

# SYNTHESIS, SPECTRAL AND BIOLOGICAL STUDIES OF TRANSITION METAL COMPLEXES OF DHA SCHIFF BASE DERIVED FROM 4-AMINO- 1, 2, 4- TRIAZOLE

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## Abstract:

The solid metal Complexes of Cu (II), Ni (II), Fe (III), Co (II) Mn (II) and Cd (II) with novel Schiff base ligand derived from DHA (3-acetyl-4-hydroxy-6-methyl-2H-pyran-2-one) and aromatic primary amine, 4-amino-1,2,4-triazole were synthesized and characterized by elemental analysis, FTIR, UV-VIS and <sup>1</sup>HNMR spectroscopic techniques. The signals of the <sup>1</sup>HNMR spectrum and important bands in IR spectra are considered and discussed in relation to the molecular structure of the ligand. The UV-VIS absorption bands are assigned to corresponding electronic transitions and are also studied by the magnetic studies. The biological (Anti-bacterial and Ant-fungal) activity of ligand and metal complexes have been screened *in vitro* against *Bacillus subtilis*, *Staphylococcus aureus*, *Aspergillus niger*, and *Candida albicans*. Schiff base ligand, as well as all metal complexes, have shown harmonious biological activities.

**Key words:** DHA, Schiff base, Metal complexes, Biological activity.

## I. INTRODUCTION

DHA (3-acetyl-4-hydroxy-6-methyl-2H-pyran-2-one) and its derivatives constitute an important class of compounds in organic synthesis, especially as starting material for the preparation of various heterocyclic systems viz. Schiff bases, Mannich bases, Chalcones, etc. Schiff bases are one of the most widely used chelating ligands in coordination chemistry.

Herein we describe the synthesis and characterization of the Schiff base derived from DHA(3-acetyl-4-hydroxy-6-methyl-2H-pyran-2-one) and aromatic primary amine, 4-amino-1,2,4-triazole as well as their synthesized metal complexes with Cu (II), Ni (II), Fe (III), Co (II), Mn (II), and Cd (II). The Schiff base and metal complexes are characterized by elemental analysis, FTIR, UV-VIS, and <sup>1</sup>HNMR spectroscopic techniques and their magnetic profiles are recorded and discussed herein. The biological (Anti-bacterial and Anti-fungal) activities of key ligand and its metal complexes have been screened *in vitro* against *Bacillus subtilis*, *Staphylococcus aureus*, *Aspergillus niger*, and *Candida albicans*.

## II. EXPERIMENTAL

DHA (3-acetyl-4-hydroxy-6-methyl-2H-pyran-2-one) for synthesis was procured from E-Merck, Germany, 4-amino-1, 2, 4-triazole was obtained from Avra and are used for the synthesis of Schiff bases. Metal chlorides were procured from E-Merck as well as from Loba chemie Pvt. Ltd. and used for the synthesis of metal complexes. The solvents were dried and distilled before use following literature reported procedure.[1]

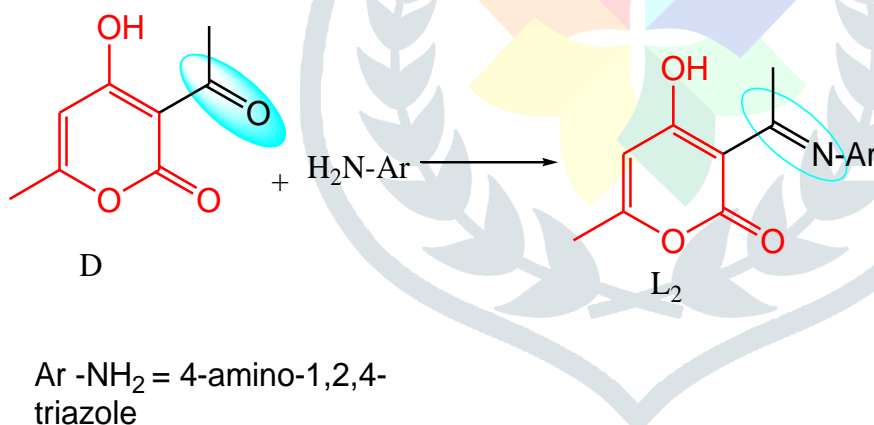
The C, H and N analyzed on Perkins Elmer CHN Analyzer (2400). The IR spectra of ligand and the metal complexes were recorded by KBr pellet method on Perkin Elmer (1430) FTIR spectrophotometer in the range 4000-400 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectrum of a ligand is recorded on Bruker FT-300 MHz NMR Spectrophotometer in CDCl<sub>3</sub> by using TMS as reference. The electronic spectral measurements were made

on Shimadzu UV–VIS Spectrophotometer UV160, Magnetic susceptibility measurement is carried out with the help of Gouy's balance at laboratory temperature by using Hg [Co(CNS)<sub>4</sub>] as standard. The biological (antibacterial and antifungal) activities of ligand and metal complexes were screened in vitro *Staphylococcus aureus* (NCIM-2079, *S. aureus*) and *Bacillus subtilis* (NCIM-2063, *B. subtilis*) as bacterial strains and *Candida albicans* (MTCC-227, *C. albicans*) and *Aspergillus niger* (NCIM- 545, *A. niger*) as fungal strains were used for the study of antibacterial activity. The suspensions in sterile peptone water from 24 h cultures of microorganisms were adjusted to 0.5 McFarland. Muller–Hinton Petri dishes of 90 ml were inoculated using these suspensions. Wells (6 mm in diameter) containing 100 µL of the substance to be tested (at a concentration of 1mg/mL in DMSO) were placed in a circular pattern in each using a ruler. Streptomycin was used as a reference substance. For antifungal activity, the same procedure was repeated with the replacement of peptone water with PBS (phosphates buffered saline) and Muller-Hinton medium with YPD (Yeast Peptone Dextrose) medium. Griseofulvin was used as a reference. The incubation of the plates was done at 37 °C for 24 h. Reading of the results was done by measuring the diameters of the inhibition zones generated by the tested substances. [2]

### III. SYNTHESIS

#### 3.1 Synthesis of Schiff Bases:

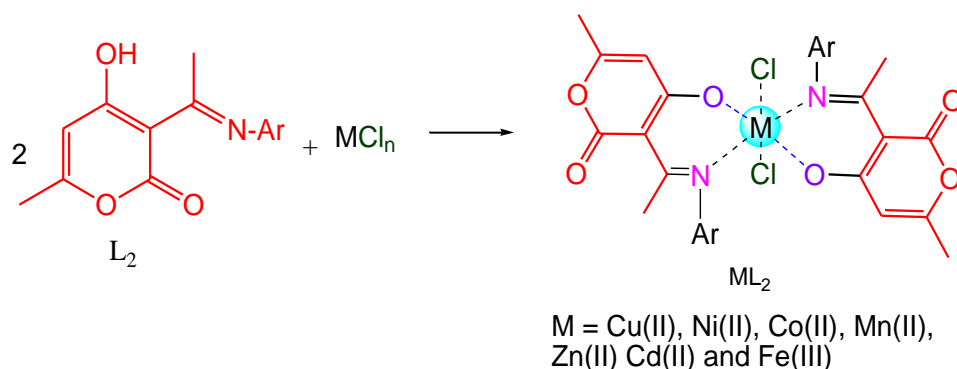
Schiff base motif was prepared by refluxing the ethanolic solution of 4-amino-1,2,4-triazole (0.05 mol ) with an ethanolic solution of DHA (0.05 mol) for 4 to 8 hours on rotamante. The Off white Schiff base separated out as solid on cooling subsequently followed by filtration and recrystallization in dry ethanol. The purity was ascertained by T.L.C. technique and melting point [3, 4]



**Fig.1. Scheme I synthesis of DHA Schiff base ligand.**

#### 3.2 Synthesis of Metal Complexes:

Methanolic solution (0.002 mol) of DHA Schiff bases derived from aromatic primary amine 4-amino-1,2,4-triazole refluxing with methanolic solution (0.001mol) of Cu(II), Ni(II),Fe(III),Co(II) and Mn (II) and Cd(II) metal chloride in 2:1 molar ratio yielded corresponding metal complexes after the addition of 10% methanolic solution of ammonia at different pH Solid metal complexes was filtered, washed with hot methanol and petroleum ether and dried over anhydrous Calcium Chloride in vacuum desiccators.



**Fig.2. Scheme II synthesis of transition metal complexes of DHA Schiff base ligand**

#### IV. RESULTS AND DISCUSSION

##### 4.1 Analytical data of synthesized motifs:

Synthesized Schiff base is off white solid, stable to air non-hygroscopic, insoluble in water and soluble in hot alcohols. The melting points determined by open capillaries. All the metal complexes were colored solids, stable to air non-hygroscopic (Table 1). They were insoluble in water, methanol, ethanol, but soluble in DMF and DMSO.

**TABLE1: Analytical data of synthesized motifs**

| Compound                       | Color     | F. Wt. | m. p. (°C) | Found (calculated) % |                |                  |                  |
|--------------------------------|-----------|--------|------------|----------------------|----------------|------------------|------------------|
|                                |           |        |            | C                    | H              | N                | M                |
| $L_2 \cdot C_{10}H_{10}N_4O_3$ | Off White | 234.00 | 120        | 51.18<br>(51.28)     | 4.30<br>(4.27) | 23.83<br>(23.93) | -----            |
| $Cu(C_{10}H_{10}N_4O_3)Cl_2$   | Green     | 638.47 | >250       | 37.8<br>(37.59)      | 3.20<br>(3.13) | 17.07<br>(17.54) | 9.91<br>(9.95)   |
| $Ni(C_{10}H_{10}N_4O_3)Cl_2$   | Greenish  | 597.70 | >250       | 40.08<br>(40.15)     | 3.22<br>(3.35) | 18.32<br>(18.74) | 9.9<br>(9.82)    |
| $Fe(C_{10}H_{10}N_4O_3)Cl_3$   | Brown     | 630.21 | >250       | 38.00<br>(38.08)     | 3.27<br>(3.17) | 17.31<br>(17.77) | 8.82<br>(8.86)   |
| $Co(C_{10}H_{10}N_4O_3)Cl_2$   | Pink      | 705.93 | >250       | 33.34<br>(33.99)     | 2.46<br>(2.83) | 14.49<br>(15.87) | 8.44<br>(8.35)   |
| $Mn(C_{10}H_{10}N_4O_3)Cl_2$   | yellowish | 522.94 | >250       | 45.53<br>(45.89)     | 3.65<br>(3.83) | 20.82<br>(21.42) | 10.53<br>(10.51) |
| $Cd(C_{10}H_{10}N_4O_3)I_2$    | Yellow    | 834.22 | >250       | 28.54<br>(28.76)     | 2.31<br>(2.39) | 13.15<br>(13.42) | 13.22<br>(13.47) |

##### 4.2 IR Spectra

The characteristic IR frequency of the ligand and metal complexes is shown in Table 2.

The IR spectrum of synthesized free ligand revealed a broad weak absorption band 3427 appear due to intramolecular hydrogen bonding of  $\nu$  (O-H---) The band at  $1719\text{cm}^{-1}$  assigned to  $\nu$  (C=O) lactone carbonyl,  $1646\text{cm}^{-1}$   $\nu$  (C=N) (azomethine),  $1358\text{cm}^{-1}$   $\nu$  (C-N) aryl azomethine &  $1256\text{cm}^{-1}$   $\nu$  (C-O) enolic. The vanishing of band at  $3400\text{--}3100\text{cm}^{-1}$  in the spectra of all complexes indicates deprotonation of enolic oxygen & azomethine nitrogen in to coordination to the metal ion. It further supported by downward shift in  $\nu$  (C=N) by  $3\text{cm}^{-1}$  from  $1646$  to  $1643\text{cm}^{-1}$  and  $15\text{cm}^{-1}$  from  $1646$  to  $1631\text{cm}^{-1}$  and upward shift in  $\nu$  (C-O) and  $\nu$  (C-N) azomethine indicate the involvement of azomethine 'N' and enolic 'O' in complex formation. The IR Spectra of the metal complexes showed new bands in the region  $650\text{--}540\text{cm}^{-1}$  &  $580\text{--}450\text{cm}^{-1}$  which can be assigned to  $\nu$  (M-O) &  $\nu$  (M-N) vibration. [5]

**TABLE 2: Characteristics IR Frequencies (Cm<sup>-1</sup>) of the Ligand and Their Metal Complexes**

| Compound  | $\nu(\text{C}=\text{O})$ | $\nu(\text{C}=\text{C})$ | $\nu(\text{C}=\text{N})$ | $\nu(\text{C}-\text{N})$ | $\nu(\text{C}-\text{O})$ | $\nu(\text{M}-\text{O})$ | $\nu(\text{M}-\text{N})$ |
|---|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| L <sub>2</sub> C <sub>10</sub> H <sub>10</sub> N <sub>4</sub><br>O <sub>3</sub> | 1719                     | 1559                     | 1646                     | 1358                     | 1256                     | ----                     | ----                     |
| Cu(II) L <sub>2</sub>   | 1709                     | 1567                     | 1640                     | 1371                     | 1269                     | 554                      | 470                      |
| Ni(II) L <sub>2</sub>   | 1714                     | 1558                     | 1639                     | 1367                     | 1265                     | 542                      | 485                      |
| Fe(III) L <sub>2</sub>  | 1701                     | 1579                     | 1637                     | 1373                     | 1267                     | 557                      | 467                      |
| Co(II) L <sub>2</sub>   | 1694                     | 1578                     | 1648                     | 1368                     | 1265                     | 546                      | 481                      |
| Mn(II) L <sub>2</sub>   | 1697                     | 1564                     | 1643                     | 1375                     | 1263                     | 558                      | 474                      |
| Cd(II) L <sub>2</sub>   | 1704                     | 1576                     | 1631                     | 1368                     | 1282                     | 598                      | 506                      |

#### 4.4 <sup>1</sup>HNMR:

The <sup>1</sup>HNMR spectra of ligand in CDCl<sub>3</sub> at laboratory temperature showed the signals at  $\delta$  (ppm) values for L<sub>2</sub> 2.28 (3H, s, C<sub>6</sub> – CH<sub>3</sub>), 15.85(1H, s, C<sub>3</sub>- H), 5.94 (1H, s, C<sub>5</sub>-H), 2.67 (3H, s, N=C-CH<sub>3</sub>) methyl hydrogen linked carbon azomethine, for DHA moiety 7.27(2H, s, C<sub>5</sub>-H) of triazole moiety.

#### 4.5 Magnetic moment and electronic absorption spectra

The magnetic moment and electronic spectral data shown (Table-3). The data is of significance for the projected structure of complexes. The electronic spectra of the Cu(II) complex in DMSO show three bands at 12953, 32154, and 40000 cm<sup>-1</sup> for ligand L<sub>2</sub> conveyable to <sup>2</sup>E<sub>g</sub>-> <sup>2</sup>T<sub>2g</sub> transition which is characteristic of distorted octahedral geometry. This further supported by magnetic moment value (1.81B.M.) within the required range for d<sup>9</sup>-system. [6] The electronic spectra of the Ni (II)-L<sub>1</sub> complex shows three bands in range 13422( $\nu_1$ ), 17543( $\nu_2$ ) and 34129( $\nu_3$ ) assigned to the transitions <sup>3</sup>A<sub>2g</sub> (F) -><sup>3</sup>T<sub>2g</sub> and a charge transfer transition, respectively, signifying octahedral geometry of the complexes[6-7]. Also, the magnetic nature supports the structure by the magnetic moment value (3.14B.M.). The electronic absorption spectrum of Co (II) complex had three bands in range 11627 ( $\nu_1$ ), 19607 ( $\nu_2$ ) and 24154( $\nu_3$ ) which may be endorsed to three spin-allowed transitions <sup>4</sup>T<sub>1g</sub> (F) -><sup>4</sup>T<sub>2g</sub> (F), <sup>4</sup>T<sub>1g</sub> (F) -><sup>4</sup>A<sub>2g</sub> (F) and <sup>4</sup>T<sub>1g</sub> (F) -><sup>4</sup>T<sub>2g</sub> (P), respectively, signifying an octahedral geometry<sup>6</sup>. The effective magnetic moment value (4.17B.M.) was found to be well within the range as expected for octahedral geometry. The electronic spectra Mn(II) complex showed three bands at 13513 cm<sup>-1</sup> ( $\nu_1$ ) and 16393 cm<sup>-1</sup> ( $\nu_2$ ) and 27027 cm<sup>-1</sup> ( $\nu_3$ ) assigned to transition <sup>6</sup>A<sub>1g</sub>-><sup>4</sup>T<sub>1g</sub> and <sup>6</sup>A<sub>1g</sub>-><sup>4</sup>T<sub>2g</sub>, respectively, indicating octahedral geometry. The magnetic moment value (5.31B.M.) which is slightly lower than the spin only value expected for octahedral Mn (II) complex .[7] This may be due to the presence of magnetic exchange and small traces of Mn (II) species. [8] The electronic spectra of the Fe (III) complex showed three bands at 13268 ( $\nu_1$ ), 21483 ( $\nu_2$ ) and 32185 cm<sup>-1</sup> ( $\nu_3$ ) assigned to transitions <sup>6</sup>A<sub>1g</sub>-><sup>4</sup>T<sub>1g</sub>(D), <sup>6</sup>A<sub>1g</sub>-><sup>4</sup>T<sub>1g</sub> and <sup>6</sup>A<sub>1g</sub>-><sup>4</sup>T<sub>1g</sub>, respectively and the magnetic moment value (4.95B.M.) signifying high spin octahedral geometry.[9,10,11,12,13]

**TABLE 3: Magnetic and electronic absorption spectral data (in DMSO) of the**

| Compound                | $\mu_{\text{eff}}$ | $\nu$ (cm <sup>-1</sup> ) | Geometry             |
|-------------------------|--------------------|---------------------------|----------------------|
| Cu(II) D L <sub>2</sub> | 1.81               | 12953, 32154, 40000       | Distorted Octahedral |
| Ni(II) L <sub>1</sub>   | 3.14               | 13422, 17543, 34129       | Octahedral           |
| Fe(III) L <sub>2</sub>  | 4.95               | 13268, 21483, 32145       | Octahedral           |
| Co(II) L <sub>2</sub>   | 4.17               | 11627, 19607, 24154       | Octahedral           |
| Mn(II) L <sub>2</sub>   | 5.31               | 13513, 16393, 27027       | Octahedral           |
| Cd(II) L <sub>2</sub>   | Diamagnetic        | 22988, 27397, 31446       | Octahedral           |

#### 4.6 Biological Evaluation

*In vitro* antibacterial and antifungal activity was screened by considering the zone of inhibition of growth. The synthesized compounds were screened and compared with standard antibiotics such as streptomycin (1 mg/mL) and Griesofluvin (1 mg/mL). It was found that metal complexes have good activity than ligand under similar condition.[14,15] All the compounds were found moderate in growth inhibition against *B. subtilis* with a maximum zone of inhibition 11 mm by compound Co L<sub>2</sub> and minimum zone of inhibition 6 mm by compound Ni L<sub>2</sub>. Compounds L<sub>2</sub>, Cu L<sub>2</sub> Fe L<sub>2</sub> Mn L<sub>2</sub>, and Cd L<sub>2</sub> were showed 10, 9, 8,8 and 7 mm

zone of inhibition. Against *S. aureus*. Compound Cu L<sub>2</sub> has showed maximum zone of inhibition 24 mm. Compound Co L<sub>2</sub>, Ni L<sub>2</sub>, L<sub>2</sub>, Mn L<sub>2</sub>, and Fe L<sub>2</sub> have shown 21, 18, 17, 15 and 14 mm zone of inhibition respectively while compound Cd L<sub>2</sub> showed a 12 mm zone of inhibition.

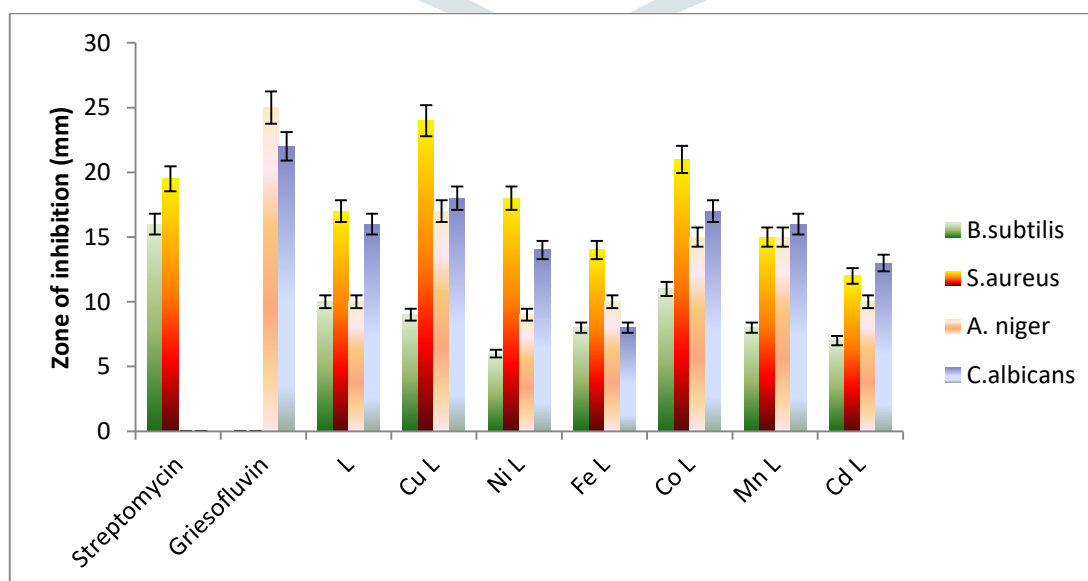
Compound Cu L<sub>2</sub> showed maximum zone of inhibition 17 mm, Co L<sub>2</sub> and Mn L<sub>2</sub> showed 15 mm, Compound L<sub>2</sub>, Fe L<sub>2</sub> Cd L<sub>2</sub> has shown 10 mm and lowest activity was showed by compound Ni L<sub>2</sub> with 9 mm zone of inhibition against *A. niger*.

The maximum zone of inhibition was shown by Compound Cu L<sub>2</sub> and Co L<sub>2</sub> 18 mm compound L<sub>2</sub> and Mn L<sub>2</sub> 16 mm Compound Ni L<sub>2</sub> and Cd L<sub>2</sub> showed 14 mm and 13 mm while Compound Fe L<sub>2</sub> showed minimum zone of inhibition; 8 mm against a human opportunistic pathogen, *C. albicans*.

**TABLE 4: Bioactivity screening data zone of inhibition in mm.**

| Sample              | <i>B.subtilis</i> <sup>b</sup> | <i>S.aureus</i> <sup>b</sup> | <i>A.niger</i> <sup>b</sup> | <i>C. albicans</i> <sup>b</sup> |
|---------------------|--------------------------------|------------------------------|-----------------------------|---------------------------------|
| <i>Streptomycin</i> | 16                             | 19.5                         | NA                          | NA                              |
| <i>Griseofulvin</i> | NA                             | NA                           | 25                          | 22                              |
| L <sub>2</sub>      | 10                             | 17                           | 10                          | 16                              |
| Cu L <sub>2</sub>   | 9                              | 24                           | 17                          | 18                              |
| Ni L <sub>2</sub>   | 6                              | 18                           | 9                           | 14                              |
| Fe L <sub>2</sub>   | 8                              | 14                           | 10                          | 8                               |
| Co L <sub>2</sub>   | 11                             | 21                           | 15                          | 18                              |
| Mn L <sub>2</sub>   | 8                              | 15                           | 15                          | 16                              |
| Cd L <sub>2</sub>   | 7                              | 12                           | 10                          | 13                              |

a. NA- Not applicable. b. Zone of inhibition in mm



**Fig. 3.** Graphical presentation antimicrobial activity of DHA Schiff base ligand and their transition metal complexes.

## V. CONCLUSION

From the analytical data composition of Schiff base ligand and their metal complexes were determined. The structure of ligand proposed was confirmed by its  $^1\text{H}$ NMR and IR spectra and its metal complexes were confirmed from electronic, and IR spectra and magnetic moment. DHA Schiff bases and their metal complexes were showed strong antifungal activity than antibacterial activity. Cobalt, Copper and Manganese complexes were among the stronger inhibitors of growth and the least growth inhibitory activity was shown by iron complexes against biological subjects.

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