



# SPECTROSCOPIC, THEORETICAL AND BIOLOGICAL STUDIES OF BINUCLEAR Mn(II), Ni(II), Cu(II) AND Cd(II) COMPLEXES WITH POLYDENTATE LIGAND DERIVED FROM DEHYDROACETIC ACID AND DIETHYLENTRIAMINE

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**Keywords:** binuclear complexes, dehydroacetic acid, biological activity; 3,3'-[iminobis(ethane-2,1-diylnitrilo-(1E)-eth-1-yl-1-ylidene)]-bis(4-hydroxy-6-methyl-2H-pyran-2-one)]

A series of binuclear acyclic polydentate complexes of Mn(II), Ni(II), Cu(II) and Cd(II) ions with a ligand derived from the condensation of dehydroacetic acid and diethylenetriamine (3,3'-[iminobis(ethane-2,1-diylnitrilo-(1E)-eth-1-yl-1-ylidene)]bis(4-hydroxy-6-methyl-2H-pyran-2-one)),  $[\text{Mn}_2\text{LCl}_2(\text{H}_2\text{O}_4)]$  and  $[\text{M}_2\text{LCl}_2]$ , M=Ni, Cd and Cu(II), have been prepared and characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, FT-IR and UV-Visible spectroscopy and micro-elemental analysis, as well as with the measurement of the magnetic moments of solid complexes and molar conductivity in DMSO solution. The new acyclic poly dentate ligand 3,3'-[iminobis(ethane-2,1-diylnitrilo-(1E)-eth-1-yl-1-ylidene)]bis(4-hydroxy-6-methyl-2H-pyran-2-one)] are identified on the basis of (CHN) elemental analysis,  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, as well as FT-IR and UV-Visible spectroscopy. The antimicrobial activity of the free ligand and its Mn(II), Ni(II), Cu(II) and Cd(II) complexes were tested against *Staphylococcus aureus* and *Escherichia coli* and fungicidal activity against *Aspergillus Niger* and *Candida albicans*. The minimum inhibitory concentration (MIC) method revealed that all metal complexes showed enhanced activity toward the selected micro-organisms compared with the free ligand  $\text{H}_2\text{L}$  and Amoxicillin. The octahedral geometry is proposed for Mn(II) complex, square planar for Ni(II) and Cu(II) complexes and tetrahedral symmetry is suggested for Cd(II) complex.

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## Introduction

The binuclear metal complexes containing heterocyclic rings are widely used as antibiotics, antifungal agents and semiconductor sensors.<sup>1-4</sup> Development of new microbicides including fungicides has increasing importance in modern medicinal chemistry<sup>5</sup> because appearance of large number of provoking factors that depress or destroy the immune system such as chemotherapy of cancer, using drugs to avoid organ rejection in transplanted patients and AIDS.<sup>6</sup>

3-Acetyl-6-methyl-2H-pyran-2,4(3H)-dione (**1**) (dehydroacetic acid or DHA) is a widely used compound usually obtained through the condensation of ethyl acetate.<sup>7</sup> It has been modest antifungal properties.<sup>8</sup> Dehydroacetic acid is an excellent chelating agent and its various derivatives including their metal complexes are promising fungicides, bactericides, herbicides and insecticides.<sup>10-11</sup> Dehydroacetic acid is also a versatile starting material for the synthesis of a wide variety of heterocyclic ring systems and other organic compounds.<sup>12</sup>

Recent studies related to coordination chemistry of (3,3'-[iminobis(ethane-2,1-diylnitrilo-(1E)-eth-1-yl-1-ylidene)]-bis(4-hydroxy-6-methyl-2H-pyran-2-one) by Al-Obaidi<sup>13</sup> motivated us to prepare and study some new binuclear metal complexes with different stoichiometry.

## Experimental

### Physical measurements

Electronic spectra of the new ligand and its metal complexes were recorded in the region 800-200 nm on a Shimadzu 670 spectrophotometer. IR-spectra were recorded on PC Shimadzu FT-IR spectrophotometer in KBr in the range of 400 - 4000  $\text{cm}^{-1}$ . The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the ligand were recorded in DMSO- $d_6$  on a 300MHz Bruker spectrometer. The effective magnetic moment measurements of the solid complexes were carried out on a Magnet Balance MG. The molar conductivity of metal complexes in DMSO solution was measured on a HPG G-3001 digital conductivity meter. The carbon, hydrogen and nitrogen analysis of ligand and its metal complexes were done on Carlo Elba 1108 instrument, the metal content in the complexes were measured on a Shimadzu 670 spectrophotometer by using standard addition method.

### Calculation method

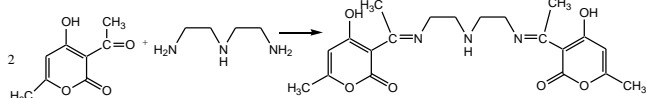
The quantum chemical calculations were made with using Hyper Chem-8 program.<sup>14</sup>

### Reagents and solvents

Dehydroacetic acid and diethylenetriamine were obtained from Aldrich Co. The hydrated metal chlorides ( $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) and  $\text{CdCl}_2$  (Fluka and Merck) were used for the synthesis of complexes without any purification.

### Synthesis of ligand 3,3'-[iminobis(ethane-2,1-diyl-nitrilo-(1E)-eth-1-yl-1-ylidene)]bis(4-hydroxy-6-methyl-2H-pyran-2-one) ( $\text{H}_2\text{L}$ )

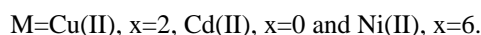
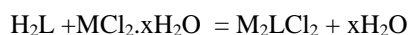
The ligand ( $\text{H}_2\text{L}$ ) was prepared by refluxing (2 g, 1.1 mol) of dehydroacetic acid in 30 ml absolute ethanol with (0.613 g, 5.91 moles) of diethylenetriamine for about 9 h on water bath. The polydentate acyclic ligand ( $\text{H}_2\text{L}$ ) formed is deposited upon cooling the mixture to room temperature overnight. (Scheme 1).



Scheme 1. Synthesis of Ligand  $\text{H}_2\text{L}$

### Synthesis of metal complexes

2 mmol of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CdCl}_2$  in 20 mL methanol was added to 0.403g, (1 mmol) of  $\text{H}_2\text{L}$  ligand dissolved in methanol containing KOH (1 %, w/v). The resulting mixture was refluxed under nitrogen atmosphere until the complex precipitated (ca. 3 h) then the solution was cooled to room temperature, the precipitate was filtered off, washed several times with 15 ml of diethyl ether and dried under vacuum to afford  $\text{Mn}_2\text{LCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{M}_2\text{LCl}_2$  ( $\text{M}=\text{Cu}$ ,  $\text{Ni}$  and  $\text{Cd}$ ) complexes in 51-65 % yield.



### Anti-bacterial Activity

The *in-vitro* biological activity of the investigated free ligand  $\text{H}_2\text{L}$  and its metal complexes were tested against the bacteria *Escherichia coli* and *Staphylococcus aureus* by disc diffusion method using nutrient agar as medium and streptomycin as control. The antifungal activities of the compounds were also tested by the well diffusion method against the fungi *Aspergillus Niger* and *Candida albicans*, on potato dextrose agar as the medium and ketaconazole as control. Each compound was dissolved in DMSO and solutions of different concentrations (25, 50 and 100 ppm) were prepared separately. In a typical procedure, a well was made on agar medium inoculated with microorganism. The well was filled with the test solution using a micropipette and the plate was incubated 24 h for bacteria at 37 °C and 72 h for fungi at 30 °C. During this period, the test solutions were diffused into the gel, the growth of the inoculated microorganism was affected, and the inhibition zone was developed. All determinations were performed three times.

The bacteria subcultures, *Staphylococcus aureus* and *Escherichia coli* were used for antibacterial test, whereas *Aspergillus flavus* and *Candida albicans* were used for antifungal test using the modified Kirby-Bayer disc diffusion method.<sup>11</sup> Briefly, 100 ml of the tested bacteria/

fungi were grown in 10 ml of breath media until they reached 100 cells  $\text{ml}^{-1}$  for bacteria and 110 cells  $\text{ml}^{-1}$  for fungi. 100 ml of microbial suspension was spread on the agar plate corresponding to the broth in which they were maintained.

## Result and Discussion

The new acyclic Schiff base [ $\text{H}_2\text{L}$ ] ligand derived from condensation of one mole diethylenetriamine with two moles of dehydroacetic acid behaves as tetradentate dibasic chelating agent towards the studied metal(II) ions. The stoichiometry of the complexes was confirmed by their elemental analysis. (Table 2). All the complexes were sparingly soluble in common organic solvents but completely soluble in DMF, DMSO, and acetonitrile. The analytical data (Table 1) indicate that the complexes are binuclear. The molar conductance (Table 3) values measured in DMF solution ( $1 \times 10^{-3}$  mol  $\text{dm}^{-3}$ ) fall in the range 9.0-22  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ . These observed values of the molar conductance agree well within the expected values for non-electrolytes.<sup>15</sup>

### $^1\text{H}$ and $^{13}\text{C}$ NMR spectra

The  $^1\text{H}$  NMR spectra of free ligand in  $\text{DMSO-d}_6$  shows six signals for the ligand in the regions 13.6-13.7, 5.96-5.60, 4.65 and 3.53- 3.10 ppm which merged with each other except high deshielded -OH proton of pyranone-ring<sup>14</sup> (Figure 1).

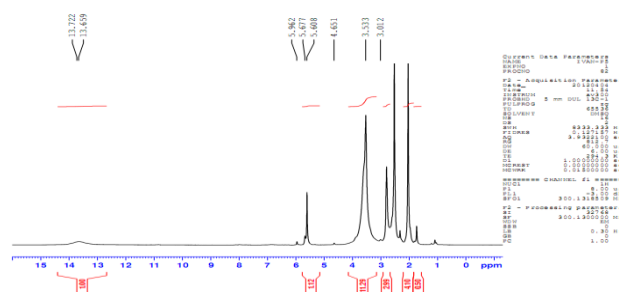


Figure 1.  $^1\text{H}$  NMR to the  $\text{H}_2\text{L}$  in  $\text{DMSO-d}_6$  solvent.

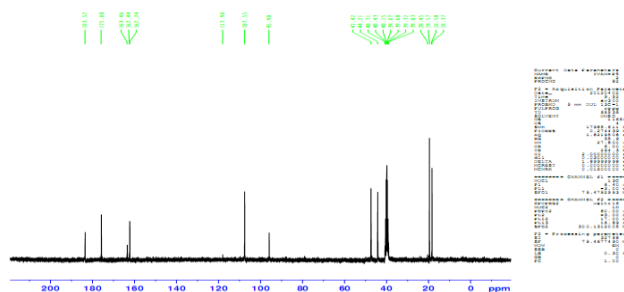


Figure 2.  $^{13}\text{C}$  NMR to the  $\text{H}_2\text{L}$  in  $\text{DMSO-d}_6$  solvent

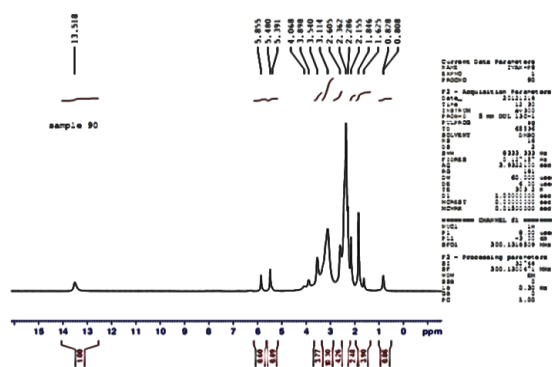
The  $^{13}\text{C}$  NMR spectrum of the free ligand in  $\text{DMSO-d}_6$  displays chemical shifts of tautomers (20 signals for twice 10 chemical environment) and the sharp Me-signals of DMSO solvent around 40 ppm. All the signals of the pyranone ring and the azomethine group could tentatively be

**Table 1.** Analytical data for ligand and its metal complexes

Formula	Molecular weight	Colour	Composition Calculated (Found)				
			C%	N%	H%	Cl%	M%
$\text{H}_2\text{L}$ , $\text{C}_{20}\text{H}_{25}\text{N}_3\text{O}_6$	403	Off white	59.55 (59.54)	11.91 (10.42)	6.20 (6.25)	-	-
$[\text{Ni}_2\text{LCl}_2]$	589.4	Brown	40.72 (39.55)	8.14 (7.20)	4.24 (3.01)	12.05 (11.88)	19.91 (18.52)
$[\text{Cu}_2\text{LCl}_2]$	599.1	Green	40.06 (39.09)	8.01 (7.96)	4.17 (4.66)	11.85 (10.98)	21.21 (20.88)
$[\text{Mn}_2\text{LCl}_2 \cdot 4\text{H}_2\text{O}]$	653.8	Brown	36.70 (35.77)	7.34 (6.61)	5.05 (4.88)	10.86 (9.97)	16.80 (15.89)
$[\text{Cd}_2\text{LCl}_2]$	696.8	Dark yellow	34.44 (33.99)	6.02 (4.98)	3.59 (3.11)	10.19 (10.09)	32.26 (31.93)

<sup>a</sup>Analysis of metal content were done on the basis of FAAS

assigned (**Me**-C6 group-107.55 ppm, **Me**-C6(ring)-163.50 ppm, **C5H**(ring)-183.5 ppm, **C4(OH)**(ring)-96.9 ppm, **C5CMeN**(ring)-162.4 ppm, **C6=O**(ring)-20.45 ppm, **C(CH<sub>3</sub>)=N**-175.8 ppm and **CH<sub>3</sub>C=N**-19.57 ppm, and methyl or methylene groups respectively.<sup>29</sup> The residual signals belong to the diethylenetriamine link and to the tautomer forms of the pyranone part. (Figure 2). The <sup>1</sup>H NMR spectra of Cd(II) complexes in DMSO-d<sub>6</sub> solution can be seen in Figure 3). The changes of <sup>1</sup>H signals belong to the Schiff base ligand reveals the coordination of nitrogen -C=N- and -OH groups with the metal ions.<sup>15,29</sup>



**Figure 3.** <sup>1</sup>H NMR of the  $[\text{Cd}_2\text{LCl}_2]$  in DMSO-d<sub>6</sub> solvent.

### Infrared Spectra

The FT-IR spectrum of the free ligand ( $\text{H}_2\text{L}$ ) in KBr disk displays broad and strong absorptions in the regions  $3400\text{ cm}^{-1}$  and  $1695\text{--}1655\text{ cm}^{-1}$  that could be assigned to -OH and C=O bands located on the pyranone ring.<sup>13,16</sup> The medium intensity absorption band at  $3571\text{--}3357\text{ cm}^{-1}$  may be assigned to  $\nu(\text{NH})$  stretching of diethylenetriamine moiety. The IR spectra of all metal complexes show bands in the regions  $3160\text{--}3550$ ,  $1655\text{--}1688$  and  $1522\text{--}1560\text{ cm}^{-1}$  that are assignable to  $\nu_{\text{NH}}$ ,  $\nu_{\text{C=O}}$  and  $\nu_{\text{C=N}}$  bands, respectively. These band positions confirm the coordination of bivalent metal ions to C=N and deprotonated C-O groups active sites. Moreover, the far infrared spectra of all metal complexes show weak

absorption bands in the range  $510\text{--}422$  and  $468\text{--}414\text{ cm}^{-1}$  which may be confirmed as  $\nu_{\text{M-N}}$  and  $\nu_{\text{M-O}}$  bands. The Mn(II) complexes show broad bands at  $3650\text{ cm}^{-1}$  and strong bands at  $1590\text{ cm}^{-1}$  that related to coordinated water molecules. The bands at  $1581$ ,  $1431$ ,  $1259\text{ cm}^{-1}$  may be assigned to bending of NH, and asymmetrical vibration modes of C=C and C-N stretching, respectively. This confirms the condensation of carbonyl group of dehydroacetic acid with amino groups of diethylenetriamine.<sup>11,13</sup> The bands around  $3400\text{ cm}^{-1}$  and  $1656\text{ cm}^{-1}$  can be assigned to  $\nu_{\text{OH}}$  and  $\nu_{\text{C=N}}$  stretchings.<sup>17</sup> The band at  $1695\text{ cm}^{-1}$  can be attributed to the  $\nu_{\text{C=O}}$  of the pyranone ring. The NH bands are probably overlapped by the OH bands and did not appear for the free NH<sub>2</sub> group bands of diethylenetriamine.<sup>16-18</sup> The Cd(II) complex shows weak bands in the far infrared spectra between  $336$  and  $370\text{ cm}^{-1}$  which probably belong to Cd-Cl bonds.

### Electronic spectra and magnetic properties

The free ligand ( $\text{H}_2\text{L}$ ) spectrum in methanol exhibits three distinct absorptions around  $42735$ ,  $37878$  and  $31847\text{ cm}^{-1}$  which are assigned to  $\pi \rightarrow \pi^*$  of benzenoid ring and  $E_1$ ,  $E_2$  and  $n \rightarrow \pi^*$  transitions of C=N, and C=O chromophores.<sup>18</sup> The diamagnetic properties of Ni(II) reveals the square planar symmetry of low spin  $d^8$  state, and agree well with the high energy absorptions in the region  $23255 - 25316\text{ cm}^{-1}$  of  ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{1g}$  and  ${}^1\text{A}_{1g} \rightarrow {}^1\text{B}_{2g}$  transitions, respectively.<sup>19</sup> However, the diamagnetic properties of binuclear copper(II) complex indicate the spin-spin coupling of Cu-Cu form.<sup>17</sup> The weak intensity peak of copper(II) complex in DMF in the region  $19500\text{ cm}^{-1}$  with a shoulder on the low energy side at  $15500\text{ cm}^{-1}$  may confirms the transitions of distorted octahedral, with LFSE= $17\ 500\text{ cm}^{-1}$ .<sup>19-20</sup> The pale pink solution of manganese(II) complex in DMF displays weak intensity peak at  $22333\text{ cm}^{-1}$  which may be assigned to  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$  and other in the UV region  $33421\text{ cm}^{-1}$  that are entirely related to LMCT transitions. The magnetic moment obtained ( $5.30\text{ B.M.}$ ) was within the range expected for magnetically high spin Mn(II) complex with octahedral symmetry.<sup>21-22</sup>

**Table 2.** IR spectral data of the free ligand and its metal complexes

Compound	$\nu_{\text{C=O, C=N}}$	$\nu_{\text{OH, NH}}$	$\delta_{\text{OH, NH, C-N}}$	$\nu_{\text{Ar-H, CH}_2\text{CH}_2}$	$\nu_{\text{M-N, M-O, M-Cl}}$
$\text{H}_2\text{L}$	1695(s), 1656, 1595	3400(br) 3571	1581 1509, 1259	2995-29249(m)	-
$[\text{Ni}_2\text{LCl}_2]$	1688, 1522(s)	3160(m)	1433, 1200, 1207	2988, 3044(w)	510(m), 440, 330(w)
$[\text{Cu}_2\text{LCl}_2]$	1680 1537,	3419 (br)	1450, 1188, 1233(m)	3030(w) 2804	468, 422, 310(w)
$[\text{Mn}_2\text{LCl}_2 \cdot 4\text{H}_2\text{O}]$	1670(s), 1505(s)	<sup>a</sup> 3550(br) <sup>a</sup> 3510 <sup>b</sup> 1590	1522, 1388, 1188(m)	2890, 3060(w)	522, 414(w), 280-333
$[\text{Cd}_2\text{LCl}_2]$	1669-1655 1560(s)	3350(m)	1544(s)	3080(w), 2966(m)	422, 414, 336-370(w)

sh=shoulder, br=broad. s=strong, m=medium, vw = very weak , w=weak and a,b=absorption of O-H for coordinated  $\text{H}_2\text{O}$ .

**Table 3.** UV-Vis spectra data, magnetic moments and molar conductance results of the prepared complexes.

Compound	Absorption bands, $\nu$ ( $\text{cm}^{-1}$ )	Assignment	Geometry	$\mu$ , BM	<sup>a</sup> $\Omega$ , $\text{S cm}^2 \text{mol}^{-1}$
$\text{H}_2\text{L}$	42735 37878 31847	INCT $\pi \rightarrow \pi^*$ $n \rightarrow \pi^*$	-	-	-
$[\text{Ni}_2\text{LCl}_2]$	23255 25316	<sup>1</sup> $\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$ <sup>1</sup> $\text{A}_{1g} \rightarrow ^1\text{B}_{2g}$	square planar	0	9
$[\text{Cu}_2\text{LCl}_2]$	19500 15500	<sup>2</sup> $\text{B}_{1g} \rightarrow ^2\text{B}_{2g}$ <sup>2</sup> $\text{B}_{1g} \rightarrow ^2\text{E}_g$	square planar	1.2	18
$[\text{Mn}_2\text{LCl}_2 \cdot 4\text{H}_2\text{O}]$	33421 27567	LMCT <sup>6</sup> $\text{A}_{1g} \rightarrow ^4\text{T}_{1g}$	octahedral	5.43	11
$[\text{Cd}_2\text{LCl}_2]$	33400 28900	LMCT $\pi \rightarrow \pi^*$	tetrahedral	0	22

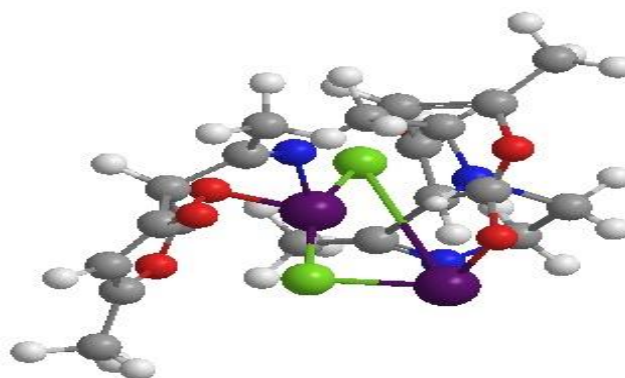
a=molar conductance in DMF solutions, INCT-intraligand field

The metal (II) complexes in DMF solutions showed nonelectrolyte properties with 15-30  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$  conductivity values indicating that there are no chloride ions in the outer sphere of metal complexes.<sup>15</sup> The cadmium(II) complex in DMF solution exhibits two sharp peak in the region 34300-29800  $\text{cm}^{-1}$  that belong to ligand to metal charge transfer and  $\pi \rightarrow \pi^*$  transitions, respectively.

### Theoretical Study

The optimized geometry of manganese-complex and some selected bond lengths and angles can be seen in Fig. 4 and Table 4 respectively.

The values of the bond lengths and angles are quite similar to the experimental results of analogous compounds.<sup>23-24</sup>



**Figure 4.** The geometry of Mn(II) complex optimized with Hyperchem MP3 semi-empirical method using Hyperchem-8 program.

**Table 4.** Structural parameters, bond lengths (Å) and angles (°) of the  $[\text{Mn}_2\text{L}_2]$  complex.

Bond lengths (Å)		Bond angles(°)		Bond angles(°)	
N(1)-C(2)	1.4700	C(20)-C(27)-H(50)	109.4993	C(16)-C(28)-H(53)	109.4999
N(1)-C(16)	1.2600	C(20)-C(27)-H(51)	109.4416	C(16)-C(28)-H(54)	109.4419
N(1)-Mn(29)	1.8460	C(20)-C(27)-H(52)	109.4617	C(16)-C(28)-H(55)	109.4618
C(2)-C(3)	1.5230	H(50)-C(27)-H(51)	109.4419	H(53)-C(28)-H(54)	109.4419
C(2)-H(35)	1.1130	H(50)-C(27)-H(52)	109.4620	H(53)-C(28)-H(55)	109.4618
C(2)-H(36)	1.1130	H(51)-C(27)-H(52)	109.5209	N(1)-Mn(29)-O(15)	72.8134
C(3)-N(4)	1.4380	C(20)-C(21)-C(22)	94.9350	N(1)-Mn(29)-Cl(32)	109.4999
C(3)-H(37)	1.1130	C(20)-C(21)-H(46)	132.5325	N(1)-Mn(29)-Cl(33)	90.0000
C(3)-H(38)	1.1130	C(22)-C(21)-H(46)	132.5324	O(15)-Mn(29)-Cl(32)	109.5001
N(4)-C(5)	1.7721	C(17)-C(22)-C(21)	115.0000	O(15)-Mn(29)-Cl(33)	90.0001
N(4)-H(31)	1.0200	C(17)-C(22)-O(23)	122.5000	Cl(32)-Mn(29)-Cl(33)	155.4959
C(5)-C(6)	1.5230	O(19)-C(18)-O(25)	130.3984	N(1)-C(16)-C(12)	115.0997
N(7)-Mn(30)	1.8460	C(18)-O(25)-Mn(30)	109.5005	N(1)-C(16)-C(28)	122.4499
C(8)-C(9)	1.3491	C(24)-C(34)-H(56)	109.5006	C(12)-C(16)-C(28)	122.4504
C(13)-C(8)	1.3510	C(24)-C(34)-H(57)	109.4422	C(2)-N(1)-C(16)	108.0001
Mn(29)-O(15)	1.7097	C(24)-C(34)-H(58)	109.4617	C(2)-N(1)-Mn(29)	119.9999
C(16)-C(28)	1.4970	H(56)-C(34)-H(57)	109.4416	C(16)-N(1)-Mn(29)	120.0000
C(17)-C(18)	1.5090	H(56)-C(34)-H(58)	109.4617	C(6)-C(5)-H(39)	113.5837
O(19)-C(20)	1.4100	H(57)-C(34)-H(58)	109.5195	C(6)-C(5)-H(40)	119.2535
C(20)-C(21)	1.6036	C(18)-C(17)-C(22)	109.4698	H(39)-C(5)-H(40)	99.9980
C(20)-C(27)	1.4970	C(18)-C(17)-C(24)	154.3598	C(3)-N(4)-C(5)	127.8364
C(21)-C(22)	1.3510	C(18)-C(17)-H(45)	65.2800	C(3)-N(4)-H(31)	116.0821
C(21)-H(46)	1.1000	C(22)-C(17)-C(24)	96.1702	C(5)-N(4)-H(31)	116.0815
C(22)-O(23)	1.2080	C(22)-C(17)-H(45)	174.7458	C(2)-C(3)-N(4)	109.4697
C(24)-C(34)	1.4970	C(24)-C(17)-H(45)	89.0805	C(2)-C(3)-H(37)	109.4491
Mn(30)-O(25)	1.8100	N(7)-Mn(30)-O(25)	109.4997	C(2)-C(3)-H(38)	109.4791
Cl(32)-Mn(29)	2.1600	N(7)-Mn(30)-Cl(32)	90.0000	N(4)-C(3)-H(37)	109.4491
Cl(33)-Mn(29)	2.1600	N(7)-Mn(30)-Cl(33)	33.3581	N(4)-C(3)-H(38)	109.4798
Cl(32)-Mn(30)	2.1600	O(25)-Mn(30)-Cl(32)	109.4999	H(37)-C(3)-H(38)	109.5005
Cl(33)-Mn(30)	4.3970	O(25)-Mn(30)-Cl(33)	89.7988	Mn(29)-Cl(33)-Mn(30)	39.4475
N(1)-Mn(29)	1.8460	Cl(32)-Mn(30)-Cl(33)	71.0216	Mn(29)-Cl(32)-Mn(30)	90.0002
N(4)-C(5)	1.7721	N(7)-C(24)-C(17)	67.6349	C(9)-C(26)-H(47)	109.5003
N(4)-H(31)	1.0200	N(7)-C(24)-C(34)	146.1829	C(9)-C(26)-H(48)	109.4421
C(5)-H(39)	1.1130	C(17)-C(24)-C(34)	146.1822	C(9)-C(26)-H(49)	109.4620
C(5)-H(40)	1.1130	C(6)-N(7)-C(24)	107.9999	H(47)-C(26)-H(48)	109.4418
C(6)-N(7)	1.4700	C(6)-N(7)-Mn(30)	120.0001	H(47)-C(26)-H(49)	109.4614
N(7)-Mn(30)	1.8460	C(24)-N(7)-Mn(30)	120.0003	H(48)-C(26)-H(49)	109.5197
Mn(29)-O(15)	1.7097	C(5)-C(6)-N(7)	110.7399	C(11)-O(15)-Mn(29)	91.9842
Mn(30)-O(25)	1.8100	C(5)-C(6)-H(41)	109.1315	C(9)-O(10)-C(11)	120.0000
Cl(32)-Mn(29)	2.1600	N(4)-C(5)-C(6)	92.1467	C(8)-C(9)-O(10)	123.3719
Cl(33)-Mn(29)	2.1600	N(4)-C(5)-H(39)	113.5836	C(8)-C(9)-C(26)	118.3141
Cl(32)-Mn(30)	2.1600	N(4)-C(5)-H(40)	119.2539	O(10)-C(9)-C(26)	118.314
Cl(33)-Mn(30)	4.3970				

### Biological Study

The inhibition zone was measured by the disc method,<sup>13,25</sup> the diameters of the inhibition zone were measured in millimeters. Standard disc of *Amoxicilline* (antibacterial agent) and *Ketoconazole* (antifungal agent) were used as controls for antimicrobial activity. However, the filter discs impregnated with 10 ml of (DMSO solvent + distilled water) were used as a negative control. The used agar (Mueller-Hinton) was rigorously tested for composition and pH.

$$RI(\%) = 100 \frac{A - B}{C - B}$$

where

A= area of inhibition sample plate.

B= area of inhibition in the DMSO (control).

C= area of inhibition in the standard plate.

The effect of free ligand  $\text{H}_2\text{L}$  and its complexes on gram-negative and gram-positive bacteria and fungi were compared and the results are given in Table 5.

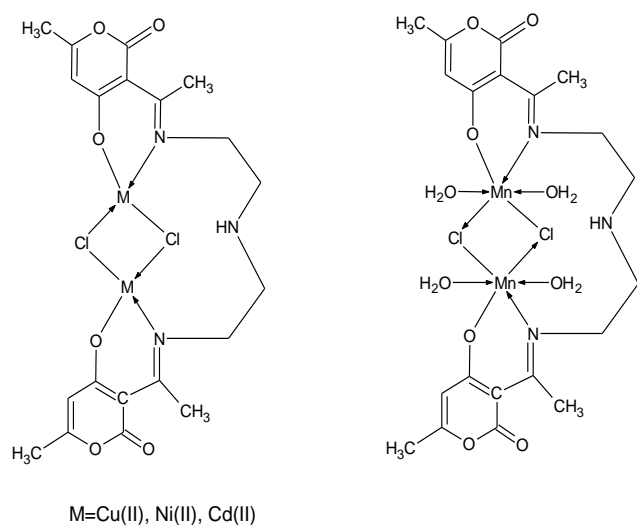
The ligand and its metal complexes were screened for their antibacterial and fungal activities at the same concentration and conditions.

**Table 5.** Antibacterial activity of ligand and its metal complexes

Compound	Inhibition, mm			
	<i>Escherichia Coli</i>	<i>Staphylococcus aurea</i>	Fungi	
	G <sup>-</sup>	G <sup>+</sup>	<i>A. flavus</i>	<i>C. albicans</i>
H <sub>2</sub> L	27.22±0.22	33.7±0.03	35.3±0.31	18.0±0.1
Mn(II)	22.01±0.55	34.51±0.11	20.91±0.09	12.11±0.1
Ni(II)	19.41±0.29	12.95±0.84	34.05±0.10	17.0±0.2
Cu(II)	34.43±0.16	39.51±0.11	42.71±0.23	20.0±0.33
Cd(II)	11±1.2	19.51±0.21	12.71±0.93	15.0±0.77
Control DMSO				
Reagent	Antibacterial		Antifungal	
	G <sup>+</sup>	G <sup>-</sup>	<i>A. flavus.</i>	<i>C. albicans</i>
<i>Amoxycilline</i>	18 ±0.2	22±0.2	-	-
<i>Ketoconazole</i>	-	-	31.89±0.2	32.5±0.2

G<sup>+</sup>, G<sup>-</sup> = gram Positive and gram negative bacteria

The ligand and all its metal complexes exhibit inhibition zone against *E. Coli* bacteria in the range 19-34 mm, supporting their activity toward gram-negative bacteria against *Amoxycilline* control.<sup>13,27</sup> It is found obviously (Table 5) that Cu(II) complex proved to be a potentially better antifungal agent against *A. Flavus* than the *Ketoconazol* (standard) and this complex has improved antimicrobial activity than the free ligand. It cannot be explained on the basis of chelation theory<sup>26,28</sup> but would rather with the releasing of Cu(II) ion from the complex. Although the decrease in the polarizing ability of the metal could enhance the lipophilicity of the complexes, which would lead to a breakdown of the permeability of the cells, resulting in interference in normal cell processes,<sup>27-29</sup> but only the Cu(II) complex showed higher value of inhibition against all types of microorganisms than the free ligand comparing it with nickel, manganese(II) or cadmium(II) chelates.

**Figure 5.** Proposed structure of metal(II) complexes.

## Conclusion

According to the results obtained from elemental analyses, spectroscopic studies and magnetic moment measurements, square planar central atom geometry was proposed for Ni and Cu(II) complexes, while the Mn(II) complex was found to be octahedral, and the Cd(II) complex was found to be tetrahedral. Theoretical study for the Mn(II) complex supported the expected structure derived from spectroscopic data. Except cadmium complex, the all studied compounds have antimicrobial activity toward gram negative and gram positive bacteria and fungi.

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