

# Original Article: Synthesis, Physicochemical and Biological Studies of Transition Metal Complexes of DHA Schiff Bases of Aromatic Amine



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## ABSTRACT

The first transition elements nickel Ni (II), copper Cu (II), iron Fe (III), cobalt Co (II), manganese Mn (II) and Cd(II) were treated with DHA Schiff base synthesized from 2-aminopyridine. The electronic absorption spectra, Thermal properties, Magnetic properties of the novel metal complex were studied. The antimicrobial (Anti-bacterial and Ant-fungal) properties metal complexes have been with 1) *Bacillus Subtilis*, 2) *Staphylococcus aureus*, 3) *Aspergillus niger*, and 4) *Candida albicans fungi*. All metal complexes were confirmed by elemental analysis, (FTIR, <sup>1</sup>HNMR, UV-VIS, and Magnetic study) spectroscopic techniques. Stability of complexes was confirmed by thermal study. The complex which were belonged to Co (II) and Cu (II) complexes exhibited the maximum and Fe (III) complex exhibited the minimum zone of inhibition.

## Introduction

In the 21<sup>st</sup> century, coordination chemistry becomes the important area of research in inorganic chemistry. It is a rapid developing branch of chemistry due to the large applications in the field of organic synthesis, asymmetric synthesis, catalysis, as bleaching agents, industries, dyes, and drugs. The metal complexes are applied in medicinal,

analytical, and diagnostic purposes in the living system. Because of the magnetic and radioactive properties, they are used in optical images and Magnetic Resonance Imaging (MRI). The metal complex of Schiff bases have a broad range of biological activities including, antiviral, synergistic, antioxidant, anti-inflammatory, antifungal analgesic, antitumor, cytotoxic, antimicrobial, antidiabetic, anti-

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fertility [1,2], anti-tumor activity [3], DNA Photocleavage activity [4], etc. Popova and Berova *et al.* reported novel metal complex, which exhibits an excellent biological activity, the complex used to cure liver function, and maintain its level in the blood. The urine can causes the side effect, which can affect during the pregnancy, Nephritis Hepatitis, the blood Leukemia, and Anemia in children [5].

Following our research on the synthesis of novel metal complex and their Schiff bases that have been described from the Dehydroacetic acid and 2-aminopyridine, all synthesized novel transition metal complex Schiff bases were characterized by elemental analysis, (FTIR, UV-VIS,  $^1\text{H}$ NMR, and XRD) spectroscopic techniques, as well as thermal and magnetic study

### Experimental Details

All the chemicals required in intermediates were purchased from E-Merck Germany and 2-aminopyridine AR grade from Loba Chemie Pvt. Ltd. The metal salts were purchased from the E-Merck and Loba chemie Pvt. Ltd. The solvent were purified before being used for the reaction with standard procedure [6]. The Perkins Elmer CHN Analyzer was used to calculate the exact percentage of C, H, and N. The FTIR of the complexes were measured by the Perkin Elmer (1430) FTIR

spectrophotometer in the range of 4000-400  $\text{cm}^{-1}$ . The himandzu UV -VISIBLE Spectrophotometer UV 160 has been applied to measure electronic spectra at Research Centre Department of Chemistry Rajarshi Shahu Mahavidyalaya, Latur (MS). The  $^1\text{H}$ NMR and  $^{13}\text{C}$ NMR were measured by using Brucker FT-500 MHz NMR Spectrophotometer in  $\text{CDCl}_3$  by solvent TMS as a reference substance, while TGA -DTA scanning at Central Instrumentation Centre, Savitribai Phule University, Pune. The biological testing has been done at Research Centre Department of Biotechnology R. S. M. Latur.

### Synthesis of schiff bases

DHA Schiff Bases are synthesized by using standard procedure [7,8] by which the equimolar solutions of Dehydroacetic acid (0.01mol) and 2-aminopyridine (0.01 mol) were dissolved in 25 mL of dry ethanol taken in a round bottomed flask. The content of flask refluxed for four to six hours on 1 RML rotamantle with magnetic stirrer. Upon cooling, the light yellow colored solid mass of separated out Schiff base was filtered, and washed with a small portion of ethanol, and then it was dried. A pure product was obtained by recrystallisation from ethanol and dried in vacuum desiccators. The purity of product was ascertained by TLC and melting point was examined.

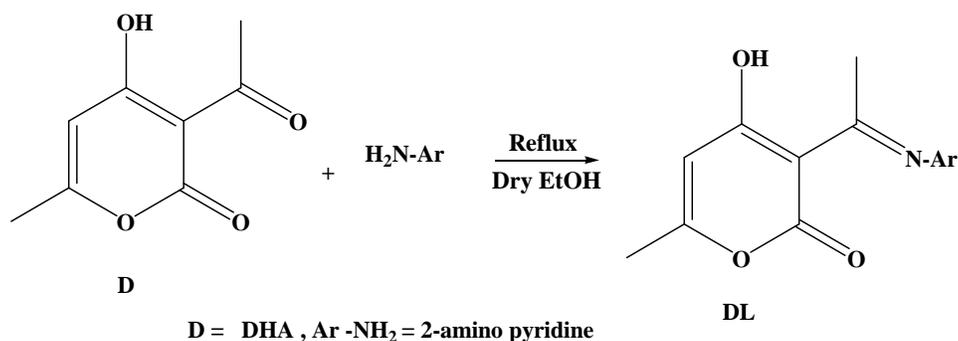
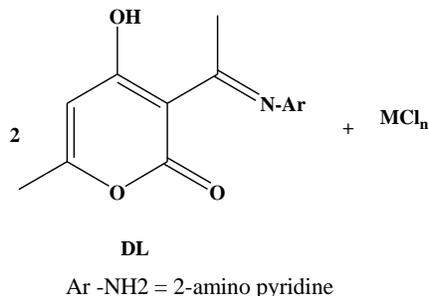


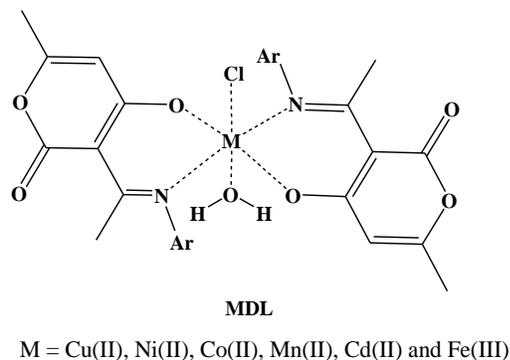
Figure 1. Synthesis of Schiff base

### Synthesis of metal complexes

The metal complexes were synthesized by the reaction of DHA Schiff bases 0.002 mol in



methanolic solution with metal chloride salt in an 2:1 molar ratio to produce the desired metal complex [8].



**Figure 2.** Synthesis of Metal Complexes

### Results and Discussion

The Schiff bases are generally orange color and air-stable, non-hygroscopic in nature, and soluble in water and in hot alcoholic solution.

The novel metal complexes are colored in nature, and non-hygroscopic, while stable in atmospheric air. The synthesized complexes

**Table 1.** Analytical Data

Compound	Color	F. Wt.	M. P. °C	Found (calculated) %				
				C	H	N	M	Cl
DL	Orange	244	90	64.01 (63.93)	04.64 (4.92)	11.41 (11.47)	-----	-----
Cu (II) DL	Green	658	>295	48.74 (48.89)	04.11 (04.04)	08.05 (08.19)	10.42 (10.54)	08.20 (08.36)
Ni (II) DL	Light Green	617.7	>290	52.18 (52.30)	04.41 (04.44)	08.57 (08.77)	11.43 (11.09)	08.62 (09.19)
Fe (III) DL	Reddish	650.21	287	49.13 (49.34)	04.19 (04.13)	08.21 (08.26)	15.35 (15.50)	08.18 (08.40)
Co (II) DL	Pink	725.93	>300	44.32 (44.55)	03.63 (03.68)	07.43 (07.23)	10.11 (09.31)	07.48 (07.72)
Mn (II) DL	Yellowish	685.9	287	46.85 (47.07)	03.82 (03.92)	07.65 (07.84)	10.14 (09.94)	07.64 (07.7)
Cd (II) DL	Yellowish	854.92	>300	38.12 (38.06)	03.12 (03.27)	06.17 (06.14)	--	12.45 (12.63)

### <sup>1</sup>H-NMR

The complex shows the characteristics peak for the metal complex in the <sup>1</sup>H-NMR. The peak signal at δ 2.2 belongs to (3H, s, C<sub>6</sub>-CH<sub>3</sub>) proton, while the signal at δ 15.82 ppm is a free hydroxyl group (OH) proton. However, the

signal at δ 2.58 (3H, s, N=C-CH<sub>3</sub>) is methyl hydrogen linked carbon azomethine for DHA moiety [7]. The remaining signal appeared around 7.4- 8.2 (4H, m) belongs to the aromatic of pyridine moiety.

### IR spectra

The details of FT-IR are indicated in Table 2. A weak band at 3419  $\text{cm}^{-1}$  appears due to intramolecular hydrogen bonding of  $\nu$  (O-H---). The IR signal appears at 1688  $\text{cm}^{-1}$  assigned to  $\nu$  (C=O) lactone carbonyl, 1644  $\text{cm}^{-1}$   $\nu$  (C=N)

(azomethine), 1333  $\text{cm}^{-1}$   $\nu$  (C-N) aryl azomethine and 1214  $\text{cm}^{-1}$   $\nu$  (C-O) enolic [7]. The absence of peak at weak band at 3419  $\text{cm}^{-1}$  in the spectra of all metal complexes suggests the deprotonating enolic oxygen and azomethine nitrogen in coordination to the metal ion.

**Table 2.** Characteristic IR Frequencies ( $\text{cm}^{-1}$ ) of the Ligand and Metal Complexes.

Compounds	$\nu$ (C=O)	$\nu$ (C=C)	$\nu$ (C=N)	$\nu$ (C-N)	$\nu$ (C-O)	$\nu$ (M-O)	$\nu$ (M-N)
DL	1688	1578	1644	1333	1214	-----	-----
Cu(II)-DL	1692	1583	1645	1347	1237	566	464
Ni(II)-DL	1704	1584	1631	1362	1240	567	477
Fe(III)-DL	1687	1590	1623	1327	1226	570	478
Co(II)-DL	1689	1583	1633	1359	1248	568	468
Mn(II)-DL	1700	1576	1638	1363	1246	630	472
Cd(II)-DL	1684	1577	1640	1347	1230	5564	465

### Magnetic measurement and electronic absorption spectra

The electronic spectra of the Cu (II) complexes in DMSO indicated the band at 11155-16450  $\text{cm}^{-1}$  for ligand D assigned to  ${}^2E_g \rightarrow {}^2T_{2g}$  transition which was a characteristic of octahedral geometry [11]. This was further supported by magnetic moment values (1.78  $\mu_B$ ) within the required range for  $d^9$ -system [12]. The electronic spectra of the Ni (II)-DL complex revealed three bands in the range of 10727( $\nu_1$ ), 15345( $\nu_2$ ), and 23730( $\nu_3$ ) assigned to the transition of  ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}$  and a charge transfer transition, respectively, suggesting the octahedral geometry of the complexes [13]. The electronic absorption spectrum of Co (II) complexes had three bands in the range of 12458 ( $\nu_1$ ), 18565( $\nu_2$ ), and 27475 ( $\nu_3$ ) which may be attributed to three spin-allowed transitions of  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ ,  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ , and  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$ , respectively, suggesting an octahedral geometry. The

effective magnetic moment values (4.41  $\mu_B$ ) were found to be well within the range, as expected for octahedral geometry [14]. The electronic spectra Mn(II) complex showed two bands at 17672  $\text{cm}^{-1}$  ( $\nu_1$ ) and 23204  $\text{cm}^{-1}$  ( $\nu_2$ ) assigned to the transition of  ${}^6A_{1g} \rightarrow {}^4T_{1g}$  and  ${}^6A_{1g} \rightarrow {}^4T_{2g}$ , respectively, indicating octahedral geometry. The magnetic moment value (5.05  $\mu_B$ ) which was slightly lower than the spin only value expected for octahedral Mn(II) complexes [15]. This may be due to the presence of magnetic exchange and small traces of Mn(II) species. The electronic spectra of the Fe(III) complexes demonstrated three bands at 16243 ( $\nu_1$ ), 22690 ( $\nu_2$ ), and 29476  $\text{cm}^{-1}$  ( $\nu_3$ ) assigned to the transitions of  ${}^6A_{1g} \rightarrow {}^4T_{1g}(D)$ ,  ${}^6A_{1g} \rightarrow {}^4T_{1g}$ , and  ${}^6A_{1g} \rightarrow {}^4T_{1g}$ , respectively, and the magnetic moment values (5.6  $\mu_B$ ) suggesting a high spin octahedral geometry [16, 17]. The Cd complex was diamagnetic. The magnetic and electronic spectral data was relevant for the proposed structure of complexes depicted in Table 3.

**Table 3.** Magnetic and electronic absorption spectral data (in DMSO) of the complexes

Compound	$\mu_{\text{eff}}$	$\nu(\text{cm}^{-1})$	Geometry
Cu(II) L <sub>1</sub>	1.78	11155 and 16450	Octahedral
Ni(II) L <sub>1</sub>	2.85	10727, 15345 and 23730	Octahedral
Fe(III) L <sub>1</sub>	5.6	16243, 22690 and 29476	Octahedral
Co(II) L <sub>1</sub>	4.41	12458, 18565 and 27475	Octahedral
Mn(II) L <sub>1</sub>	5.05	17672 and 23204	Octahedral
Cd(II) L <sub>1</sub>	1.72	-----	Octahedral

### Thermo-analytical techniques

There was no mass loss up to 200 °C indicating the absence of lattice and coordinated water in the TG curve of Ni (II)-DL metal complex and exhibited a high initial thermal stability. The TG thermo gram showed the first step decomposition in the temperature range of 200-440 °C with mass loss of 38.00% and the corresponding exothermic peaks at 195 °C and 370 °C in the DTA curve specified the decomposition of non-coordinated part of ligand in a relatively fast but moderate oxidation process. The second step of decomposition occurred in the temperature range of 500-700 °C with a further mass loss of the next 52.08% indicating the decomposition of the coordinated part of a ligand of the complex through a slow process. The organic part decomposed in the temperature range of 500-700 °C that was also shown by broad exotherms in this range in the DTA curve. Finally, the residue of Nickel oxide remained at 720 °C [18].

### XRD powder diffraction

The unit cell of Fe (III)-DLcomplex yielded the constant values of lattice as  $a=24.7805(\text{Å})$ ,  $b=7.5469(\text{Å})$ ,  $c=24.788(\text{Å})$ , and unit cell volume of  $V=624.8765(\text{Å}^3)$ .  $\alpha=\gamma=90^\circ$  and  $\beta=104.32^\circ$  were required for the sample to be

crystal system monoclinic and lattice type-P was found to be satisfactory [19].

### Antibacterial and antifungal activity

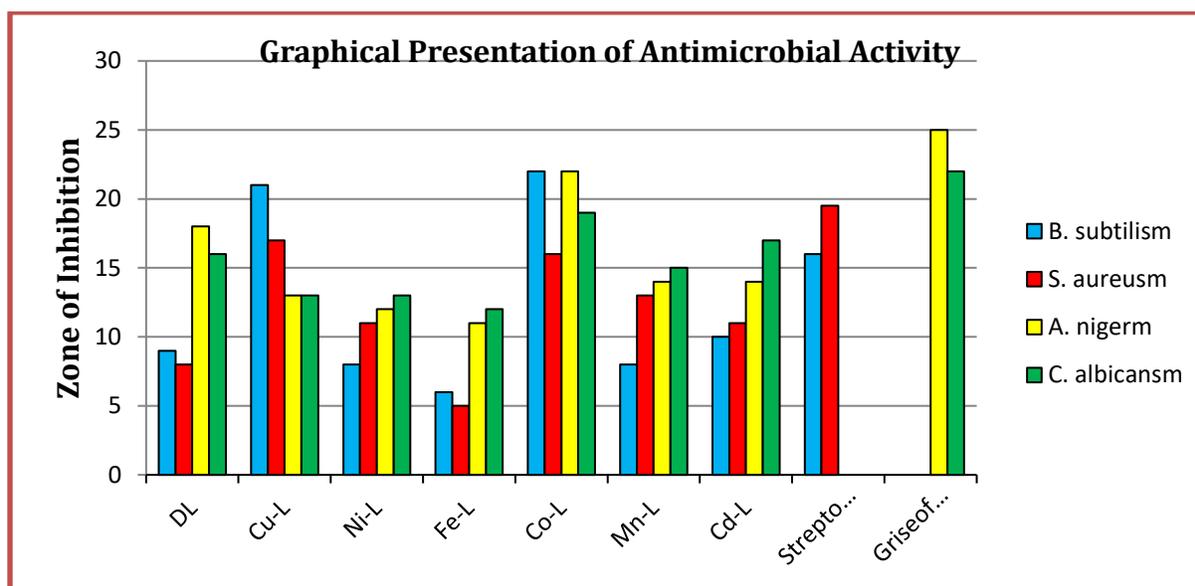
The antimicrobial potentiality of DHA Schiff base ligands and their metal complexes was carried out by the agar well diffusion method [20]. The minimum inhibitory concentration of DHA Schiff base ligands and their metal complexes was determined by adopting the standard procedure of the National Committee for Clinical Laboratory standard (2004) [21]. In vitro antibacterial and antifungal activity was screened by considering the zone of growth inhibition. The synthesized Schiff base L and its metal complexes were screened with their different concentrations and the standard antibiotics such as streptomycin (1 mg/mL) and griseofluvin (1 mg/mL).

However, DHA Schiff base ligand weak antibacterial revealed a strong antifungal activity. Antibacterial activity significantly increased on coordination because it reduced the polarity of metal ion due to the partial sharing of positive charge with ligands that increase the lipophilic nature of metal ion in complex [4, 22]. This enhanced antimicrobial activity of metal complexes is due to the lipophilic nature of metal ion in complex [23]. The Antimicrobial activity data is presented in Table 4 and Figure 4.

**Table 4.**Antibacterial and Antifungal Activities Data

Sample	<i>B. subtilis</i> <sup>m</sup>	<i>S. aureus</i> <sup>m</sup>	<i>A. niger</i> <sup>m</sup>	<i>C. albicans</i> <sup>m</sup>
DL	9	8	18	16
Cu(II)-DL	21	17	13	13
Ni(II)-DL	8	11	12	13
Fe(III)-DL	6	5	11	12
Co(II)-DL	22	16	22	19
Mn(II)-DL	8	13	14	15
Cd(II)-DL	10	11	14	17
Streptomycin	16	19.5	0	0
<i>Griseofulvin</i>	0	0	25	22

*m*=Zone of inhibition in mm

**Figure 4.** Graphical presentation of antibacterial and antifungal activities

### Conclusion

Composition of Schiff base and metal complexes was confirmed by elemental analysis. The structure of Schiff base and metal complexes was confirmed by IR and <sup>1</sup>H-NMR study. The magnetic susceptibility measurement and electronic spectral data of the complexes suggested the octahedral geometry. Thermal study showed thermal stability, and X-Ray diffraction studies concluded that all transition metal complexes synthesized having monoclinic crystal structure and lattice type-P. The DHA Schiff base ligand exhibited a weak activity against bacteria, but it revealed a strong antifungal

activity. Antibacterial activity significantly increased on coordination due to the increase in lipophilic nature of metal ion in complex. Co (II) and Cu (II) complexes exhibited the maximum zone of inhibition, while Fe (III) complex indicated the minimum zone of inhibition.

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### References

- [1] S. Kumar, D. N. Dhar, P. N. Saxena, *Journal Scientific and Industrial Research*, **2009**, *68*, 181-187. [Crossref], [Google Scholar], [Publisher]
- [2] V. K. Gaikwad, Urmila M. Yadav, *Scholarly Research Journal for Interdisciplinary Studies*; 2225-2234. [Crossref], [Google Scholar], [Publisher]
- [3] S. Shia, ShiuYua, Lixa Quana, Zilu Chena, Fupeli Liyang, *Journal of Inorganic Biochemistry*; 2020, *210*, 2599-2604.. [Crossref], [Google Scholar], [Publisher]
- [4] A. K. Gupta, S. Saini, R. Pal, R. Kumar and V. Benniwal, *World Journal of Pharmacy and Pharmaceutical Sciences*, **2014**, *3*, 1621-1636. [Crossref], [Google Scholar], [Publisher]
- [5] A. Prakash, D. Adhikari, *International Journal of Chem. Tech. Research*, **2011**, *3*, 1891-1896. [Crossref], [Google Scholar], [Publisher]
- [6] A. I. Vogel, *Text book of practical Organic Chemistry*, 5<sup>th</sup> ed., Longman, London, **1989**. [Crossref], [Google Scholar], [Pdf]
- [7] S. B. Biradar, D. V. Narte, R. P. Kale, K. I. Momin, M. S. Sudewad, K. C. Tayade, D.G. Palke, *Journal of Applied Organometallic Chemistry*, **2021**, *1*, 41-47. [Crossref], [Google Scholar], [Publisher]
- [8] S. Salunke, *Lap Lambert Academic Publishing*, **2015**, *6*. [Publisher]
- [9] K. Namkamoto, *Infrared Spectra of Inorganic and Coordination Compounds*. Wiley Interscience, New York, **1970**, *159*, 167-714. [Google Scholar], [Publisher]
- [10] J. Singh, P. Singh, *International Scholarly Research Network*; , 2012, 1-6. [Crossref], [Google Scholar], [Publisher]
- [11] A. Noor Al-Shareef, S. Hadi Kadhim, W. Abbas Jawad, *Journal of Applicable Chemistry*, **2013**, *2*(3), 438-446. [Crossref], [Google Scholar], [Publisher]
- [12] B. N. Figgs, Michael A. Hitchman, *Ligand Field Theory and its Applications*, John Wiley and Sons, Wiley India Edition, **2000**. [Crossref], [Google Scholar], [Publisher]
- [13] S. Jyothi, K. Sreedhar, D. Nagaraju, S.J. Swamy *Canadian Chemical Transactions*, **2015**, *3*, 368-380. [Crossref], [Google Scholar], [Publisher]
- [14] K. S. Abou-Melha, *Journal of Coordination Chemistry*, **2008**, *61*, 2053-2067. [Crossref], [Google Scholar], [Publisher]
- [15] L. A., Saghatforoush, A. Aminkhani, F. Chalabian, [Crossref], [Google Scholar], [Publisher]
- [16] M.; Sunjuk, L.; Al-Najjar, M.; Shtaiwi, B.; El-Eswed, M.; Al-Noaimi, L.; Al-Essa, K. Sweidan, [Crossref], [Google Scholar], [Publisher]
- [17] P. S. Mane, S.M. Salunke, B.S. More and T.K. Chondhekar, *Asian Journal of chemistry*, **2012**, *24*, 2235-2238. [Crossref], [Google Scholar], [Publisher]
- [18] H. H. Horowitz, G. Metzger, *Anal. Chem.*, **1963**, *35*, 1464-1468. [Crossref], [Google Scholar], [Publisher]
- [19] D. G. Palke, S.D. Salunke, *Asian Journal of Chemistry*; 2017, *29*, 10, 2167-2170. [Crossref], [Google Scholar], [Publisher]
- [20] D.G. Palke, S.D. Salunke, *Der Pharma Chem.*, **2018**, *10*, 46-49. [Crossref], [Google Scholar], [Publisher]
- [21] National Committee for Clinical Laboratory standard. Methods for dilution antimicrobial susceptibility test for bacteria that grow aerobically, *Approved Standard Document*, **2004**, *M7-76*. [Crossref], [Google Scholar], [Publisher]

[22] S. Saini, R. Pal, A. K. Gupta, V. Beniwal, *Der Pharma Chemica*, **2014**, 6(2),330-334.

[Crossref], [[Google Scholar](#)], [[Publisher](#)]

[23] L. Mishra, V. K. Singh, *Indian Journal of Chemistry*; **1993**, 32(A), 446. [[Crossref](#)],

[[Google Scholar](#)], [[Publisher](#)]