc(II) and Cadmium (II) is Diamagnetic in nature while Cu (II) is paramagnetic in nature. Molar conductance of metal complexes was observed at room temperature in $1\times10^{-3}$M DMSO Solution. Show negligible molar conductance value in range 8-12 $ohm^{-1}cm^{2}mol^{-1}$results shows in table 4.All metal complexes are non-electrolytic in nature[19].

**Electronic absorption Spectra**: The electronic spectral data of the ligands and metal complexes in DMSO shown in Table 4. Geometry and Nature of the ligand field around the metal ion has been concluding from the electronic spectral data of metal complexes and ligand. The band at 220-315 is due to transition of benzene ring of the ligand. Band of free ligands 320-382 nm due to transition for phenolic -OH and azomethine moieties (-C=N-).These band shifts longer wavelength formation of ligand to metal complexes[20,21] The spectral data of the complexes band at 422-500 nm assigned to charge transfer transition from ligands to metal[17].The magnetic moment value for Cu (II) complexes is 1.82 B.M is close to octahedral complex spectra shows two band at 360 nm and 560 nm shows that octahedral geometry of Cu (II) complex[22]. Spectra of Zn (II) complexes shows band 266 nm,370-432 nm does not show d-d transition suggest octahedral geometry[23]. Spectra of Cd (II) shows two peak at 326 nm and 306-360 ligand to metal donation with diamagnetic suggest octahedral geometry[24].

**Antimicrobial activtity:** Antimicrobial activity In vitro of the ligand and their corresponding metal complexes on two gram positive *bacteria S. aureus and B. Subtlis* two fungi *A. niger* and *F. Oxysporum* was screened shown in table 5. The observation shows that Cu (II) shows more bactericidal and fungicidal activity than Zn (II) and Cd (II) Complexes as compare to ligand hence activity of metal complexes increases due to chelation enhance the penetration of complexes in lipid membrane of microbes and blocks the binding site enzymes of microorganism there are some other factors increases the activity of complexes i.e. M-L bond length solubility, lipophilicity/hydrophilicity and Conductivity.[15,25-29].

**Table 1: Analytical Data and physical properties of ligand and its metal complexes.**

| Comp. | Empirical Formula | Mol. Wt. | Color | M.P (°C) | Yield (%) | Elemental Analysis/ Found (Calc.) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | C | H | N | S | I | M |
| Ligand (HL) | Ligand $C_9H_5I_2N_3OS_2$ | 489 | Light Yellow | 208 | 75% | 23.50 (22.10) | 1.60 (1.03) | 7.98 (8.59) | 14.02 (13.11) | 52.03 (51.89) | -- |
| Cu(II) Complex | C18H12CuI4N6O4S4 | 1075 | green | >300 | 71% | 19.02 (20.10) | 1.33 (1.12) | 7.92 (7.81) | 11.62 (11.92) | 47.0 (47.19) | 5.22 (5.91) |
| Zn(II) Complex | C18H12I4N6O4S4Zn | 1077 | Lemon Yellow | >300 | 70% | 20.20 (20.06) | 1.08 (1.12) | 7.98 (7.80) | 11.83 (11.90) | 47.25 (47.11) | 5.97 (6.07) |
| Cd(II) Complex | C18H12CdI4N6O4S4 | 1124 | Gray | >300 | 69% | 19.08 (19.22) | 1.11 (1.08) | 7.96 (7.47) | 11.81 (11.40) | 47.56 (45.14) | 6.02 (5.69) |

**Table 2: Infrared Spectra of the Schiff base and Complexes in $Cm^{-1}$.**

| Compound | νOH/$H_2O$ | νC-O | νC=N | νM-N | νM-O | νC-S-C | ν-C=N-N=C | νN-N |
|---|---|---|---|---|---|---|---|---|
| Ligand | 3320 | 1267 | 1651 | ___ | ___ | 751 | 1479 | 1028 |
| Cu(II) Complex | 3471 | 1271 | 1623 | 484 | 584 | 757 | 1470 | 1039 |
| Zn(II) Complex | 3445 | 1291 | 1624 | 481 | 575 | 754 | 1487 | 1033 |
| Cd(II) Complex | 3444 | 1315 | 1604 | 484 | 549 | 753 | 1453 | 1026 |

**Table 3: $^1$H NMR Signals (δ, ppm) and their assignments.**

| Compound | $^1$H NMR Signals (δ,ppm) and their assignments |
|---|---|
| Ligand(HL) | 11.50 (s,1H,Ar-OH), 8.92 (s,1H,CH=N),7.18-8.10 (s,2H,Ar-CH), 13.21 (s,1H,SH) |

**Table 4: Electronic spectral Magnetic and Molar conductance Data.**

| Compounds | Wavelength in nm | Magnetic moment μeff (BM) | Molar conductance ($ohm^{-1}$ $cm^2$ $mol^{-1}$) |
|---|---|---|---|
| Ligands(HL) | 260,370 | -- | 6.68 |
| $C_{18}H_{12}Cl_4CuN_6O_4S_4$ | 270-320,360,560 | 1.82 | 8.1 |
| $C_{18}H_{12}Cl_4ZnN_6O_4S_4$ | 266,370-432 | Diamagnetic | 10.1 |
| $C_{18}H_{12}C_{l4}CdN_6O_4S_4$ | 265,306-360 | Diamagnetic | 12 |

**Table 5: Antimicrobial activity of ligand and its Metal Complexes.**

| Compounds | Antibactrial Activity | | | | Antifungal Activity | | | |
|---|---|---|---|---|---|---|---|---|
| | *S.aureus* | | *B.subtilis* | | *A.niger* | | *F.oxysporum* | |
| | Diameter of inhibition Zone in mm | % Activ-ity Index | Diameter of inhibition Zone in mm | % Activ-ity Index | Diameter of inhibition Zone in mm | % Activ-ity Index | Diameter of inhibition Zone in mm | % Activ-ity Index |
| | 500ppm | 500ppm | 500ppm | 500ppm | 500ppm | 500ppm | 500ppm | 500ppm |
| Ligands(HL) | 23 | 68 | 22 | 67 | 23 | 74 | 19 | 70 |
| Cu(II) | 26 | 76 | 26 | 79 | 26 | 84 | 21 | 78 |
| Zn(II) | 22 | 64 | 22 | 67 | 19 | 61 | 18 | 67 |
| Cd(II) | 19 | 56 | 21 | 64 | 21 | 68 | 12 | 44 |
| Ciprofloxacin (Standard) | 34 | 100 | 33 | 100 | -- | -- | --- | -- |
| Miconazole (Standard) | -- | -- | -- | | 31 | 100 | 27 | 100 |

**CONCLUSION:** The ligand, 2,4-diiodo-6-(((5-mercapto-1,3,4-thiadiazol-2-yl)imino)methyl)phenol HL was coordinated to three different metal ions via oxygen and nitrogen atoms to afford the corresponding complexes. All the complexes were six coordinated and exhibited octahedral geometry. Preliminary *in vitro* antibacterial study indicated that all the complexes obtained showed moderate to excellent activity against the tested bacterial strains and slightly higher activity compared to the ligand, HL.

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