

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

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(Received 8/ 7/ 2018 ; Accepted 25/ 10/ 2018)

### ABSTRACT

Unsymmetrical Schiff bases  $H_2L^1 = [1-((E)-(3-((E)-2\text{-hydroxybenzylidene) amino)phenyl)imino)methyl) naphthalene-2-ol]$  and  $H_2L^2 = [1-((E)-(3-((E)-1-(2\text{-hydroxyphenyl) ethylidene) amino) phenyl) imino) methyl) naphthalene - 2 - ol]$  which derived from *m*-phenylenediamine and 2-hydroxynaphthaldehyde and then with salicylaldehyde or 2-hydroxyacetophenone, and their complexes of the type  $[M_2L^n_2]$ , where  $n = 1, 2$  and  $M = Mn(II), Co(II), Ni(II)$  and  $Cu(II)$  have been synthesized. Adduct complexes of the type  $[M_2L^n_2(py)_4]$  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- v.s,  $^1H$ -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 indicat that the complexes have either tetrahedral or octahedral geometry while  $[Ni_2L^n_2]$  complexes have square planer geometry. The legends and their complexes were screened for antibacterial activity against *Staphylococcus- aureus* and *Escherichia coli*. The ligands and their complexes showed some biological activities.

**Keywords:** Antibacterial activity, *m*-phenylenediamine, Schiff base, Unsymmetrical tetradentate.

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$H_2L^1 = [1-((E)-(3-((E)-2\text{-hydroxybenzylidene) amino)phenyl)imino)methyl) naphthalene- 2- ol]$ ,  $H_2L^2 = [1-((E)-(3-((E)-1-(2\text{-hydroxyphenyl) ethylidene) amino) phenyl) imino) methyl) naphthalene - 2 - ol]$ ,  
*m*- phenylenediamine ethylidene) amino) phenyl) imino) methyl) naphthalene - 2 - ol],  
 $[M_2L^n_2]$  2-hydroxyacetophenone Salicylaldehyde 2 - hydroxynaphthaldehyde  
 $[M_2L^n_2]$   $M = Mn(II), Co(II), Ni(II), Cu(II), n = 1, 2$   
(C.H.N) .( : ) (1 : 4) (py)<sub>4</sub>)  
- )  
( (ONNO)

## DMSO



### 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).

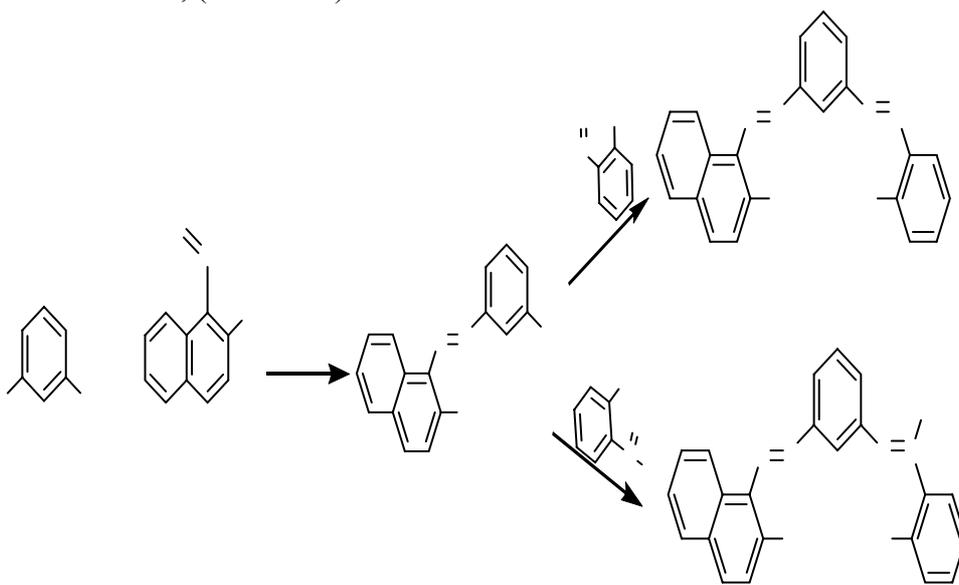
Generally, *m*-phenylenediamine Schiff bases have the ability to acquire the formation of dimer complexes, where the Schiff bases act as bridges connecting the two metal cations (Clarke *et al.*, 1998) thus producing dinuclear complexes. The uniqueness of such behaviour however has never been applied 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  $\text{cm}^{-1}$ ) 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.<sup>1</sup> H-NMR Spectra were recorded in DMSO - $\text{d}_6$  using NMR edy 60 prrouser, Manual Version 1.0 (Nanalysis Crop, 2015). Melting point was recorded on Electro - thermal 9300 Engineering LTD. The magnetic measurements were carried out at 25  $^{\circ}\text{C}$  on the solid state by (Magnetic Susceptibility Balance Sherwood Scientific Cambridge / U K).

### Preparation of the Ligands

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 (0.01mole, 1.72g) and refluxed for 1h, then followed by addition of salicylaldehyde (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).



### Preparation of the Complexes

The ligands  $H_2L^1$  (0.01 mole, 3.66 g) or  $H_2L^2$  (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) [  $MnCl_2 \cdot 4H_2O$  (1.97 g),  $CoCl_2 \cdot 6H_2O$  (2.37 g),  $NiCl_2 \cdot 6H_2O$  (2.37 g),  $CuCl_2 \cdot 2H_2O$  (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 (Osovole, 2008).

### Antibacterial Activity

Antibacterial activity was evaluated using agar diffusion method (Kethicum, 1988), Gram - positive bacteria *Staphylococcus aureus* and Gram - negative bacteria *Escherichia coli* were cultivated in nutrient agar 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 °C, diameter of zones of inhibition was determined. DMSO was inactive under applied conditions.

*m*-phenylenediamine, 2-hydroxy-1-naphthaldehyde

Methanol 2 h

Reflux, H<sub>2</sub>O

HC N

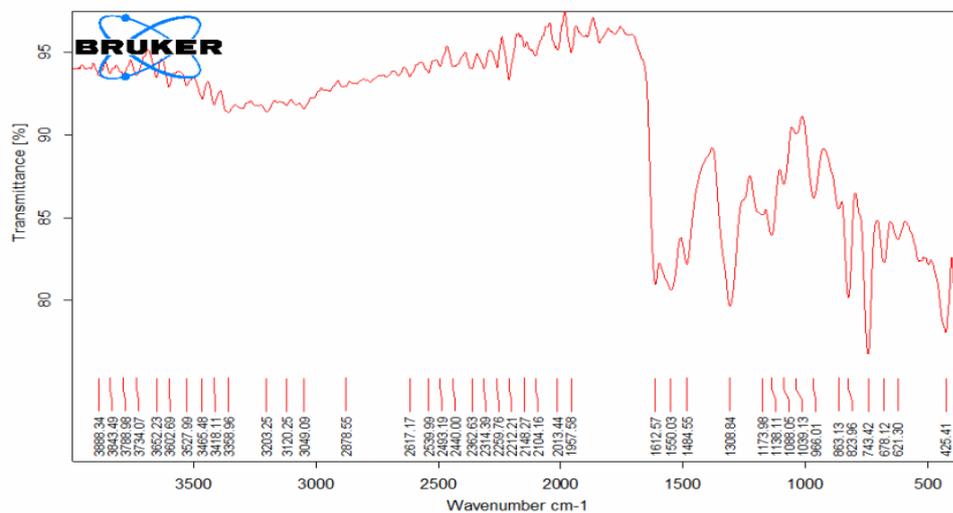
OH

## 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  $[M_2 L^n_2]$  and (2 : 2 : 4)  $[M : L^n : py]$  molar ratio for  $[M_2 L^n_2 (PY)_4]$ . 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  $(14.4 - 20.0) \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , 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  $(3465 \text{ and } 3498) \text{ cm}^{-1}$  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  $(1245 - 1273) \text{ cm}^{-1}$  in the spectra of all complexes (Nagajothi *et al.*, 2013). The IR spectrum of  $(H_2L^1$  and  $H_2L^2)$  show band at  $(1612 \text{ and } 1582) \text{ cm}^{-1}$  due to  $\nu(C=N)$  stretch. On complexation this band shifted to higher frequency in all complexes by  $(10 - 34) \text{ cm}^{-1}$  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  $(1484 - 1506) \text{ cm}^{-1}$  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  $(417-463) \text{ cm}^{-1}$  and  $(491 - 553) \text{ cm}^{-1}$  respectively (Pathan *et al.*, 2012). The I.R Spectra of ligands and Mn(II), Cu(II) have been shown Fig. (1).



( a )

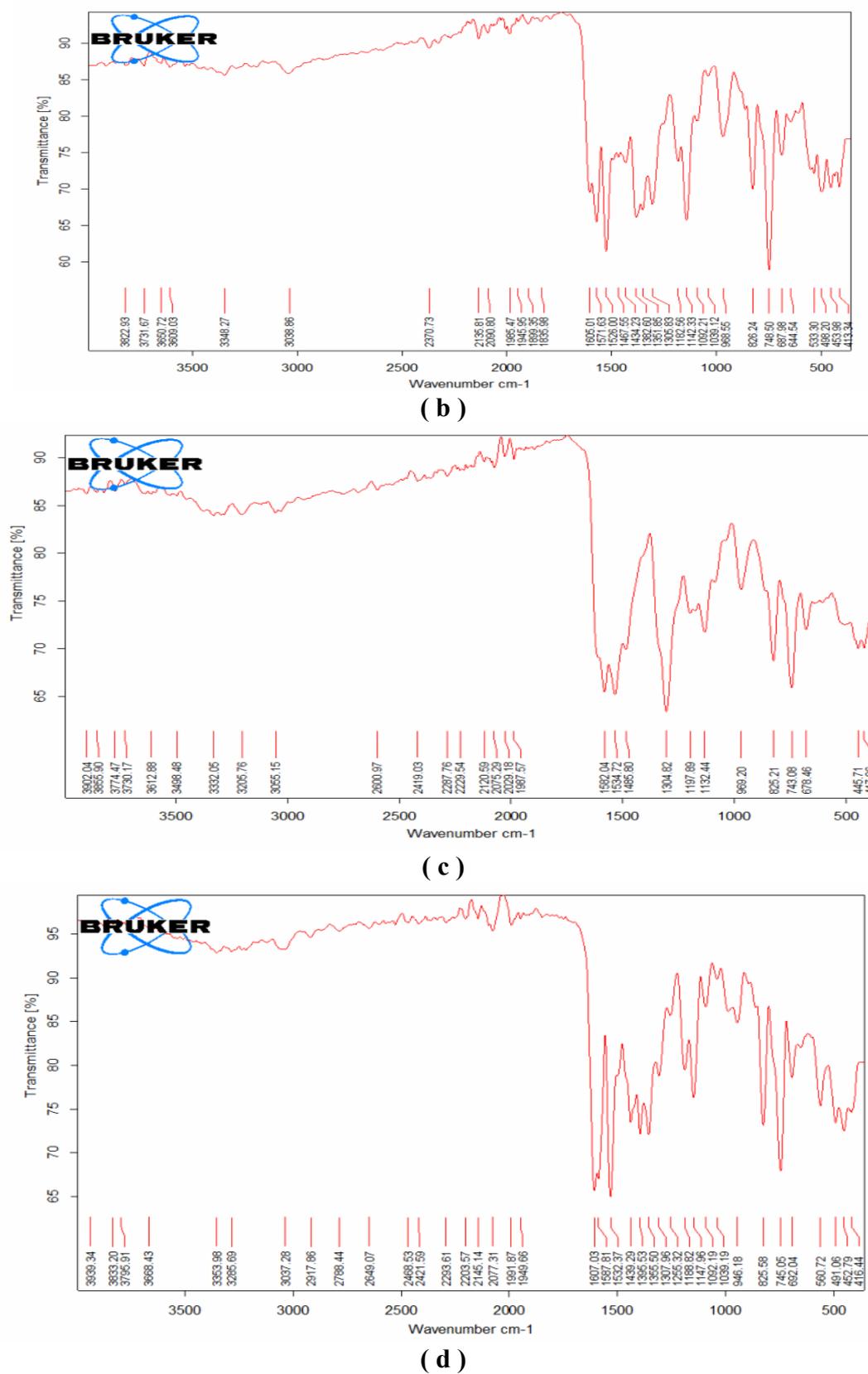


Fig. 1: IR – Spectra of (a)  $H_2L^1$  (b)  $[Mn_2L^1_2]$  (c)  $H_2L^2$  and (d)  $[Cu_2L^2_2]$

### 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)  $cm^{-1}$  region 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  $^1A_{1g} \rightarrow B_{1g}$  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).

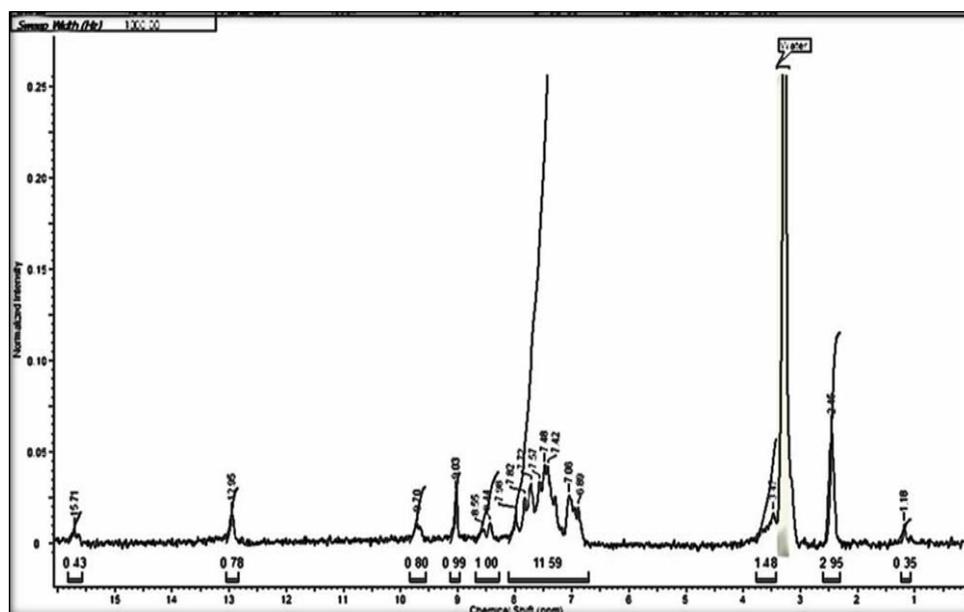
The obtained magnetic moment values of Cu(II) complexes (4 , 8,12 and 16) has been found in the range (1.83 – 2.20) B.M, which indicate the presence of one unpaired electron for Cu (II). The electronic spectra of Cu (II) complexes (4, 12) showed a broad band at (10686, 10566)  $cm^{-1}$  attributed to  $^2T_2 \rightarrow ^2E$  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).

### $^1H$ -NMR - Spectra of Ligands

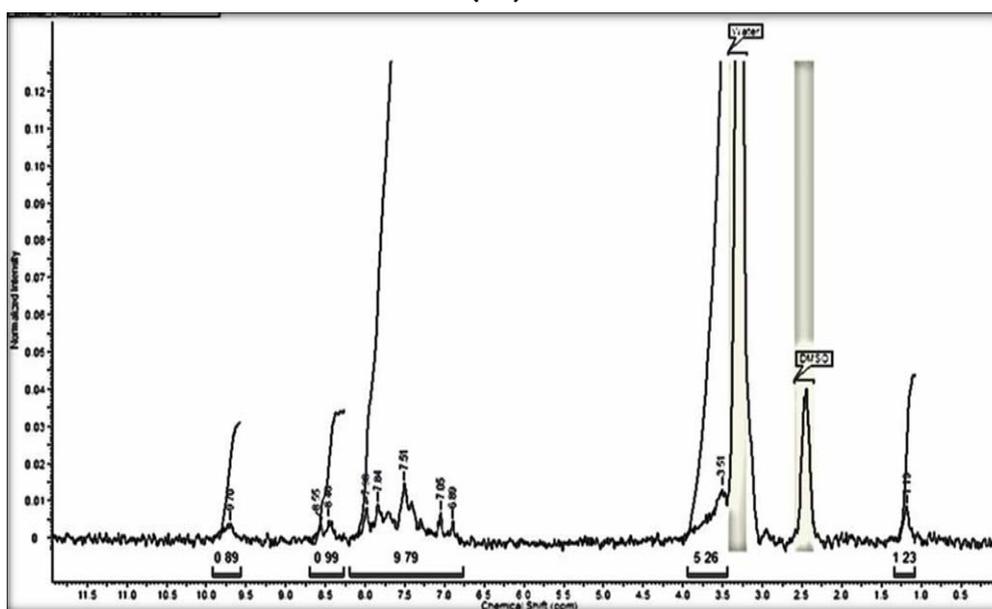
The  $^1H$ -NMR- Spectra of free ligands at room temperature in DMSO –  $d_6$  shows the following signals (Garces *et al.*, 1988).

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, -CH<sub>3</sub>),  $\delta = 9.70$  ppm (s, 2H, phenolic),  $\delta = (6.89- 8.45)$  ppm (m, 14H, Aromatic),  $\delta = 8.55$  ppm (s, 1H, azomethine). The  $^1H$ -NMR - Spectra of ligands have been shown Fig. (2).



(a)



(b)

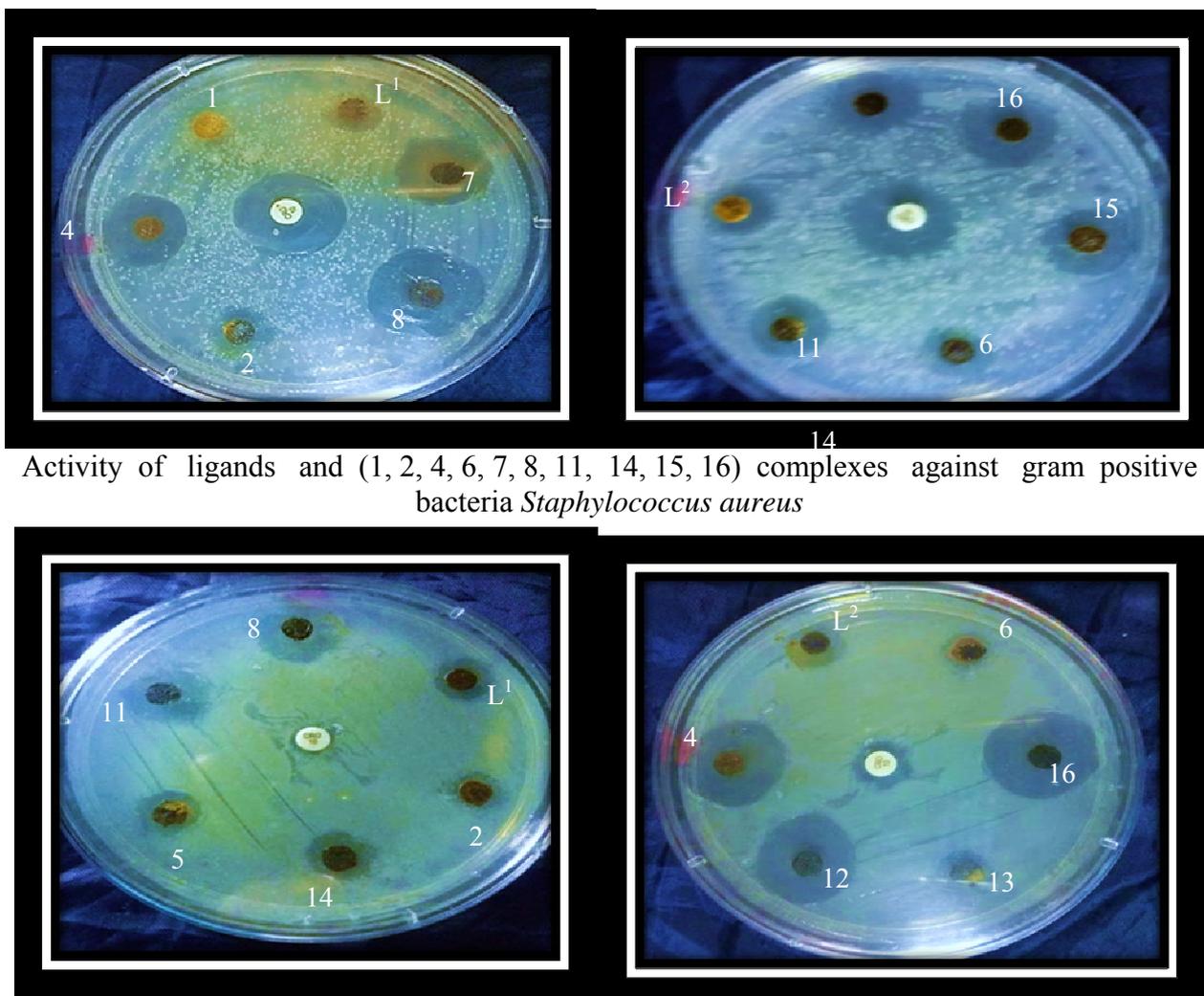
Fig. 2:  $^1\text{H}$ -NMR For (a)  $\text{H}_2\text{L}^1$  (b)  $\text{H}_2\text{L}^2$ 

s = singlet, m = multiplate

### 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 *Escherichia coli* of the synthesized compounds is as follows :-  $\text{CuL} > \text{NiL} > \text{MnL} > \text{CoL} > \text{H}_2\text{L}^2 = \text{H}_2\text{L}^1$ .



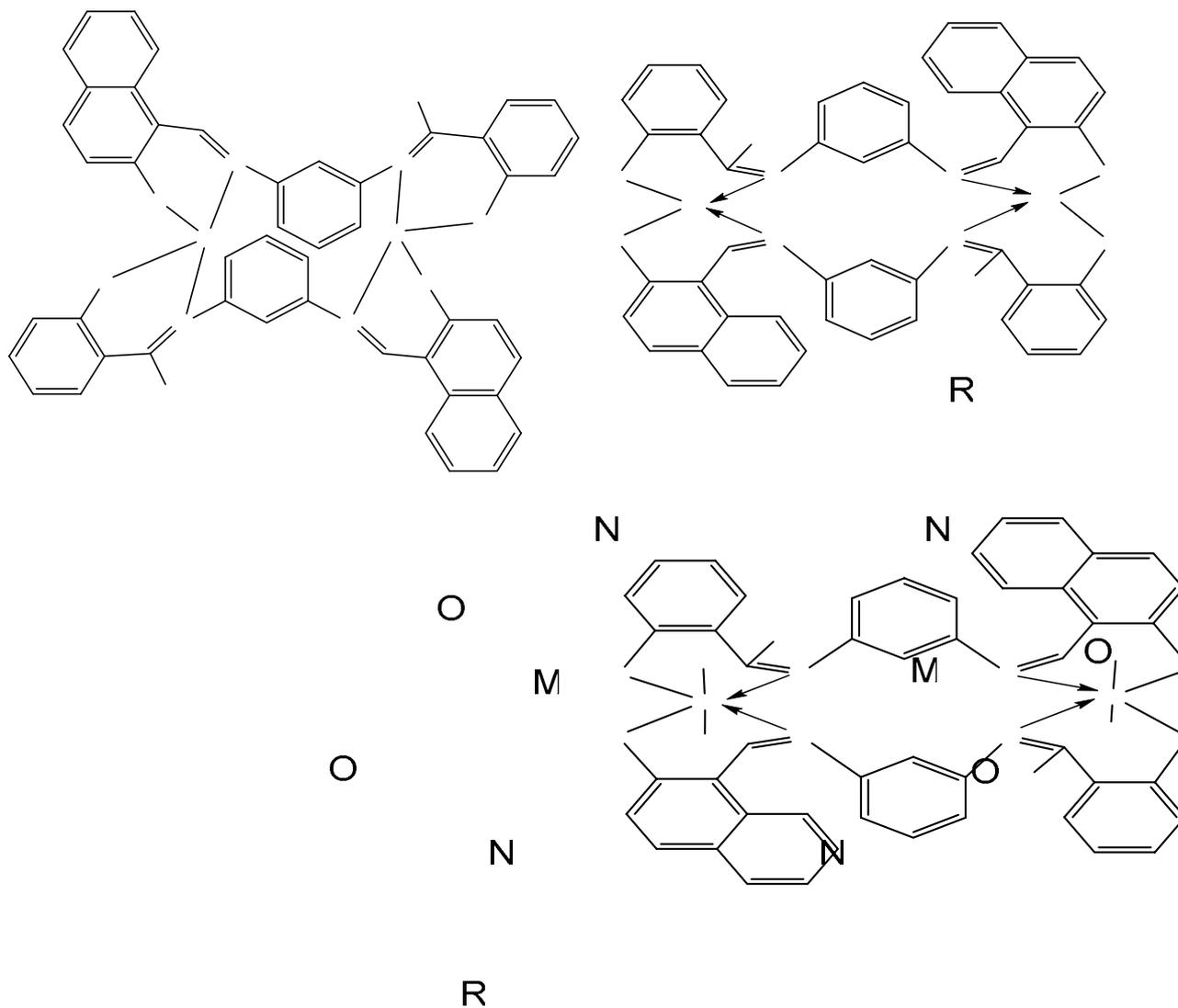
Activity of ligands and (1, 2, 4, 6, 7, 8, 11, 14, 15, 16) complexes against gram positive bacteria *Staphylococcus aureus*

Activity of ligands and (2, 4, 5, 6, 8, 11, 12, 13, 14, 16) complexes against gram negative bacteria *Escherichia coli*

**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  $[M_2L^n_2]$  and  $[M_2L^n_2(py)_4]$**

Complexes(1, 2, 4, 9, 10, 12)

M = Mn(II), Co(II) and Cu(II)

R = H , CH<sub>3</sub>

**Table 1: The physical properties and analytics of the ligands and their complexes**

NO.	COMPOUND	COLOUR	m.p(C <sup>0</sup> )	Am(ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )	M% Calc. (found)	Analysis calc. (found) %		
						C%	H %	N %
H <sub>2</sub> L <sup>1</sup>	C <sub>24</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub>	Green yellow	175	-----	-----	78.67 (77.73)	4.95 (4.78)	7.65 (8.18)
1	[Mn <sub>2</sub> L <sup>1</sup> <sub>2</sub> ]	Pale yellow	250	19.5	13.1 (13.69)	68.74 (68.89)	3.85 (3.90)	6.68 (6.08)
2	[Co <sub>2</sub> L <sup>1</sup> <sub>2</sub> ]	Green olive	188	17.6	-----	-----	-----	-----
3	[Ni <sub>2</sub> L <sup>1</sup> <sub>2</sub> ]	Orange yellow	190	12.8	13.87 (13.60)	-----	-----	-----
4	[Cu <sub>2</sub> L <sup>1</sup> <sub>2</sub> ]	Brown	185	20.4	-----	-----	-----	-----
5	[Mn <sub>2</sub> L <sup>1</sup> <sub>2</sub> (py) <sub>4</sub> ]	Pale yellow	220	11.3	9.51 (9.11)	70.70 (69.98)	4.55 (4.50)	9.70 (8.89)
6	[Co <sub>2</sub> L <sup>1</sup> <sub>2</sub> (py) <sub>4</sub> ]	Light green	200	20.0	-----	-----	-----	-----
7	[Ni <sub>2</sub> L <sup>1</sup> <sub>2</sub> (py) <sub>4</sub> ]	Brown	190	14.4	-----	-----	-----	-----
8	[Cu <sub>2</sub> L <sup>1</sup> <sub>2</sub> (py) <sub>4</sub> ]	Green	195	19.8	-----	-----	-----	-----
H <sub>2</sub> L <sup>2</sup>	C <sub>25</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub>	Brown red	180	-----	-----	78.93 (78.87)	5.30 (5.02)	7.36 (7.51)
9	[Mn <sub>2</sub> L <sup>2</sup> <sub>2</sub> ]	Pale yellow	232	19.7	-----	-----	-----	-----
10	[Co <sub>2</sub> L <sup>2</sup> <sub>2</sub> ]	Green olive	198	18.5	-----	-----	-----	-----
11	[Ni <sub>2</sub> L <sup>2</sup> <sub>2</sub> ]	Olive	193	19.7	13.43 (13.10)	68.69 (68.45)	4.16 (4.59)	6.41 (6.97)
12	[Cu <sub>2</sub> L <sup>2</sup> <sub>2</sub> ]	Gray	195	19.4	14.38 (14.90)	67.93 (67.87)	4.11 (4.32)	6.34 (5.77)
13	[Mn <sub>2</sub> L <sup>2</sup> <sub>2</sub> (py) <sub>4</sub> ]	Pale yellow	250	14.9	-----	-----	-----	-----
14	[Co <sub>2</sub> L <sup>2</sup> <sub>2</sub> (py) <sub>4</sub> ]	Green	200	20.0	9.89 (9.60)	70.58 (70.21)	4.75 (4.48)	9.41 (9.70)
15	[Ni <sub>2</sub> L <sup>2</sup> <sub>2</sub> (PY) <sub>4</sub> ]	Green yellow	205	16.7	-----	-----	-----	-----
16	[Cu <sub>2</sub> L <sup>2</sup> <sub>2</sub> (PY) <sub>4</sub> ]	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<sup>-1</sup>) of the ligands and their complexes**

NO.	(O-H) cm <sup>-1</sup> υ	(C-O) cm <sup>-1</sup> υ	υ (C=N) <sub>imine</sub> cm <sup>-1</sup> υ (C=N) <sub>py-ring</sub>	(M-O) cm <sup>-1</sup> υ	(M-N) cm <sup>-1</sup> υ
H <sub>2</sub> L <sup>1</sup>	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 1488	533	420
6	-----	1255	1623 1488	535	440
7	-----	1265	1622 1488	518	433
8	-----	1260	1623 1506	533	417
H <sub>2</sub> L <sup>2</sup>	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 1488	540	457
14	-----	1245	1619 1500	530	420
15	-----	1250	1616 1489	553	418
16	-----	1245	1616 1506	520	418

**Table 3: Magnetic moments and the electronic spectral data of the ligands and their complexes**

NO.	$\mu_{eff}$ (B.M)	Assignment	Band maxima $\lambda$ (cm <sup>-1</sup> )	Structure
H <sub>2</sub> L <sup>1</sup>	-----	n → π*, π → π*	31446 , 37037	-----
1	5.75	C . T	27397	Td
2	3.81	<sup>4</sup> A <sub>2</sub> (F) → <sup>4</sup> T <sub>1</sub> (P), C . T	16393, 287501	Td
3	Diamagnetic	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> A <sub>2g</sub> , <sup>1</sup> A <sub>1g</sub> → <sup>1</sup> B <sub>1g</sub> , C . T	18518, 24396, 28134	Sq.pl
4	2.11	<sup>2</sup> T <sub>2</sub> → <sup>2</sup> E , C . T	10686, 27954	Td
5	5.85	C . T	277701	Oh
6	5.75	<sup>4</sup> A <sub>2g</sub> (F) → <sup>4</sup> T <sub>1g</sub> (F), <sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> T <sub>1g</sub> (p) ,C.T	16806, 21052, 29411	Oh
7	2.92	<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>2g</sub> (F), <sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (F) <sup>3</sup> T <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (p), C . T	21186, 24271, 27691	Oh
8	1.83	T , C . <sup>2</sup> E <sub>g</sub> → <sup>2</sup> T <sub>2g</sub>	151515, 27998	Oh
H <sub>2</sub> L <sup>2</sup>	-----	n → π* , π → π*	31545, 37313	-----
9	5.8	C . T	28091	Td
10	3.79	<sup>4</sup> A <sub>2</sub> (F) → <sup>4</sup> T <sub>1</sub> (P), C . T	16260, 27397	Td
11	Diamagnetic	<sup>1</sup> A <sub>1g</sub> → <sup>1</sup> A <sub>2g</sub> , <sup>1</sup> A <sub>1g</sub> → <sup>1</sup> B <sub>1g</sub> , C . T	16666, 24096, 29061	Sq.pl
12	1.87	<sup>2</sup> T <sub>2</sub> → <sup>2</sup> E, C . T	10566, 28365	Td
13	5.90	C . T	28559	Oh
14	5.80	<sup>4</sup> A <sub>2g</sub> (F) → <sup>4</sup> T <sub>1g</sub> (F), <sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> T <sub>1g</sub> (p) ,C.T	15480, 21276, 26993	Oh
15	2.79	<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>2g</sub> (F), <sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (F) <sup>3</sup> T <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (p), C . T	20618, 23529, 29050	Oh
16	2.20	<sup>2</sup> E <sub>g</sub> → <sup>2</sup> T <sub>2g</sub> , C . T	15625, 28792	Oh

**Table 4: The antibacterial activity of ligands and their complexes**

NO.	COMPOUND	Gram (+) bacteria	Gram (-) bacteria
		<i>Stphylococcus aureus</i> (m m)	<i>Escherichia coli</i> (m m)
H <sub>2</sub> L <sup>1</sup>	C <sub>24</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub>	7	14
1	[Mn <sub>2</sub> L <sub>2</sub> <sup>1</sup> ]	6	10
2	[Co <sub>2</sub> L <sub>2</sub> <sup>1</sup> ]	12	7
3	[Ni <sub>2</sub> L <sub>2</sub> <sup>1</sup> ]	15	12
4	[Cu <sub>2</sub> L <sub>2</sub> <sup>1</sup> ]	24	27
5	[Mn <sub>2</sub> L <sub>2</sub> <sup>1</sup> (py) <sub>4</sub> ]	12	15
6	[Co <sub>2</sub> L <sub>2</sub> <sup>1</sup> (py) <sub>4</sub> ]	13	12
7	[Ni <sub>2</sub> L <sub>2</sub> <sup>1</sup> (py) <sub>4</sub> ]	23	14
8	[Cu <sub>2</sub> L <sub>2</sub> <sup>1</sup> (py) <sub>4</sub> ]	30	20
H <sub>2</sub> L <sup>2</sup>	C <sub>25</sub> H <sub>20</sub> N <sub>2</sub> O <sub>2</sub>	14	14
9	[Mn <sub>2</sub> L <sub>2</sub> <sup>2</sup> ]	13	13
10	[Co <sub>2</sub> L <sub>2</sub> <sup>2</sup> ]	16	12
11	[Ni <sub>2</sub> L <sub>2</sub> <sup>2</sup> ]	18	18
12	[Cu <sub>2</sub> L <sub>2</sub> <sup>2</sup> ]	22	28
13	[Mn <sub>2</sub> L <sub>2</sub> <sup>2</sup> (py) <sub>4</sub> ]	13	12
14	[Co <sub>2</sub> L <sub>2</sub> <sup>2</sup> (py) <sub>4</sub> ]	22	15
15	[Ni <sub>2</sub> L <sub>2</sub> <sup>2</sup> (PY) <sub>4</sub> ]	23	14
16	[Cu <sub>2</sub> L <sub>2</sub> <sup>2</sup> (PY) <sub>4</sub> ]	27	30
Standard drug	Ciprofloxacin	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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