RJC

**RASĀYAN *J. Chem.***
Vol. 15 | No. 3 |1718-1727| July - September | 2022
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

# SYNTHESIS, SPECTRAL, THERMAL AND ANTIMICROBIAL STUDIES OF NEW METAL COMPLEXES OF SUBSTITUTED HYDROXY PROPIOPHENONE

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**ABSTRACT**

A new series of metal complexes of innovative bisketimines ($L_1$ - $L_5$) have been synthesized. Schiff base ligands were synthesized by condensing substituted 2'- hydroxy propiophenone and ethylene diamine. The synthesized Schiff bases act as tetradentate ligands with two nitrogen and two phenolic oxygen groups and co-ordinates with Co (II), Ni (II), Cu (II) and Zn (II) salts. Ligands and their metal complexes have been studied using $^1H$ NMR, IR, UV-Vis and thermogravimetric techniques. The complexes were crystalline, according to the XRD pattern. The thermogravimetric data revealed the thermal stability of the complexes. The study of antibacterial and antifungal activities of the ligands and their metal complexes showed more effectiveness of metal complexes than Schiff base ligands.

**Keywords: -**Schiff Bases, Substituted Hydroxy Propiophenones, Transition Metal Complexes, TGA analysis, XRD Analysis.

RASĀYAN *J. Chem.*, Vol. 15, No.3, 2022

## INTRODUCTION

Schiff base ligands named after the scientist Hugo Schiff[1], are produced by combining an aldehyde or ketone with a primary amine. These Schiff bases and their metal complexes have received a great deal of attention in recent decades and they have made substantial contributions to the advancement of coordination chemistry.[2-4] Schiff bases with a -OH group close to the –CH=N- act as an effective ligand and can serve as a location for biochemically active molecules. The Schiff base ligand and its transition metal complexes have been used in a wide range of applications.[5,6] Transition metal complexes have been widely used as a catalyst, [7,8] DNA binding agents[9] and corrosion inhibitors.[10] Most transition metal complexes have been found to be effective against ulcers, rheumatoid arthritis and cancers.[11-14] Recently, tetradentate $N_2O_2$ Schiff bases are gaining more attention due to their interaction with several metal ions. So, considering the research potential of the present topic, we reported the synthesis, physicochemical characterization and antimicrobial studies of Co (II), Ni (II), Cu (II) and Zn (II) complexes with ligands derived from 5'-methyl -2'- hydroxy propiophenone ($L_1$), 5'-Bromo-2'-hydroxy propiophenone ($L_2$), 5'-chloro-2'-hydroxy propiophenone ($L_3$), 5'- Bromo-3'iodo-2'-hydroxy propiophenone ($L_4$) and 5'-chloro-3'-iodo-2'-hydroxy propiophenone ($L_5$) with ethylenediamine.

## EXPERIMENTAL

### Material and Methods

All analytical grade chemicals were employed without additional purification. 2'-hydroxy propiophenone (Sigma Aldrich) was used as starting material. The literature approach was used to synthesize substituted 2'- hydroxy propiophenones. The melting points were determined using an open capillary tube and are uncorrected. $^1H$ NMR spectra were recorded on Brucker Avance Neo 500 MHz spectrophotometer in DMSO solvent, UV spectra were recorded on W-1800 series spectrometer and FTIR spectra were recorded on Shimadzu IR spectrometer. The molar conductance ($10^{-3}$ M in DMSO) was measured using a Systronic CM 304 conductivity bridge. Thermal analysis was carried out by using Shimadzu (TGA-50 H) at room temperature to 800 $^0$C at a heating rate of 20 $^0$C per minute.


http://doi.org/10.31788/RJC.2022.1536355

**Preparation of Ligands**

All of the ligands $L_1$, $L_2$, $L_3$, $L_4$, and $L_5$ were synthesized by refluxing the mixture of corresponding substituted 2'hydroxy propiophenone (0.02M) and ethylenediamine (0.01M) in ethanol solvent for 3-6 hours. A catalytic amount of glacial acetic acid was introduced into the reaction mixture. Thin-layer chromatography was used to monitor the progress of the reaction mixture. After completion of the reaction, the reaction mixture was cooled at room temperature and 25 ml of ice-cold water was added to it. The yellow solid separates. The separated solid was filtered, washed with cold water, and recrystallized by ethanol to obtain pure crystals. (Fig.-1)

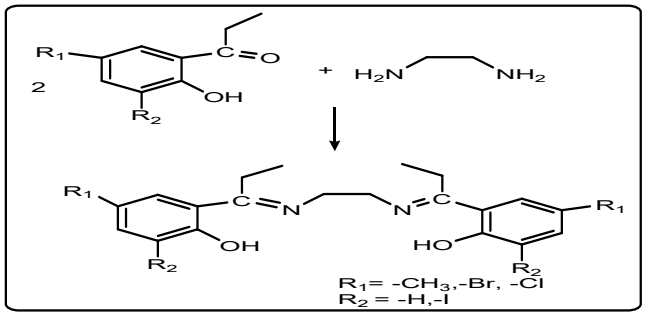


Fig.-1: Synthesis of Schiff Base Ligand

**Synthesis of Metal Complexes**

The metal complexes were synthesized by mixing ethanolic solutions of Co (II), Ni (II), Cu (II) and Zn (II) salts with an ethanolic solution of Schiff base in a 1:1 ratio. The resulting mixture of metal salts and Schiff base in ethanol was refluxed for 3-4 hours. The pH of the solution was adjusted by adding a dilute alcoholic solution of ammonia. After digestion for half an hour, the precipitated complex was filtered, washed with ethanol and finally dried over fused $CaCl_2$. (Fig.-2)

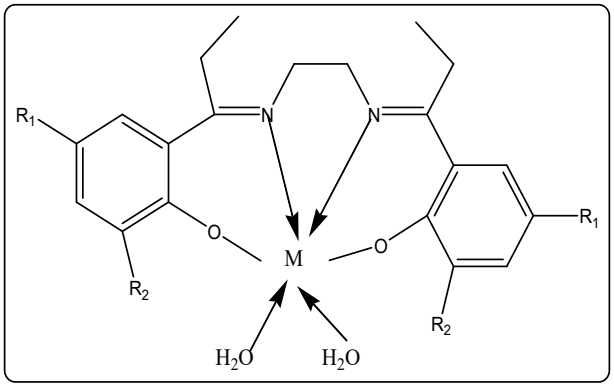


Fig.-2: Probable Structure of the Complex
[M=Ni (II), Cu (II), Co (II), Zn (II)]

**Microbial Assay**

**Test organisms**

All the synthesized metal complexes were screened against nine microbial strains which include six bacteria, three gram-positive (*S. aureus, S. pneumonia and B. subtilis*), three-gram negative bacteria (*E. coli, S. typhi and P. vulgaris*), and three fungi (*C. albicans, A. niger and T. rubrum).*

**In Vitro Microbial Activity**

The disc diffusion method was used to study the antimicrobial activity of newly synthesized compounds.[15] The Mueller Hinton plate was inoculated with the bacterial suspension and the sterile discs were impregnated with the test compounds. The assay was inoculated at 37 $^0$C for 24 hours and the zone of inhibition was measured. Ofloxacin was used as the standard antibacterial drug for gram-positive bacteria, ciprofloxacin was used for gram-negative bacteria. A similar procedure was carried out for fungi using fluconazole. Instead of Mueller Hinton agar, PDA was utilized.

## RESULT AND DISCUSSION

Table-1 summarises the analytical and physical data of the Schiff base ligand and its metal complexes. At room temperature, all of the metal complexes are coloured, solid and stable to air and moisture. According to the statistics, all complexes are formed in a 1:1 ratio. The general formula for the prepared complex is [ML $(H_2O)_2$].

Table-1: Physical and Analytical Data of Metal complexes

| Compound | Mol. Formula | Color | % Yield | M.P .$^0$C | Elemental Analysis % Found (Calculated) | | | | $\Lambda_m$ ($\Omega^{-1}$ $cm^{-2}$ $mol^{-}$) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | C | H | N | M | - |
| $L_1$ | $C_{22}H_{28}N_2O_2$ | Yellow | 68 | 135 | 74.97 (75.00) | 8.01 (7.95) | 7.92 (7.95) | -- | -- |
| [$NiL_1$ $(H_2O)_2$] | $C_{22}H_{30}N_2O_4Ni$ | Green | 55 | 250 | 59.39 (59.36) | 6.71 (6.74) | 6.25 (6.29) | 13.18 (13.19) | 19.8 |
| $CoL_1$ $(H_2O)_2$ | $C_{22}H_{30}N_2O_4Co$ | Brick Red | 57 | 230 | 59.23 (59.20) | 6.69 (6.72) | 6.30 (6.27) | 13.15 (13.21) | 24.5 |
| $CuL_1$ $(H_2O)_2$ | $C_{22}H_{30}N_2O_4Cu$ | Green | 60 | 185 | 58.69 (58.72) | 6.70 (6.67) | 6.19 (6.22) | 14.20 (14.13) | 16.5 |
| $ZnL_1$ $(H2O)_2$ | $C_{22}H_{30}N_2O_4Zn$ | Dark yellow | 59 | >250 | 58.58 (58.61) | 6.62 (6.66) | 6.24 (6.21) | 14.47 (14.51) | 15.2 |
| $L_2$ | $C_{20}H_{22}N_2O_2Br_2$ | Bright Yellow | 72 | 165 | 49.98 (50.00) | 4.62 (4.58) | 5.79 (5.83) | -- | -- |
| $NiL_2$ $(H_2O)_2$ | $C_{20}H_{24}N_2O_4Br_2Ni$ | Pale green | 60 | >250 | 41.88 (41.90) | 4.21 (4.19) | 4.85 (4.88) | 10.20 (10.24) | 17.5 |
| $CoL_2$ $(H_2O)_2$ | $C_{20}H_{24}N_2O_4Br_2Co$ | Red | 50 | >250 | 41.86 (41.88) | 4.22 (4.18) | 4.85 (4.88) | 10.17 (10.28) | 21.8 |
| $CuL_2$ $(H_2O)_2$ | $C_{20}H_{24}N_2O_4Br_2Cu$ | Green | 63 | >250 | 41.59 (41.62) | 4.12 (4.16) | 4.82 (4.85) | 10.97 (11.02) | 12.8 |
| $ZnL_2$ $(H_2O)2$ | $C_{20}H_{24}N_2O_4Br_2Zn$ | Yellow | 60 | >250 | 41.52 (41.56) | 4.18 (4.15) | 4.79 (4.84) | 11.29 (11.32) | 13.4 |
| $L_3$ | $C_{20}H_{22}N_2O_2$ $Cl_2$ | Yellow | 65 | 160 | 61.20 (61.22) | 5.68 (5.61) | 7.11 (7.14) | -- | -- |
| $NiL_3$ $(H_2O)_2$ | $C_{20}H_{24}N_2O_4Cl_2Ni$ | Bluish-green | 58 | >250 | 49.49 (49.51) | 4.91 (4.95) | 5.72 (5.77) | 12.06 (12.10) | 12.1 |
| $CoL_3$ $(H_2O)_2$ | $C_{20}H_{24}N_2O_4Cl_2Co$ | Red | 48 | >250 | 49.42 (49.38) | 4.89 (4.93) | 5.80 (5.76) | 12.14 (12.12) | 14.9 |
| $CuL_3$ $(H_2O)_2$ | $C_{20}H_{24}N_2O_4Cl_2Cu$ | Mehandi | 62 | 215 | 48.98 (49.02) | 4.86 (4.90) | 5.68 (5.71) | 12.95 (12.97) | 15.8 |
| $ZnL_3$ $(H_2O)_2$ | $C_{20}H_{24}N_2O_4Cl_2$ Zn | Yellow | 58 | >250 | 48.90 (48.94) | 4.91 (4.89) | 5.69 (5.70) | 13.30 (13.33) | 18.5 |
| $L_4$ | $C_{20}H_{20}N_2O_2$ $Br_2I_2$ | Yellow | 67 | 205 | 32.75 (32.78) | 2.79 (2.73) | 3.79 (3.82) | -- | -- |
| $NiL_4$ $(H_2O)_2$ | $C_{20}H_{22}N_2O_4Br_2$ $I_2Ni$ | Black | 55 | >250 | 29.10 (29.13) | 2.69 (2.67) | 3.35 (3.39) | 7.10 (7.12) | 20.4 |
| $CoL_4$ $(H_2O)_2$ | $C_{20}H_{22}N_2O_4Br_2$ $I_2Co$ | Brown | 54 | >250 | 29.07 (29.10) | 2.63 (2.66) | 3.36 (3.39) | 7.17 (7.14) | 22.6 |
| $CuL_4$ $(H_2O)_2$ | $C_{20}H_{22}N_2O_4Br_2$ $I_2Cu$ | Pale green | 58 | 215 | 28.91 (28.95) | 2.62 (2.65) | 3.35 (3.37) | 7.63 (7.66) | 14.1 |
| $ZnL_4$ $(H_2O)_2$ | $C_{20}H_{22}N_2O_4Br_2$ $I_2Zn$ | Pale yellow | 56 | >250 | 28.89 (28.92) | 2.60 (2.65) | 3.34 (3.37) | 7.82 (7.87) | 16.9 |
| $L_5$ | $C_{20}H_{20}N_2O_2$ $Cl_2I_2$ | Yellow | 70 | 186 | 37.24 (37.26) | 3.13 (3.10) | 4.29 (4.34) | -- | -- |
| $NiL_5$ $(H_2O)_2$ | $C_{20}H_{22}N_2O_4Cl_2I_2Ni$ | Green | 53 | >250 | 32.58 (32.61) | 3.01 (2.98) | 3.84 (3.80) | 7.95 (7.97) | 22.5 |
| $CoL_5$ $(H_2O)_2$ | $C_{20}H_{22}N_2O_4Cl_2I_2Co$ | Brown | 53 | >250 | 32.55 (32.57) | 3.03 (2.98) | 3.76 (3.80) | 7.*96* *(7.99)* | 18.2 |
| $CuL_5$ $(H_2O)_2$ | $C_{20}H_{22}N_2O_4Cl_2I_2Cu$ | Green | 55 | 215 | 32.66 (32.61) | 3.01 (2.98) | 3.77 (3.80) | 8.60 (8.63) | 13.4 |
| $ZnL_5$ $(H_2O)_2$ | $C_{20}H_{22}N_2O_4Cl_2I_2Zn$ | Yellow | 58 | >250 | 32.56 (32.57) | 2.95 (2.98) | 3.86 (3.80) | 8.86 (8.87) | 18.7 |

### Molar Conductance

The molar conductance of the complexes was measured in DMSO solvent with 0.001 M concentration. The low value of molar conductance indicated the nonelectrolyte nature of all the complexes.[16,17]

**Infra-Red Spectra and Mode of Bonding**

Table-2 displays the IR spectra of the ligand and complexes. To confirm the involvement of the coordination site in the complex, the IR spectra of the complexes were compared to those of the free ligand. The IR spectrum of Schiff base ligand showed a strong absorption at 3000-3300 $cm^{-1}$ which is a characteristic band of the phenolic –OH group and 1570-1670 $cm^{-1}$ attributed to azomethine (–-C=N-). The frequencies were slightly shifted towards lower values in the spectra of metal complexes indicating the co-ordination of nitrogen of the azomethine group to the central metal ion in the complexes.[18] In all the complexes, the absence of the characteristic –OH band in the metal complexes indicates the coordination of oxygen to the metal. All the complexes showed broadband in the region 3200-3453 $cm^{-1}$ indicating the presence of coordinated water in the complex.[19,20] The presence of coordinated water was further confirmed by the appearance of a strong and sharp band at 890-740 $cm^{-1}$ due to rocking -OH vibration.[21] The weak bands in the low-frequency region are attributed to M-N and M-O bonds.[22,23]

Table-2: IR Bands of Schiff Base Ligands and Their Complexes in $cm^{-1}$

| Ligand / Complex | υ(OH) Water | υ(OH) Phenolic | υ (C=N) | υ (C-O) | υ(M-N) | υ(M-O) |
|---|---|---|---|---|---|---|
| $L_1$ | ---- | 3063.09 | 1647.28 | 1242.21 | ---- | ---- |
| $L_1$ Co | 3441.16 | ---- | 1597.13 | 1360.23 | 523.13 | 432.07 |
| $L_2$ | ---- | 3070.81 | 1573.98 | 1226.78 | --- | ----- |
| $L_2$ Cu | 3302.27 | ----- | 1512.26 | 1257.64 | 532.38 | 447.50 |
| $L_3$ | --- | 3066.95 | 1604.84 | 1280.79 | --- | ---- |
| $L_3$ Co | 3364.00 | --- | 1589.41 | 1311.65 | 516.94 | 432.07 |
| $L_4$ | ---- | 3294.56 | 1643.42 | 1276.93 | ---- | --- |
| $L_4$Zn | 3564.80 | ---- | 1608.84 | 1342.51 | 594.10 | 416.64 |
| $L_5$ | --- | 3051.52 | 1612.26 | 1234.50 | ---- | ---- |
| $L_5$ Cu | 3300.20 | ---------- | 1571.99 | 1319.31 | 550.42 | 474.43 |

**$^1$H NMR**

The $^1$H NMR spectrum of the Schiff base ligand was recorded in the DMSO $d_6$ solution using TMS as an internal standard. The $^1$H NMR spectra of all the three ligands revealed phenolic –OH peaks in the range of δ 15.5 to 16.5 ppm which disappear in the spectra of complexes. The lack of phenolic -OH signal in the metal complexes confirmed the eventual participation of the phenolic -OH group in the chelation with a metal ion.[24] The spectrum also exhibited multiplets in the range of 6.5 to 7.9 ppm due to aromatic proton. The $^1$H NMR spectrum of the $L_2$ ligand is shown in Fig.-3.

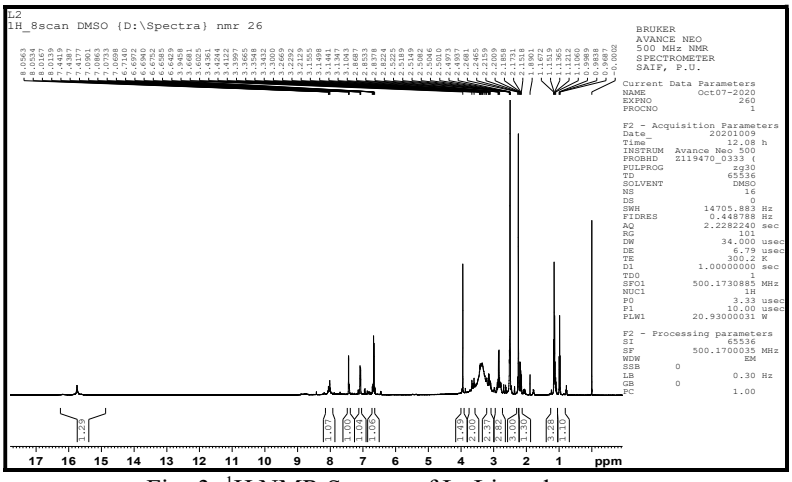


Fig.-3: $^1$H NMR Spectra of $L_2$ Ligand

**Electronic Spectra and Magnetic Properties**

The electronic spectrum of the Schiff base ligand exhibits a strong absorption band at 333 nm and 288 nm which are attributed to n-n* and π-π* transitions respectively.[25] The electronic spectra of Ni(II) complexes showed three bands in the range 9488-9775 $cm^{-1}$,14265-16000 $cm^{-1}$ and 22222-24161 $cm^{-1}$ assigned to $^3A_{2g}\rightarrow{}^3T_{2g}(F)$, $^3A_{2g}\rightarrow{}^3T_{1g}(F)$ and $^3A_{2g}\rightarrow{}^3T_{1g}(P)$ respectively indicating an octahedral geometry around Ni (II) ion.[26] The Racah interelectronic repulsion parameters B, β were calculated for Ni (II) complexes and were found to be in the range 660.87-718.33 $cm^{-1}$ and 0.612–0.665 respectively. Because of decreased interelectronic repulsions caused by electron delocalization, the value of B was found to be less than the free ion value (1080 $cm^{-1}$) indicating the covalent nature of the bond between metal and ligand. The octahedral geometry of the Ni (II) complex was further supported by the magnetic moment value (3.13-3.30 B.M.). Fig.-4 indicated the electronic spectrum of $L_2Ni$ complex.

The electronic spectra of Co (II) complexes revealed three bands in the ranges 9346-9597 $cm^{-1}$, 16863-17857 $cm^{-1}$ and 21739-22728$cm^{-1}$ which were ascribed to $^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$, $^4T_{1g}(F)\rightarrow{}^4A_{2g}(F)$ and $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$ respectively which suggest the octahedral geometry around Co (II) ion.[27] The Racah interelectronic repulsion parameters B, β for Co(II) complexes were computed and found to be in the range 690.8-798.53 $cm^{-1}$ and 0.712–0.823, respectively indicating the covalent nature of the bond between metal and ligand. The magnetic moment of the Co (II) complex (4.31-4.91B.M.) also supported the octahedral geometry. The electronic spectra of Cu (II) complexes showed a band in the range 14684-15480 $cm^{-1}$ assigned to $^2Eg\rightarrow{}^2T_{2g}$ and a charge transfer transition in the range 25974-37878 $cm^{-1}$. The ligand field parameters viz ligand field splitting energy (10 Dq) and LFSE were found in the range14684-15480 and 42.03 - 44.78 resp. All of these elements contribute to the formation of the distorted octahedral complex.[28] The magnetic moment of the Cu (II) complex (1.88-2.01B.M.) further confirmed the distorted cathedral geometry. The electronic spectra of Zn (II) complexes showed a charge transfer band in the range 24510-26178 $cm^{-1}$ indicating octahedral structure.[29] The magnetic moment was found to be zero indicating the diamagnetic nature of Zn (II) complexes. The electronic transition data and the ligand field parameters are depicted in Tables-3 and 4.

Table-3: Electronic Transitions in Metal Complexes

| Complex | $\mu_{eff}$ (B.M.) | Electronic transitions ($Cm^{-1}$) | Assignments | Geometry |
|---|---|---|---|---|
| $NiL_1(H_2O)_2$ | 3.20 | 9532<br>15361<br>23148 | $^3A_{2g}\rightarrow{}^3T_{2g}(F)$<br>$^3A_{2g}\rightarrow{}^3T_{1g}(F)$<br>$^3A_{2g}\rightarrow{}^3T_{1g}(P)$ | Octahedral |
| $CoL_1(H_2O)_2$ | 4.99 | 9597<br>17094<br>22472 | $^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$<br>$^4T_{1g}(F\rightarrow{}^4A_{2g}(F)$<br>$^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$ | Octahedral |
| $CuL_1(H_2O)_2$ | 2.07 | 14749<br>25974 | $^2Eg\rightarrow{}^2T_{2g}$<br>Charge transfer | Distorted octahedral |
| $ZnL_1(H_2O)_2$ | diamagnetic | 25316 | Charge transfer | Octahedral |
| $NiL_2(H_2O)_2$ | 3.30 | 9606<br>15432<br>24161 | $^3A_{2g}\rightarrow{}^3T_{2g}(F)$<br>$^3A_{2g}\rightarrow{}^3T_{1g}(F)$<br>$^3A_{2g}\rightarrow{}^3T_{1g}(P)$ | Octahedral |
| $CoL_2(H_2O)_2$ | 5.02 | 9434<br>16863<br>22222 | $^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$<br>$^4T_{1g}(F)\rightarrow{}^4A_{2g}(F)$<br>$^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$ | Octahedral |
| $CuL_2(H_2O)_2$ | 2.01 | 15015<br>27701 | $^2Eg\rightarrow{}^2T_{2g}$<br>Charge transfer | Distorted octahedral |
| $ZnL_2(H_2O)_2$ | diamagnetic | 26178 | Charge transfer | Octahedral |
| $NiL_3(H_2O)_2$ | 3.13 | 9488<br>16000<br>23148 | $^3A_{2g}\rightarrow{}^3T_{2g}(F)$<br>$^3A_{2g}\rightarrow{}^3T_{1g}(F)$<br>$^3A_{2g}\rightarrow{}^3T_{1g}(P)$ | Octahedral |
| $CoL_3(H_2O)_2$ | 4.91 | 9452<br>17606<br>22728 | $^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$<br>$^4T_{1g}(F)\rightarrow{}^4A_{2g}(F)$<br>$^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)$ | Octahedral |

| | | | | |
|---|---|---|---|---|
| $CuL_3(H_2O)_2$ | 1.88 | 15198<br>28090 | $^2Eg \rightarrow {}^2T_{2g}$<br>Charge transfer | Distorted<br>Octahedral |
| $ZnL_3(H_2O)_2$ | diamagnetic | 24510 | Charge transfer | Octahedral |
| $NiL_4(H_2O)_2$ | 3.18 | 9662<br>14265<br>23364 | $^3A_{2g} \rightarrow {}^3T_{2g}(F)$<br>$^3A_{2g} \rightarrow {}^3T_{1g}(F)$<br>$^3A_{2g} \rightarrow {}^3T_{1g}(P)$ | Octahedral |
| $CoL_4(H_2O)_2$ | 5.39 | 9551<br>17181<br>21834 | $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$<br>$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$<br>$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ | Octahedral |
| $CuL_4(H_2O)_2$ | 1.94 | 15480<br>25974 | $^2Eg \rightarrow {}^2T_{2g}$<br>Charge transfer | Distorted octahedral |
| $ZnL_4(H_2O)_2$ | diamagnetic | 25063 | Charge transfer | Octahedral |
| $NiL_5(H_2O)_2$ | 3.38 | 9775<br>15432<br>23981 | $^3A_{2g} \rightarrow {}^3T_{2g}(F)$<br>$^3A_{2g} \rightarrow {}^3T_{1g}(F)$<br>$^3A_{2g} \rightarrow {}^3T_{1g}(P)$ | Octahedral |
| $CoL_5(H_2O)_2$ | 5.22 | 9346<br>17857<br>21739 | $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$<br>$^4T_{1g}(F \rightarrow {}^4A_{2g}(F)$<br>$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ | Octahedral |
| $CuL_5(H_2O)_2$ | 1.97 | 14684<br>37878 | $^2Eg \rightarrow {}^2T_{2g}$<br>Charge transfer | Distorted octahedral |
| $ZnL_5(H_2O)_2$ | diamagnetic | 24814 | Charge transfer | Octahedral |

Table-4: Ligand Field Parameters of Metal Complexes

| Complex | Ligand Field Splitting Energy 10 Dq (cm-1 | Racah Interelectronic Repulsion Parameter B (cm'1) | Covalent Factor $\beta = B / B'$ | % β | $\upsilon_2/\upsilon_2$ | Ligand Field Splitting Energy LFSE (Kcal mol'1) |
|---|---|---|---|---|---|---|
| Ni- $L_1$ | 9532 | 660.87 | 0.612 | 63.4 | 1.612 | 27.21 |
| Co- $L_1$ | 7497 | 718.33 | 0.741 | 34.95 | 1.781 | 21.40 |
| Cu- $L_1$ | 14749 | --- | --- | --- | --- | 42.03 |
| Ni - $L_2$ | 9606 | 718.33 | 0.665 | 50.37 | 1.606 | 27.43 |
| Co- $L_2$ | 7429 | 718.87 | 0.741 | 34.95 | 1.757 | 21.21 |
| Cu - $L_2$ | 15015 | --- | --- | --- | --- | 42.87 |
| Ni - $L_3$ | 9488 | 712.27 | 0.660 | 51.5 | 1.686 | 27.09 |
| Co- $L_3$ | 8154 | 798.53 | 0.823 | 21.51 | 1.863 | 23.28 |
| Cu - $L_3$ | 15198 | --- | --- | --- | --- | 43.39 |
| Ni - $L_4$ | 9662 | 576.2 | 0.534 | 87.3 | 1.476 | 27.59 |
| Co- $L_4$ | 7630 | 690.8 | 0.712 | 40.44 | 1.799 | 21.78 |
| Cu- $L_4$ | 15480 | --- | --- | --- | --- | 44.20 |
| Ni - $L_5$ | 9775 | 672.53 | 0.623 | 60.5 | 1.579 | 27.91 |
| Co- $L_5$ | 8511 | 770.53 | 0.794 | 25.95 | 1.910 | 24.30 |
| Cu - $L_5$ | 14684 | --- | --- | --- | --- | 44.78 |

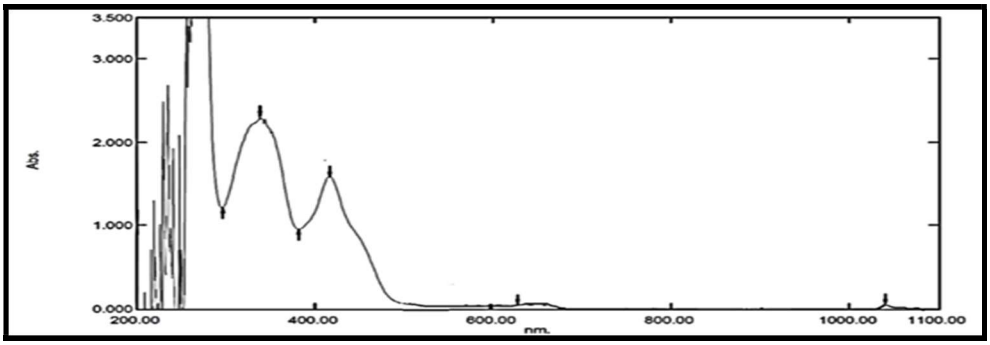


Fig.-4: Electronic Spectra of $L_2$ Ni complex

**X-Ray Diffraction Analysis**

The powder x-ray diffraction method was used to identify the structures of the complexes. The data revealed that all of the complexes had monoclinic structures except for the Ni (II) complex of the $L_2$ ligand, which has a triclinic structure. Table-5 summarises the XRD data of the Ni (II) (Fig.-5) and Cu (II) complexes (Fig.-6) of the $L_2$ ligand.

Table-5: XRD Data of Ni (II) and Cu( II) Metal Complexes

| Compound | NiL $(H_2O)_2$ | CuL $(H_2O)_2$ |
|---|---|---|
| Empirical formula | $C_{20}H_{24}N_2O_4Br_2Ni$ | $C_{20}H_{24}N_2O_4Br_2Cu$ |
| Formula weight | 558.65 | 577.54 |
| Wavelength (Å) | 1.541874 | 1.541871 |
| Crystal system | triclinic | monoclinic |
| Space group | P-1 | P 1 21/n 1 |
| Unit cell dimensions | | |
| A ( Å) | 10.1670 | 14.0540 |
| b( Å) | 16.1190 | 23.6330 |
| C( Å) | 9.4720 | 16.5250 |
| β (º) | 100.910 | 102.557 |
| Z | 2 | 8 |
| Unit Cell Volume | 1402.781 $Å^3$ | 5357.29 $Å^3$ |
| Calc. density | 1.355 g/cm³ | 1.4295 g/cm³ |

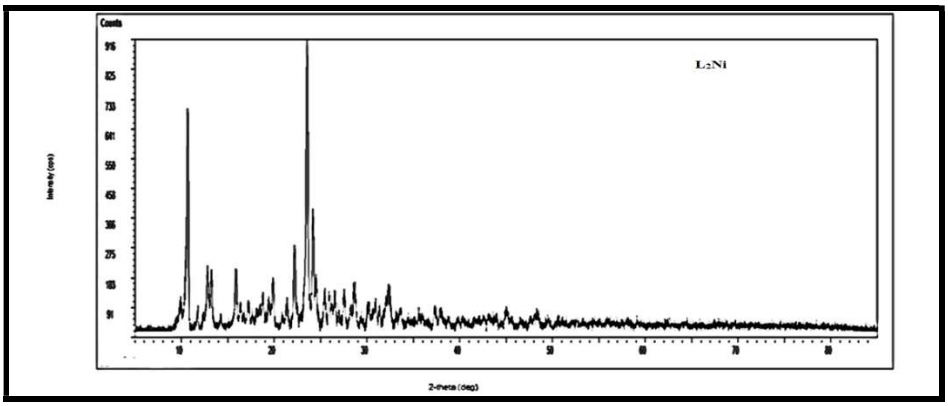


Fig.-5: X-Ray Diffraction of Ni (II) Complex of $L_2$Ligand

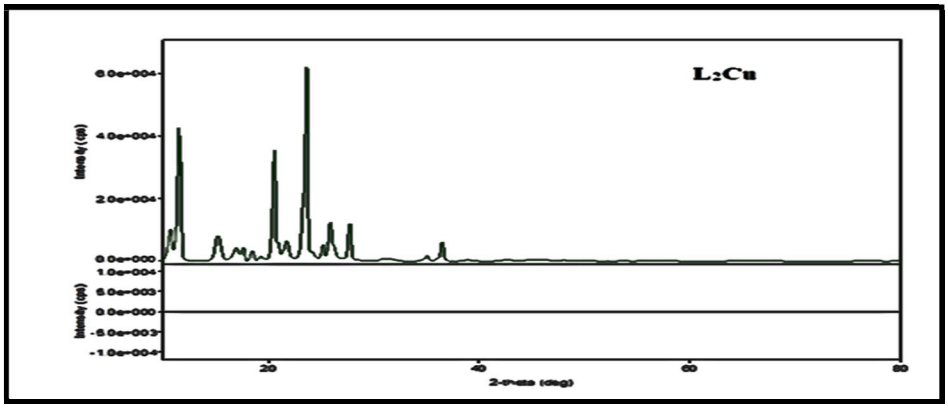


Fig.-6: XRD diffraction of Cu (II) Complex of $L_2$ ligand

**Thermogravimetric Analysis**

Thermal studies aid in determining the existence of water molecules in complexes as well as studying the decomposition pattern. Thermal studies of the complexes were conducted in the range of 50-900 $^0$C by controlling the heating rate of 15 $^0$C/min. The TGA curve of Co (II) complex of $L_2$ ligand (Fig.-7) was

found to be stable almost up to 230 $^0$C indicating the absence of lattice water. At about 300 $^0$C, the TG curve of the Co (II) complex of the $L_2$ ligand showed weight loss. The weight loss corresponds to the two coordinated water molecules. (Actual 6.309%, cal.6.28%). The loss of water molecules was confirmed by the exothermic peak obtained in DTA. The other exothermic peak was observed at 388.8 $^0$C which corresponds to the loss of some organic moiety. Following this, the complexes displayed a sharp drop in the weight loss suggesting that the organic moiety of the complex is eliminated and then decomposition continues up to 900 $^0$C showing the formation of stable metal complex oxides.

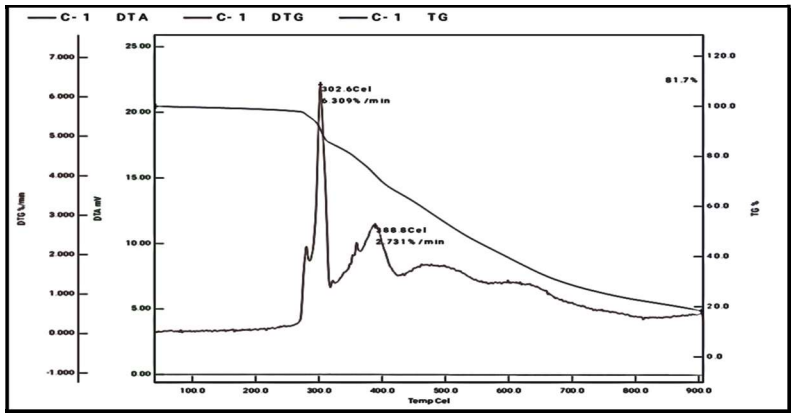


Fig.-7: TGA of $L_2$ Co complex

**Biological Evaluation**

The Schiff bases and their metal complexes were screened for antimicrobial activity against three strains of gram-positive (*S. aureus, S. pneumoniae, and B. subtilis*), three strains of gram-negative (*E. coli, S. typhi, and P. vulgaris*) and three fungi (*C. albicans, A. niger and T. rubrum*). Table-6 displayed the antimicrobial activity of the $L_2$ ligand and its metal complexes. (Fig.-8) According to the data, all of the metal complexes had low to moderate antimicrobial activity. The standards used for the gram-positive strain were ofloxacin, the gram-negative strain was ciprofloxacin and fungi were fluconazole. Among all the complexes Zn possesses higher activity and was also found to be active against fungi.

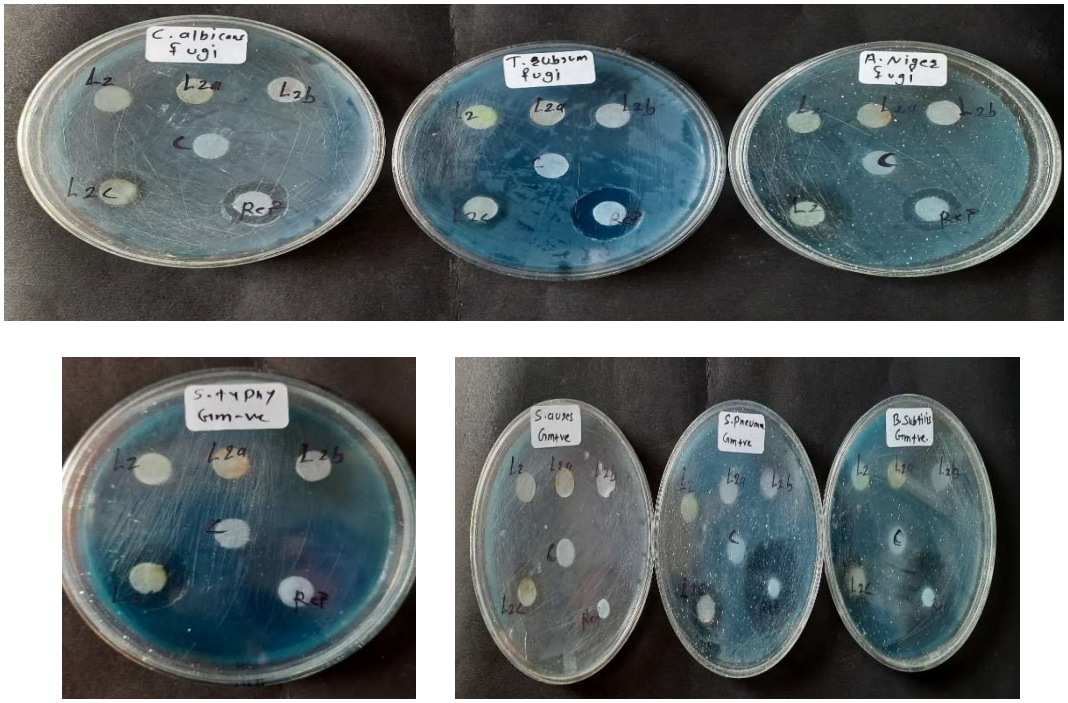


Fig.-8: Antimicrobial Activity of $L_2$ Ligand and its Metal Complexes. ($L_2$c -Zn(II) Complex

Table-6: Zone of Inhibition of Ligand and Metal Complexes

| | Zone of inhibition in mm | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Gram-Negative bacteria | | | Gram-Positive bacteria | | | Fungi | | |
| | *E. coli* | *S. typhi* | *P. vulgaris* | *S. aureus* | *S. pneumoniae* | *B. subtilis* | *C. albicans* | *A. niger* | *T. rubrum* |
| $L_2$ | 12 | 10 | 08 | 11 | 08 | 07 | NR | NR | NR |
| $L_2Co$ | 10 | 08 | 08 | 07 | 09 | 07 | NR | NR | NR |
| $L_2Ni$ | 16 | 11 | 10 | 12 | 10 | 12 | NR | NR | NR |
| $L_2Cu$ | 12 | 08 | 08 | 10 | 09 | 10 | NR | NR | NR |
| $L_2Zn$ | 16 | 20 | 12 | 18 | 14 | 20 | 14 | 23 | 15 |
| Reference | 38 Ofloxacin | 39 Ofloxacin | 34 Ofloxacin | 34 ciprofloxacin | 35 ciprofloxacin | 35 ciprofloxacin | 26 Fluconazole | 16 Fluconazole | 20 Fluconazole |
| Control | - | - | - | - | - | -- | | | |

## CONCLUSION

The synthesis, characterization, and molecular structure of new Ni (II), Co (II), Cu (II) and Zn (II) complexes of the tetradentate (2-N and 2 –O donor) Schiff base ligand have been reported and characterized by magnetic and spectral data. All the complexes except Cu (II) exhibited octahedral geometry. The molar conductance values of the complexes imply the non-electrolytic structure, thermal analysis indicates the presence of two coordinated molecules and x-ray diffraction studies indicate the crystalline nature of the complexes. Zn (II) complexes possess higher antimicrobial activity compared to other metal complexes.

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[RJC-6355/2021]