Preparation, Characterization and Biological Activities of some Unsymmetrical Schiff Bases Derived from m-phenylenediamine and their Metal Complexes

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ABSTRACT
Unsymmetrical Schiff bases \(H_2L^1 = [1-((E)-((3-(((E)-2-hydroxybenzylidene)amino)phenyl)imino)methyl) naphthalene-2-ol]\) and \(H_2L^2 = [1-((E)-((3-(((E)-1-(2-hydroxyphenyl)ethylidene)amino)phenyl)imino)methyl) naphthalene-2-ol]\) which derived from \(m\)-phenylenediamine and 2-hydroxynaphthaldehyde and then with salicyaldehyde or 2-hydroxyacetophenone, and their complexes of the type \([M_2Ln^2]\), where \(n = 1, 2\) and \(M = \text{Mn(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}\) have been synthesized. Adduct complexes of the type \([M_2Ln^2(py)_4]\) were also prepared in \((1:4)\) (complex : py) molar ratio. The complexes and adducts were characterized by elemental analysis (C, H, N), metal content, (IR, UV-\(\mathrm{v.s.}\), \(^1\text{H}-\text{NMR}\)) spectroscopy, conductivity and magnetic measurements. The resulted data suggested that the Schiff bases containing ONNO donor atoms acts as dibasic tetradentate ligands through coordinated with metal ions. Conductivity data in DMSO solution showed that all complexes are non-electrolyte. Magnetic moment and electronic spectra data indicate that the complexes have either tetrahedral or octahedral geometry while \([\text{Ni}_2L^n_2]\) complexes have square planer geometry. The legends and their complexes were screened for antibacterial activity against \(\text{Staphylococcus-aureus}\) and \(\text{Escherichia coli}\). The ligands and their complexes showed some biological activities.

Keywords: Antibacterial activity, \(m\)-phenylenediamine, Schiff base, Unsymmetrical tetradentate.
INTRODUCTION

Both symmetrical and unsymmetrical Schiff bases have been widely used as ligands to prepare metal complexes (Prakash et al., 2011). These complexes have played a major role in the advancement of coordination chemistry whose field of application varies from physicochemical studies (Luo et al., 2003), to biological aspects (El-Motalb et al., 2011).

In biological systems, transition metal ions are usually bound to a macrocycle such as a heme ring or to donor atoms of peptide chains in distorted environment (Li et al., 2015), and this unsymmetrical coordination of ligands around central metal ions had lead to a growing interest in the design and synthesis of transition metal complexes of unsymmetrically substituted Schiff base ligands as synthetic models (Hernandez et al., 2004).

Aromatic diamines have the ability to coordinate to a metal directly on their relative ortho, meta or para positions (Hernandez et al., 1997), m– phenylenediamine derived Schiff bases can only coordinate one nitrogen atom to any metal ion. This is due to the big proximity range between the nitrogen atoms of m- phenylenediamine and its rigid structure (Torayama et al., 1998).

Generally, m-phenylenediamine Schiff bases have the ability to acquire the formation of dimer complexes, where the Schiff bases act as bridges connecting the two metal cations (Clarke et al., 1998) thus producing dinuclear complexes. The uniqueness of such behaviour however has never been applied and studied in the biological field as compared the Schiff bases derived from the other two aromatic diamines namely its ortho and para – analogues. Such complexes were suggested to have an even better biological activity due to the presence of two metal ions compared to complexes with one metal ion. Therefore synthesis, characterization and the biological activity of two unsymmetrical tetradentate Schiff bases derived from m- phenylenediamine and their Mn(II), Co(II), Ni(II) and Cu(II) complexes are described in this work.

EXPERIMENTAL

All reagents and solvents were of analytical grade used as supplied from fluka or BDH chemical companies, Infrared spectra were recorded on BRUKER mauf. U.K. (400-4000 cm$^{-1}$) using KBr disc. Conductivity measurements were carried out on (10$^{-3}$) M solution of the complexes in DMSO using Conductivity meter Model PCM3 - JENWAY at ambient temperature. The electronic spectra were recorded in DMSO (10$^{-3}$) M solution on SPECTRO UV-VIS AUTO, 110 v 60 HZ using 1cm quartz cell (200-1000)nm. Metal content was determined using instrument, AA-7000- UN. BG. IBN- H.C.S.L Atomic Absorption (Flamecont). Elemental analysis were performed on Euro EAE Elemental Analyzer Euro EA 3000 Italy. H-NMR Spectra were recorded in DMSO –d$_{6}$ using NMR edy 60 prrouser, Manual Version 1.0 (Nanalysis Crop, 2015). Melting point was recorded on Electro - thermal 9300 Engineering LT D. The magnetic measurements were carried out at 25 °C on the solid state by (Magnetic Susceptibility Balance Sherwood Scientific Cambridge / U K).
Preparation of the Legends

The unsymmetrical Schiff base ligands were prepared according to the reported procedure (Pethe et al., 2017) by reacting equimolar amounts of m-phenylenediamine (0.01 mole, 1.08 g) in methanol (10 ml) was added slowly to methanolic solution (10 ml) containing 2-hydroxynaphthaldehyde (0.01 mole, 1.72 g) and refluxed for 1 h, then followed by addition of salicyaldehyde (0.01 mole, 1.22 g) or 2-hydroxyacetophenone (0.01 mole, 1.36 g), each one dissolved in methanol (10 ml), the resulting coloured mixture was refluxed with stirring for 4 h and cooled, then the precipitate was filtered off and washed with cold methanol and dried under vacuum, (Schem 1).

![Chemical structure](image1)

Preparation of the Complexes

The ligands H$_2$L$^1$ (0.01 mole, 3.66 g) or H$_2$L$^2$ (0.01 mole, 3.80 g) was dissolved in methanol (30 ml) in 100 ml round bottom flask. A solution of metal chloride (0.01 mole) [MnCl$_2$.4H$_2$O (1.97 g), CoCl$_2$.6H$_2$O (2.37 g), NiCl$_2$.6H$_2$O (2.37 g), CuCl$_2$.2H$_2$O (1.70 g)] in methanol (20 ml) was added drop wise for 10-15 min. with continues stirring at room temp. The mixture was refluxed for (3 - 4) h, after cooling the precipitate filtered off and washed with cold methanol then dried under vacuum.

Preparation Base Adduct Complexes

These complexes were prepared by the addition of pyridine (0.04 mole, 3.16 g) to (0.01 mole) the prepared complexes in methanol (50 ml) with continuous stirring until complete precipitation. The precipitate was filtered off, washed with cold methanol and dried under vacuum (Osowole, 2008).

Antibacterial Activity

Antibacterial activity was evaluated using agar diffusion method (Kethcum, 1988), Gram - positive bacteria Staphylococcus aureus and Gram – negative bacteria Escherichia coli were cultivated in nutrient agar on petri dishes. The test solution was prepared by dissolving (10 mg) of the tested substances in DMSO (1 mL). A6 mm diameter filter discs were soaked in the tested solutions. After 24 h cultivation at 37$^\circ$C, diameter of zones of inhibition was determined. DMSO was inactive under applied conditions.
RESULTS AND DISCUSSION

All the metal complexes are quite stable in dry air and insoluble in common organic solvents but soluble in DMF and DMSO. The elemental analysis shows \((2 : 2)\) \((M : L)\) molar ratio for \([M_2 L_2^n]\) and \((2 : 2 : 4)\) \([M : L^n : py]\) molar ratio for \([M_2 L_2^n (PY)_4]\). Some physical properties of ligands and their complexes are listed (Table 1.). The molar conductance in \((10^{-3})\) M DMSO solution of complexes are in the range \((14.4 - 20.0)\) ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\), indicating a non electrolytic nature of the complexes (Gerry, 1971).

Infrared Spectra

The IR Spectrum of the free ligands was studied and assigned on the bases of careful comparison of the complex spectra with that of the free legends, (Table 2). The IR Spectrum of the ligand show characteristic band at \((3465\) and \(3498)\) cm\(^{-1}\) attributed to the phenolic hydroxyl group in \(H_2L_1\) and \(H_2L_2\) respectively (Alias et al., 2014). The absence of this band in the spectra of the complexes indicates the coordination of phenolic oxygen to the metal ion after deprotonation (Pethe et al., 2017). This is further supported by the shifting of \(\nu (C-O)\) phenolic band to lowers frequency \((1245 -1273)\) cm\(^{-1}\) in the spectra of all complexes (Nagajothi et al., 2013). The IR spectrum of \((H_2L_1\) and \(H_2L_2\)) show band at \((1612\) and \(1582 )\) cm\(^{-1}\) due to \(\nu (C=N)\) stretch. On complexation this band shifted to higher frequency in all complexes by \((10 - 34)\) cm\(^{-1}\) indicating participation of azomethine nitrogen in complexation (Ramesh et al., 1996). The stretching vibration of \(\nu (C=N)\) bond of pyridine ring was observed at the region \((1484 - 1506 )\) cm\(^{-1}\) in complexes \((5,6,7, 8,13,14,15\) and \(16)\) which indicates the coordination of the nitrogen atom of pyridine ring with the metal ions (Ceraldo et al., 2011). Some new bands apper in the spectra of the complexes which include of the stretching vibrations of \(\nu (M-N)\) and \(\nu (M-O )\). These bands apper in the ranges \((417-463)\) cm\(^{-1}\) and \((491 - 553)\) cm\(^{-1}\) respectively (Pathan et al., 2012). The I.R Spectra of ligands and Mn(II), Cu(II) have been shown Fig. (1).
Fig. 1: IR – Spectra of (a) $\text{H}_2\text{L}^1$ (b) $[\text{Mn}_2\text{L}^1_2]$ (c) $\text{H}_2\text{L}^2$ and (d) $[\text{Cu}_2\text{L}^2_2]$
Electronic Spectra and Magnetism

The magnetic moments and electronic spectra data at 25 °C of the ligands and their complexes are listed (Table 3). The electronic spectra of the ligands $H_2L_1$ and $H_2L_2$ in DMSO solution show intense bands at (37037, 37313) cm$^{-1}$ and (31446, 31545) cm$^{-1}$ attributed to benzene $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition of the non-bonding electrons present on the nitrogen of the azomethine group respectively, these transitions are also found in the spectra of the complexes but they are shifted to confirmed the coordination of the ligand to the metal ion (Elmali et al., 2005). New bands in spectra of all complexes at range (26993- 29411) cm$^{-1}$ may be associated with the charge transfer transition (Aranha et al., 2016).

The dinuclear Mn(II) complexes (1,5,9 and 13) show magnetic moment values at the range (5.75 - 5.90) B.M, which are appreciably close to the calculated spin-only value (5.91) B.M, for five unpaired electrons and reveals a high spin state (Cotton et al., 1999). The electronic spectra of extremely pale colour high spin Mn (II) complexes don’t show any d–d transitions bands due to spin forbidden as well as parity–forbidden transitions in tetrahedral and octahedral environments (Cotton et al., 1999; Al-Kattan and Al-Nidaa, 2013), therefore, the structures of the prepared Mn(II) complexes were proposed depending on the data of other measurements namely metal content and IR spectra.

The magnetic moment values of dinuclear Co(II) complexes (2, 10) are (3.81 and 3.79) B.M, and their electronic spectra exhibit an absorption peak at (16393 and 16260) cm$^{-1}$ which was assigned to $^4A_2(F) \rightarrow ^4T_1(P)$ transition, and the absence of $^4A_2(F) \rightarrow ^4T_2(F)$ and $^4A_2(F) \rightarrow ^4T_1(F)$, are due to the sensitivity of the instrument used, the magnetic measurement and the electronic spectra of these complexes indicating a tetrahedral geometry (Ejidike et al., 2015). The magnetic moment values of dinuclear Co(II) complexes (6, 14) are (5.75 and 5.80) B.M, and their electronic spectra showed bands at (16806, 21052) cm$^{-1}$ and (15480, 21276) cm$^{-1}$ assigned to $^4T_{1g}(F) \rightarrow ^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$ respectively, these observation indicates an octahedral geometry around Co(II) ions (Siddiqi et al., 2007).

The magnetic measurements indicates that dinuclear Ni (II) complexes (3, 11) are diamagnetic and the electronic spectra of these complexes showed two bands at (18518, 24396) cm$^{-1}$ and (16666, 24096) cm$^{-1}$, which assigned to $^1A_1g \rightarrow ^1A_2g$ and $^1A_1g \rightarrow ^1B_1g$ transition respectively, these results suggest a square planar geometry around Ni (II) (Raman et al., 2007), while the magnetic measurements of complexes (7, 15) were found to be (2.92 and 2.79) B.M, and the electronic spectra of these complexes show two bands at (21186, 24271) cm$^{-1}$ and (20618, 23529) cm$^{-1}$ assigned to $^3A_2g(F) \rightarrow ^3T_{1g}(F)$ and $^3A_2g(F) \rightarrow ^3T_{1g}(P)$ transition respectively, which indicating an octahedral geometry around the Ni(II) ions. (Jayaseelan et al., 2011; Al-Daher et al., 2018).

The obtained magnetic moment values of Cu(II) complexes (4, 8,12 and 16) has been found in the range (1.83 – 2.20) B.M, which indicate the presence of one unpaired electron for Cu (II). The electronic spectra of Cu (II) complexes (4, 12) showed a broad band at (10686, 10566) cm$^{-1}$ attributed to $^2T_2 \rightarrow ^2E$ transition which is comparable with complexes having a tetrahedral structure (Turan et al., 2009), while complexes (8, 16) showed a broad absorption band at (151515, 15625) cm$^{-1}$ arises due to d–d transition $^2E_g \rightarrow ^2T_{2g}$ suggest that the Cu(II) ion exhibits an octahedral geometry (Jayaseelan et al., 2010).

$^1$H-NMR - Spectra of Ligands

The $^1$H-NMR- Spectra of free ligands at room temperature in DMSO – d$_6$ shows the following signals (Garces et al., 1988).

For $H_2L_1$: $\delta$ = 12.95 ppm (s, 2H, phenolic), $\delta$ = (6.89 - 8.55) ppm (m, 14 H, Aromatic), $\delta$ = 9.03 ppm (s, 2H, azomethine).

For $H_2L_2$: $\delta$ = 3.51 ppm (s, 3H, -CH3), $\delta$ = 9.70 ppm (s, 2H, phenolic), $\delta$ = (6.89- 8.45) ppm (m, 14H, Aromatic), $\delta$ = 8.55 ppm (s, 1H, azomethine). The $^1$H-NMR - Spectra of ligands have been shown Fig. (2).
Antibacterial Activity

The tested compounds were screened in vitro for their antibacterial activity against Gram-negative and Gram-positive (Escherichia coli, Staphylococcus aureus) bacteria, the antibacterial results are given in (Table 4), compared with those of the standard drug (Ciprofloxacin). The results evidently show that the ligands and all tested complexes were active against the Gram-positive and Gram-negative bacteria. On the other hand, Cu(II) complexes (4, 8, 12 and 16) exhibited higher inhibition activity as compared with their corresponding ligands and other complexes, generally the activity order against Staphylococcus aureus of the
synthesized compounds is as follows: \( \text{CuL} > \text{NiL} > \text{CoL} > \text{H}_2\text{L}^2 > \text{H}_2\text{L}^1 > \text{MnL} \), while the activity order against \textit{Escherichia coli} of the synthesized compounds is as follows: \( \text{CuL} > \text{NiL} > \text{MnL} > \text{CoL} > \text{H}_2\text{L}^2 = \text{H}_2\text{L}^1 \).

![Activity of ligands and complexes](image)

**Fig. 3: Antibacterial Activity of Schiff base ligands and complexes**

**CONCLUSION**

New Mn (II), Co (II), Ni (II), and Cu (II) complexes of unsymmetrical tetra dentate Schiff bases ligand (\( \text{H}_2\text{L}^1 \) and \( \text{H}_2\text{L}^2 \)) have been prepared and characterized by conventional measurements. The data revealed that all the complexes are dinuclear and have an either tetrahedral or octahedral geometry while \([\text{Ni}_2\text{L}_2]\) complexes have square planer configuration Fig. (4). The ligands act as \( \text{N}_2\text{O}_2 \) tetra dentate dibasic chelating ligands coordinated through phenolic oxygen and imine nitrogen atoms. The ligands and their complexes were tested against Gram–positive and Gram–negative bacteria which indicate that ligands and all complexes are active against Gram-negative bacteria as compared with standard drugs. The highest activity exhibited by Cu (II) complexes.
Fig. 4: Suggested structure of complexes \([M_2L^a_2]\) and \([M_2L^a_2(py)_4]\)

Complexes(1, 2, 4, 9, 10, 12)
M = Mn(II), Co(II) and Cu(II)
R = H, CH3
Table 1: The physical properties and analytics of the ligands and their complexes

| NO. | COMPOUND | COLOUR       | m.p(C⁰) | Am(ohm⁻¹ cm² mol⁻¹) | M% Calc. (found) | Analysis calc. (found) | % C% | H % | N % |
|-----|----------|--------------|---------|--------------------|------------------|-----------------------|------|-----|-----|
|     |          |              |         |                    |                  |                       |      |     |     |
| 1   | [Mn₂L₁²] | Pale yellow  | 250     | 19.5               | 13.1 (13.69)     | 68.74 (68.89)         | 3.85 (3.90) | 6.68 (6.08) |
| 2   | [Co₂L₁²] | Green olive  | 188     | 17.6               | --------         | -----                  | ----- | ----- | ----- |
| 3   | [Ni₂L₁²] | Orange yellow| 190     | 12.8               | 13.87 (13.60)    | -----                  | ----- | ----- | ----- |
| 4   | [Cu₂L₁²] | Brown        | 185     | 20.4               |                   | -----                  | ----- | ----- | ----- |
| 5   | [Mn₂L₁²(py)₄] | Pale yellow | 220     | 11.3               | 9.51 (9.11)      | 70.70 (69.98)         | 4.55 (4.50) | 9.70 (8.89) |
| 6   | [Co₂L₁²(py)₄] | Light green  | 200     | 20.0               |                   | -----                  | ----- | ----- | ----- |
| 7   | [Ni₂L₁²(py)₄] | Brown     | 190     | 14.4               |                   | -----                  | ----- | ----- | ----- |
| 8   | [Cu₂L₁²(py)₄] | Green     | 195     | 19.8               |                   | -----                  | ----- | ----- | ----- |
| 9   | [Mn₂L₂²] | Pale yellow  | 232     | 19.7               |                   | -----                  | ----- | ----- | ----- |
| 10  | [Co₂L₂²] | Green olive  | 198     | 18.5               |                   | -----                  | ----- | ----- | ----- |
| 11  | [Ni₂L₂²] | Olive        | 193     | 19.7               | 13.43 (13.10)    | 68.69 (68.45)         | 4.16 (4.59) | 6.41 (6.97) |
| 12  | [Cu₂L₂²] | Gray         | 195     | 19.4               | 14.38 (14.90)    | 67.93 (67.87)         | 4.11 (4.32) | 6.34 (5.77) |
| 13  | [Mn₂L₂²(py)₄] | Pale yellow | 250     | 14.9               |                   | -----                  | ----- | ----- | ----- |
| 14  | [Co₂L₂²(py)₄] | Green     | 200     | 20.0               | 9.89 (9.60)      | 70.58 (70.21)         | 4.75 (4.48) | 9.41 (9.70) |
| 15  | [Ni₂L₂²(PY)₄] | Green yellow | 205     | 16.7               |                   | -----                  | ----- | ----- | ----- |
| 16  | [Cu₂L₂²(PY)₄] | Brown green | 195     | 17.5               | 10.59 (10.56)    | 70.03 (69.51)         | 4.71 (4.55) | 9.34 (8.87) |
### Table 2: Characteristic Infrared spectral data (cm$^{-1}$) of the ligands and their complexes

| NO. | (O-H) cm$^{-1}$ | (C-O) cm$^{-1}$ | (C=N)$_{imine}$ cm$^{-1}$ | (M – O) cm$^{-1}$ | (M-N) cm$^{-1}$ |
|-----|-----------------|-----------------|--------------------------|------------------|-----------------|
|     |                 |                 |                         |                  |                 |
| H$_2$L$^1$ | 3465 | 1275 | 1612 | ------- | ------- |
| 1   | ------- | 1250 | 1622 | 533 | 453 |
| 2   | ------- | 1270 | 1626 | 520 | 433 |
| 3   | ------- | 1265 | 1623 | 454 | 425 |
| 4   | ------- | 1273 | 1622 | 522 | 463 |
| 5   | ------- | 1260 | 1623 | 533 | 420 |
| 6   | ------- | 1255 | 1623 | 535 | 440 |
| 7   | ------- | 1265 | 1622 | 518 | 433 |
| 8   | ------- | 1260 | 1623 | 533 | 417 |
| H$_2$L$^2$ | 3498 | 1265 | 1582 | ------- | ------- |
| 9   | ------- | 1255 | 1612 | 535 | 463 |
| 10  | ------- | 1250 | 1616 | 520 | 418 |
| 11  | ------- | 1265 | 1614 | 531 | 453 |
| 12  | ------- | 1255 | 1607 | 491 | 452 |
| 13  | ------- | 1260 | 1598 | 540 | 457 |
| 14  | ------- | 1245 | 1619 | 530 | 420 |
| 15  | ------- | 1250 | 1616 | 553 | 418 |
| 16  | ------- | 1245 | 1616 | 520 | 418 |
Table 3: Magnetic moments and the electronic spectral data of the ligands and their complexes

| NO. | µeff (B.M) | Assignment | Band maxima λ (cm⁻¹) | Structure |
|-----|------------|------------|-----------------------|-----------|
| H₂L¹ | . . . . . . | n → π*, π → π* | 31446, 37037 | . . . . . . |
| 1   | 5.75       | C, T       | 27397                | Td        |
| 2   | 3.81       | ¹A₂(F) → ²T₁(P), C, T | 16393, 287501 | Td        |
| 3   | Diamagnetic | 'A₁g → 'A₂g, 'A₁g → 'B₁g, C, T | 18518, 24396, 28134 | Sq.pl     |
| 4   | 2.11       | ²T₂ → ²E, C, T | 10686, 27954 | Td        |
| 5   | 5.85       | C, T       | 277701               | . . . . . . |
| 6   | 5.75       | ¹A₂g (F) → ²T₁g (F), ³T₁g (F) → ³T₁g (p), C, T | 16806, 21052, 29411 | Oh        |
| 7   | 2.92       | ¹A₂g (F) → ³T₂g (F), ³A₂g (F) → ³T₁g (F) | 21186, 24271, 27691 | Oh        |
| 8   | 1.83       | T, C, ²Eg → ²T₂g | 151515, 27998 | Oh        |
| H₂L² | . . . . . . | n → π*, π → π* | 31545, 37313 | . . . . . . |
| 9   | 5.8        | C, T       | 28091                | Td        |
| 10  | 3.79       | ¹A₂(F) → ²T₁(P), C, T | 16260, 27397 | Td        |
| 11  | Diamagnetic | 'A₁g → 'A₂g, 'A₁g → 'B₁g, C, T | 16666, 24096, 29061 | Sq.pl     |
| 12  | 1.87       | ²T₂ → ²E, C, T | 10566, 28365 | Td        |
| 13  | 5.90       | C, T       | 28559                | . . . . . . |
| 14  | 5.80       | ¹A₂g (F) → ²T₁g (F), ³T₁g (F) → ³T₁g (p), C, T | 15480, 21276, 26993 | Oh        |
| 15  | 2.79       | ¹A₂g (F) → ³T₂g (F), ³A₂g (F) → ³T₁g (F) | 20618, 23529, 29050 | Oh        |
| 16  | 2.20       | ²Eg → ²T₂g , C, T | 15625, 28792 | Oh        |

Table 4: The antibacterial activity of ligands and their complexes

| NO. | COMPOUND | Gram (+) bacteria | Gram (-) bacteria |
|-----|----------|-------------------|-------------------|
|     |          | Staphylococcus aureus (mm) | Escherichia coli (mm) |
| H₂L¹ | C₂₅H₂₀N₂O₂ | 7                  | 14                |
| 1   | [Mn₂L₂]  | 6                  | 10                |
| 2   | [Co₂L₂]  | 12                 | 7                 |
| 3   | [Ni₂L₂]  | 15                 | 12                |
| 4   | [Cu₂L₂]  | 24                 | 27                |
| 5   | [Mn₂L₂(py)₄] | 12               | 15                |
| 6   | [Co₂L₂(py)₄] | 13               | 12                |
| 7   | [Ni₂L₂(py)₄] | 23               | 14                |
| 8   | [Cu₂L₂(py)₄] | 30               | 20                |
| H₂L² | C₂₅H₂₀N₂O₂ | 14                | 14                |
| 9   | [Mn₂L₂]  | 13                 | 13                |
| 10  | [Co₂L₂]  | 16                 | 12                |
| 11  | [Ni₂L₂]  | 18                 | 18                |
| 12  | [Cu₂L₂]  | 22                 | 28                |
| 13  | [Mn₂L₂(py)₄] | 13               | 12                |
| 14  | [Co₂L₂(py)₄] | 22               | 15                |
| 15  | [Ni₂L₂(py)₄] | 23               | 14                |
| 16  | [Cu₂L₂(py)₄] | 27               | 30                |
| Standard drug | Ciprofloxacain | 27 | 16 |

Inhibition zone diameter (mm) (% inhibition): 6 - 10 (27 - 45%); 10 - 14 (45 - 64%); 14 - 18 (64 - 82%); 18 - 22 (82 - 100%).
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