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Synthesis, Characterization and Biological Activity of Binuclear Cu(II) Complexes with Unsymmetrical Brighted Tetradentate Schiff Bases

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Abstract: Unsymmetrically brighted tetradentate Schiff bases H2L1= [1-(E)-((3-((E)-2hydroxybenzlidene) amino) phenyl)imino) methyl), naphthalene-2-ol], H2l2= [2-((E)-1-((3(((E) 2hydroxybenzlidene) amino)phenyl) imino) phenyl) imino)ethyl)phenol], H2L3= [2-((E)-1-((3(((E) 2hydroxybenzlidene) amino)phenyl)methyl)-5methoxyphenol] Which derived from m-phenylenediamine with salicyaldehyde and 2-hydroxynaphthaldehyde or 2-hydroxyacetophenone or 2-hydroxy-4methoxybenzophenone and their complexes of the type [Cu2Ln2], where n=1,2,3 have been synthesized. Adduct complexes of the type [Cu2Ln2 (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-Vis, 1H-NMR) spectroscopy, conductivity and magnetic measurements. The resulted data suggested that the Schiff bases containing ONNO donor atoms acts as dibasic tetradendetate ligands through coordinated with Cu(II). 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. The ligands and their complexes were screened for antibacterial activity against Bacillus and Morganella Morgani. 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 prepare metal complexes (Prakash et al., 2011). These complexes have played ligands to 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 as a heme ring or to donor atoms of peptide chains in distorted enviromment (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 unsymmetrically substituted Aromatic diamines have the ability to coordinate to a metal directly on their relative ortho meta or para positions (Hernandez et al., 1997), m- phenyelenediamine 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 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 bases derived from the other two aromatic diamines namely its ortho and para - analogues. Such complexes were suggested to have an even better 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- described in this work usually bound to a macrocycle such transition metal complexes of Schiff base ligands as synthetic models (Hernandez et al., 2004) phenylenediamine and its rigid structure (Torayama et al, -u compared the Schiff biological activity due to the phenylenediamine and their Mn(II), Co(II), Ni(II) and Cu(II) complexes are described in this work.

- Selection and peer-review under responsibility of the Organizing Committee of the Conference

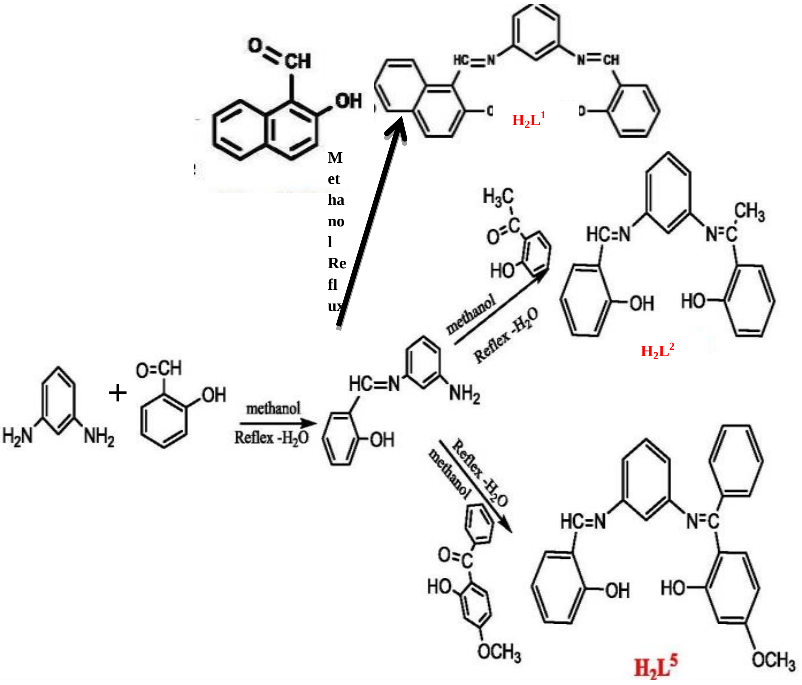
Experimental

All reagents and solvents were of analytical grade used as 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 of the supplied from fluka or (10-3) M solution complexes in DMSO using Conductivity meter Model PCM3-JENWAY at ambient DMSO (10-3) M solution on temperature.The electronic spectra were recorded SPECTRO UV-VIS AUTO, 110 v 60 HZ using lcm 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-d6 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/UK)

Method

Preparation of the ligands. H2L1, H2L2 , H2L3

Schiff base ligands were prepared according procedure (Pethe et al., 2017) by reacting equimolar amounts of m-phenylenediamine (0.01 mole, 1.08g) in methanol (15 ml) was added slowly to methanolic solution (15 ml) containing (0.01 mol, 1.22g) of salicyaldehyde and refluxed for 2h, then, fllowed by addition of 2-hydroxynaphthaldehyde (00.1 mole, 1.72g) or a 2-hydroxacetophenone (00.1 mole, 1.36g) or 2-hydroxy-4-methoxybeenzphenone (00.1 mole, 2.28g) each one dissolved in methanol (15 ml) the resulting cdoured mixture was refluxed with stirring for 3h and cooled, then the precipitate was filtered and washed with cold methanol and dried under vacuum, (schem-1-)



Scheme 1. Synthesis of Schiff bases ligands (H2L1, H2L2 and H2L3)

Preparation of the complexes. [Cu2Ln2]

The ligands H2L1 (00.1 mole, 3.66g) or H2L2 (001 mole, 3.30g) or H2L3 (00.1 mole, 4.22g), was dissolved in methanol (25 ml) in (50 ml) round bottom flask. Solution of Cu2L2. 2H2O (00.1 mole, 1.70 g) in methanol (15 ml) was added dropwise for 10-15 min. with continuos 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 of base adduct complexes. [Cu2Ln2 (py)2]

These complexes were prepared by the addition of pyridine (0.04 mole, 3.16g) to (0.01 mole) of 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 Bacillus and Gram - negative bacteria Morgaella Morgani 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 socked in the tested solutions. After 24 h cultivation at 37 °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) (Cu:L) molar ratio for [Cu2 Ln2] and (2:2:4) (Cu: Ln: py) molar ratio for [Cu2 Ln2 (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 (16.0-20.4) ohm-1 cm2 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, 3416, and 3498) cm-1 attributed to the phenolic hydroxyl group in H2L1 H2L2 and H2L3 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 ν (C-O) phenolic band to lowers frequency (1240-1260) cm-1 in the spectra of all complexes (Nagajothi et al., 2013). The IR spectrum of ligands show band at (1612, 1583 and 1582) cm-1 due to ν (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 ν (C=N) bond of pyridine ring was observed at the region (1506-1515) cm-1 in complexes (2,4,6) 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 ν (M-N) and ν (M-O). These bands apper in the ranges (425-463) cm-1 and (491-429) cm-1 respectively (Pathan et al., 2012). The I.R Spectra of ligands H2L2, H2L3 and complexes (3, 5) had been shown Fig. 1 and 2.

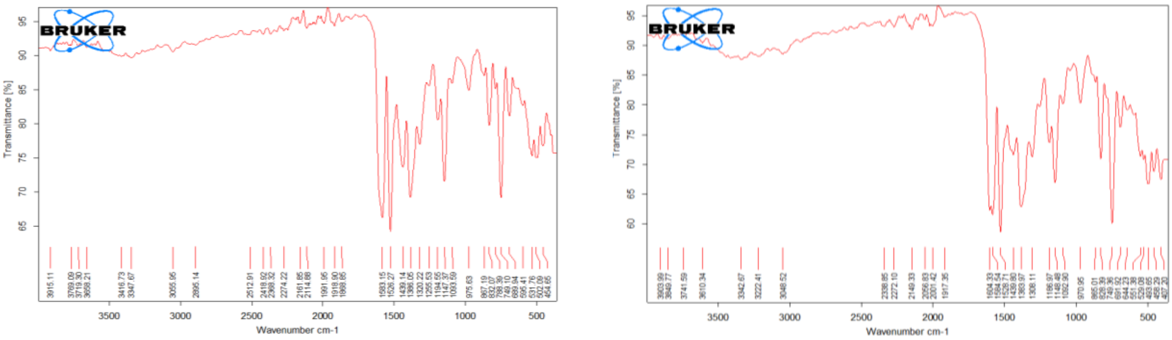


Fig (1) I.R spectra of (H_2L^2) and complex (3)

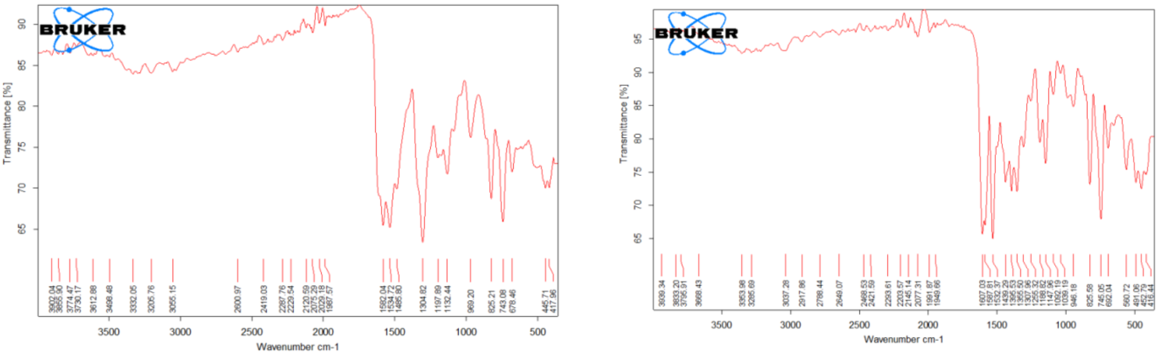
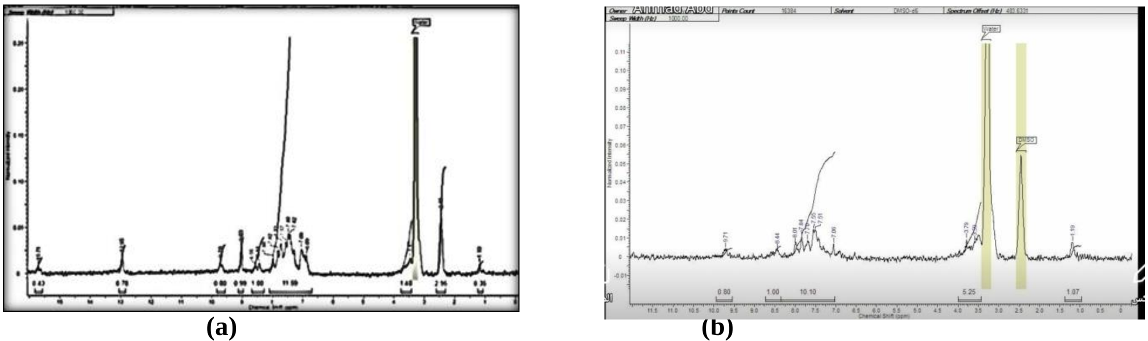


Fig (2) I.R spectra of (H_2L^3) and complex (5)

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 H2L1, H2L2 and H2L3 in DMSO solution show intense bands at (37037–38167) cm-1 and (28985-31948) cm-1 attributed to benzene $\pi\rightarrow\pi^*$ and n → π^* transition of the non-bonding electrons present on the nitrogen of the acomethine group respectively, these transitions are also found in the spectra of the complexes but they are shifited to confirmed the coordination of the ligand to the metalion (Elmali et al 2005). New bands in spectra of all complexes at range (26221–38167) cm-1 may be associated with the charge transfer transition (Aranha et al 2016).

The obtained magnetic moment values of Cu (II) complexes (1-6) has been found in the range (1.83-2-11) B.M, which indicate the presence of one unpaired electron of for Cu (II). The electroic. spectra of Cu (II) complexes (1,3,5) showed a broad band at (10427-10686) cm-1 attributed to 2T2→ 2E transition which is comparable with complexes having a tetrahedral structure (Turan et al., 2009) while complexes (2, 4, 6) showed a broad absorption band at (14816 15157) cm-1arises due to d-d transition 2Eg →2T2g suggest that the Cu (II) ion exhibits an octahedral geometry (Jayaseelan et al., 2010).

^{1}H-NMR Spectra of H_2L^1 and H_2L^2 : The H-NMR spectra of free ligands to at room temperature in DMSO-d6 shows the following signals (Garces et al., 1988) For H2L1. δ = 12.95 ppm (s, 2H, phenolic) δ = (6.89 - 8.55) ppm (m, 14 H, Aromatic) δ =9.03 ppm (s, 2H, a zomethine). For H2L2 . δ =9.71 (s, 2H, phendic), δ =(7.06-8.01) ppm (m, 17H, Aromatic), δ =8. 44ppm (s, 2H, azomethine), δ = 3.79 ppm (s, 3H, O-CH3).



(a) (b)

Fig. 3: ^{1}H-NMR Spectra of (a) H_2L^1; (b) H_2L^2

Antibacterial Activity

The tested compounds were screened in vitro of their antibacterial activity against Gram-negative and Gram-positive (Morganella Morgani, Bacillus) bacteria, the antibacterial rusults are given in (Table 4) compared with those of standard drug (Ciprofloxacin). The results evidently. show that all tested complexes were active against the Gram-positive and Gram-negative bacteria a generally the activity order against (Bacillus) of the synthesized compounds is as follows:

$[Cu_2L^3{}_2 > Cu_2L^2{}_2\ (Py)_4] = [Cu_2L^2{}_2\ (Py)_4] > [Cu_2L^1{}_2] > [Cu_2L^3{}_2] > [Cu_2L^3{}_2] > [Cu_2L^2{}_2\ (Py)_4] > [Cu_2L^3{}_2] > [Cu_2L^2{}_2]$

While the activity order against (Morganella *Morgani*) of the synthesized compounds is as follows:
$[Cu_2L^1{}_2] > [Cu_2L^1{}_2\ (Py)_4] > [Cu_2L^2{}_2] = [Cu_2L^3{}_2\ (Py)_4] > [Cu_2L^2{}_2(Py)_4] = [Cu_2L^3{}_2] > H_2L^3 > H_2L^1$

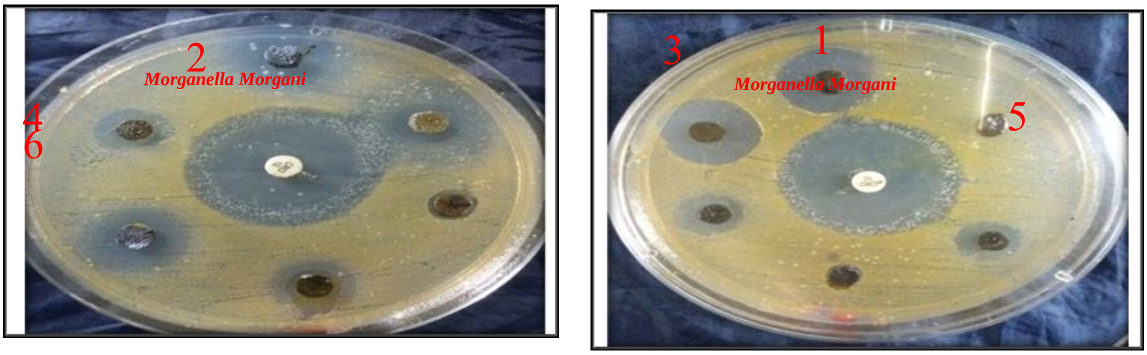


Fig.4 (a): Antibacterial activity of complexes agents gram negative bacteria *Morganella Morgani*

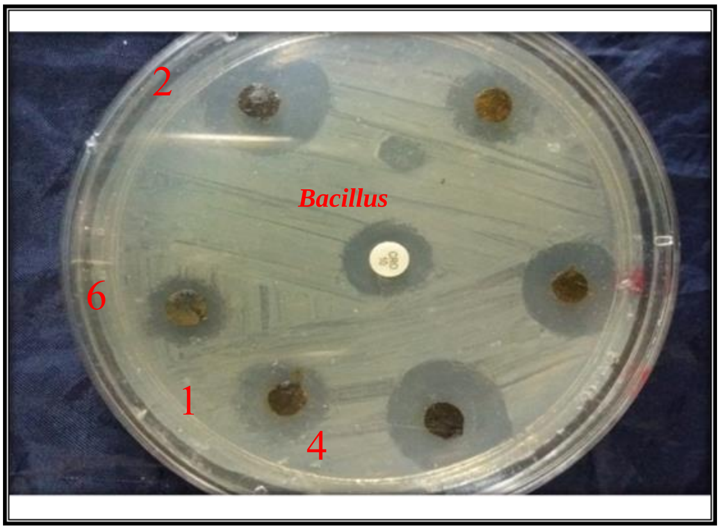
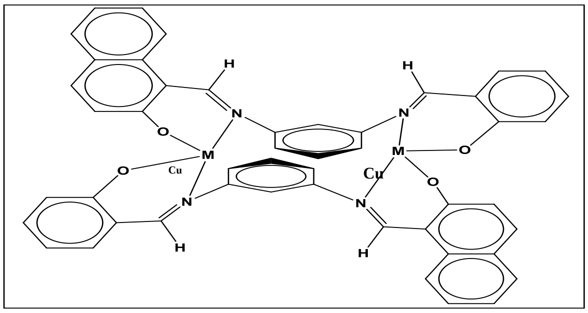


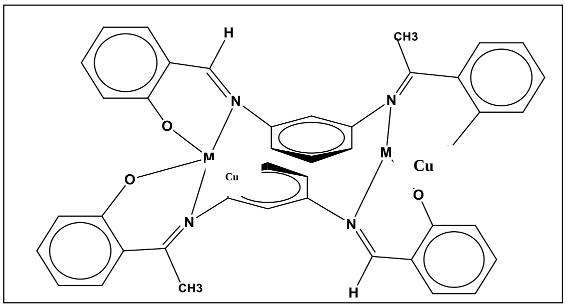
Fig.4 (b): Antibacterial activity of complexes agents gram positive bacteria *Bacillus*

Conclusion

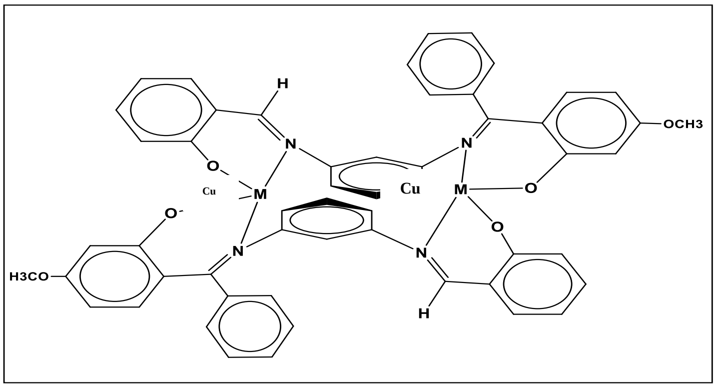
New cu (II) complexes of unsymmetrical brighted tetra dentate Schiff bases ligands H2L1, H2L2 , H2L3 have been prepared and characterized by conventional measurements. The data revealed that all the complexes are dinuclear and have an either tetrahedral or octahedral geometry Fig (4). The ligands act as N2O2 tetra dentate dibasic chelating e 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 all complexes are active against this bacteria as compared with standard drug (Ciprofloxaic).



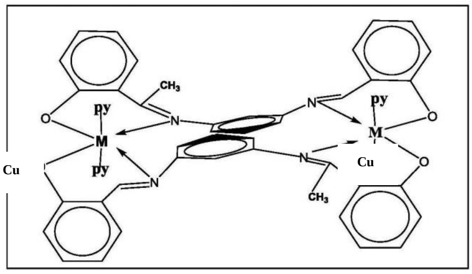
Complex (1)

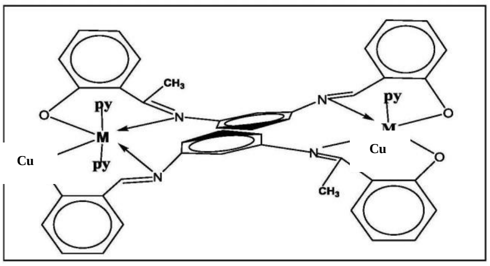


Complex (2)



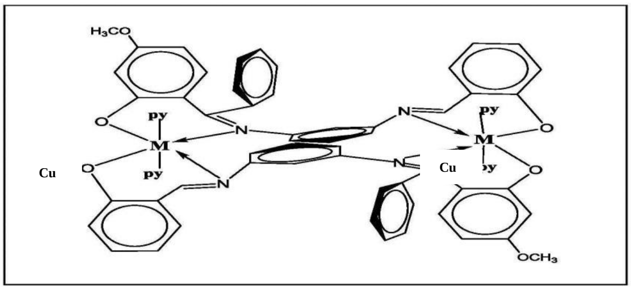
Complex (3)





Complex (4)

Complex (5)



Complex (6)
Fig (5) Suggested Structure of complexes

Table 1.Tthe physical properties and analytical data of the ligands and their complexes

NO.	COMPOUND	COLOUR	m.p (°C)	Am ohm^{-1} Cm^2 mol^{-1} DMSO	M% Calc (found)	Analysis calc (found) %		
						C%	H%	N%
H_2L^1	$C_{24}H_{18}N_2O_2$	Green Yellow	175	--------	--------	78.67 (77.73)	4.95 (4.78)	7.65 (8.18)
1	$Cu_2L^1_2$	Brown	185	20.4	14.86 (15.22)	67.42 (68.11)	3.74 (4.12)	6.54 (7.21)
2	$[Cu_2L^1_2(Py)_4]$	Green	195	19.8	--------	--------	-------	--------
H_2L^2	$C_{21}H_{18}N_2O_2$	Silver	180	--------	--------	76.38 (77.12)	5.45 (5.95)	8.74 (9.12)
3	$Cu_2L^2_2$	Gray	220	17.0	11.50	67.68	4.77	10.19

					(10.05)	(66.81)	(4.55)	(9.87)
4	$[Cu_2L^2_2\,(Py)_4]$	Green	195	17.3	--------	--------	-------	--------
H_2L^3	$C_{27}H_{22}\,N_2O_2$	Gray	195	--------	--------	76.73 (77.41)	5.21 (5.91)	6.63 (7.36)
5	$Cu_2\,L^3_2$	Pale green	290	16.0	13.18 (14.00)	67.30 (68.21)	4.15 (4.91)	5.81 (6.21)
6	$[Cu_2L^3_2\,(Py)_4]$	Brown Green	225	19.4	--------	--------	-------	--------

Table 2. Characteristic Infrared Spectral data (cm-1) of the ligands and their complexes

NO.	**υ (O-H) cm^{-1}**	**υ (C-O) cm^{-1}**	**υ (C=N) imine** **υ (C=N) py-ring**	**υ (M-O) cm^{-1}**	**υ (M-O) cm^{-1}**
H_2L^1	3465	1275	1612		
1		1270	1622	522	463
2		1260	1623 1506	523	458
H_2L^2	3416	1270	1583		
3		1240	1604	529	458
4		1251	1616 1515	496	425
H_2L^3	3498	1265	1582		
5		1255	1602	491	452
6		1245	1616 1506	420	465

Table 3. Magnetic moments and the electronic spectral data of theligands and Cu (II) complexes

No.	**Meff (B.M)**	**Assignment**	**Band maxima λ (Cm^{-1})**	**structure**
H_2L^1	…….	$n \longrightarrow \pi^*,$ $\pi \longrightarrow \pi^*$	31446 , 37037	……
1	2.11	$T_2^2 \longrightarrow E^2, C.T$	10686 , 27954	Th
2	1.83	$E_g^2 \longrightarrow E_{2g}^2, C.T$	15151, 27977	Oh
H_2L^2	……	………	31948, 38167	…….
3	2.09	$T_2^2 \longrightarrow E^2, C.T$	10480, 29011	Th
4	1.99	$E_g^2 \longrightarrow E_{2g}^2, C.T$	15157, 31152	Oh
H_2L^2	……..	……	28985, 37735	………
5	1.89	$T_2^2 \longrightarrow E^2, C.T$	10427, 26221	Th
6	2.09	$E_g^2 \longrightarrow E_{2g}^2, C.T$	14826, 26873	oh

Table 4. The antibacterial activity of ligand and their complexes

No.	**Compound**	**Gram (+) bacteria Bacillus (mm)**	**Gram (-) bacteria Morga.**
H_2L^1	$C_{24} H_{18} N_2O_5$	0	3
1	$[cu_2 L_2^1]$	14	22
2	$[cu_2 L_2^1 (py)_4]$	20	20
H_2L^2	$C_{21} H_{18} N_2O_5$	0	0
3	$[cu_2 L_2^2]$	7	18
4	$[cu_2 L_2^2 (py)_4]$	20	12
H_2L^3	$C_{27} H_{22} N_2O_3$	0	6
5	$[cu_2 L_2^3]$	10	12
6	$[cu_2 L_2^3 (py)_4]$	12	18

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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