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Microwave Assisted Rapid Synthesis, Spectroscopic Characterization, and Antimicrobial Significance of New Derivative of 1,4 -Dihydropyridines

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Abstract

An efficient one-pot three-component synthesis of 1,4-dihydropyridine derivatives were synthesized by a Hantzsch reaction of dehydroacetic acid with benzaldehyde or furfural by using microwave irradiation technique in basic alumina. The prepared ligands used to yield various complexes with Co(II), Ni(II), Mn(II), Cu(II), Zn(II) and Cd(II). The isolated solid compounds were elucidated by elemental analysis (C, H, N, M, Cl), physical measurements (magnetic susceptibility and molar conductance) and spectroscopy (^{1}H NMR, ^{13}C NMR, IR, UV-visible, MS). Also, the synthesized compounds were tested against Gram-positive bacteria (*Staphylococcus aureus*, *Enterococcus faecalis*) and Gram-negative bacteria (*Escherichia coli, Proteus*) by disc diffusion method.

Keywords: 1,4-dihydropyridine complexes, Microwave, Spectroscopic, Antibacterial activity**.**

1. Introduction

Microwave-assisted synthesis considered a technique for accelerating the organic as well as inorganic reactions. Where, it enhanced the reaction selectivity and utilization of the inexpensive reagents. Also, this method characterized with shorter reaction times, low cost, high yield and simplicity in processing and handling together. Moreover, the microwave deliberated an eco-friendly technique where it was free of environmental impacts [1-5]. The application of microwave irradiation towards the acceleration of wide range of organic, organometallic and coordination chemistry was received concealable attention [6-9].

Hantzsch reaction is an significant technique for synthesis the 1,4-dihydropyridines (1,4-DHPs) which exhibited important antimicrobial activity in the treatment of various disease as cardiovascular disease [10]. There are several commercial drugs such as Amlodipine, Nifedipin, Nimodipin, Felodipine and Isradipine involving the 1,4-dihydropyridine as mother nucleus [11-14]. All these fact encouraged us to synthesis a new complexes with 1,4-dihydropyridines derivatives and evaluate their biological activity against four pathogenic bacteria.

2. Results and discussion

The prepared compounds were stable in air and soluble in DMF and DMSO. The values of molar conductance indicated that all complexes were non-electrolytes. The physical properties and elemental analyses of the isolated solid compounds were registered in Table 1.

Table 1. Elemental analysis and physical data of H_2L_1, H_2L_2 and their metal complexes

Compound Empirical Formula F.W. Found(Calculate)	Colour	M.p. °C	Yield (%)	% Calculate (Found)			
				C	H	N	M
H_2L **(1)** $C_{23}H_{19}NO_6$ 405.41	Yellow	163	79	68.14 (68.18)	4.72 (4.76)	3.46 (3.49)	-
$[CoL(N(Et)_3)(H_2O)_2].H_2O$ **(2)** $CoC_{29}H_{38}N_2O_9$ 617.525	Greenish-Brown	82	67	56.41 (56.54)	6.20 (6.02)	4.54 (4.56)	9.54 (9.51)
$[NiL(N(Et)_3)].2H_2O$ **(3)** $NiC_{29}H_{36}N_2O_8$ 599.30	Dark-Yellow	110	78	58.12 (57.98)	6.05 (6.16)	4.67 (4.67)	9.79 (9.63)
$[MnL(N(Et)_3)(H_2O)_2].H_2O$ **(4)** $MnC_{29}H_{38}N_2O_9$ 613.585	Brown	139	73	56.77 (56.78)	6.24 (6.11)	4.57 (4.59)	8.95 (8.86)
$[CuL(N(Et)_3)].2H_2O$ **(5)** $CuC_{29}H_{36}N_2O_8$ 604.16	Dark-Green	188	54	57.65 (57.42)	6.01 (6.14)	4.64 (4.67)	10.52 (10.43)
$[ZnL(N(Et)_3)(H_2O)_2].H_2O$ **(6)** $ZnC_{29}H_{38}N_2O_9$ 624.01	Pale-Yellow	141	77	55.82 (55.76)	6.14 (6.01)	4.49 (4.47)	10.47 (10.42)
$[CdL(N(Et)_3)(H_2O)_2].H_2O$ **(7)** $CdC_{29}H_{38}N_2O_9$ 671.03	Yellow	181	76	51.91 (52.05)	5.71 (5.67)	4.18 (4.17)	16.75 (16.77)
H_2L^2 **(8)** $C_{21}H_{17}NO_7$ 395.370	Yellow	155	88	63.80 (63.84)	4.33 (4.38)	3.54 (3.51)	-
$[Co(H_2L^2)(N(Et)_3)Cl_2]$ **(9)** $CoC_{27}H_{32}N_2O_7Cl_2$ 626.490	Green	96	63	51.17 (51.34)	515 (5.22)	4.47 (4.50)	9.41 (9.41)
$[Ni(H_2L^2)(N(Et)_3)Cl_2]$ **(10)** $NiC_{27}H_{32}N_2O_7Cl_2$ 626.250	Yellow	167	81	51.78 (51.78)	5.15 (5.18)	4.47 (4.54)	9.37 (9.39)
$[Mn(H_2L^2)(N(Et)_3)Cl_2].H_2O$ **(11)** $MnC_{27}H_{34}N_2O_8 Cl_2$ 640.515	Brown	169	59	50.63 (50.68)	5.35 (5.30)	4.37 (4.39)	8.58 (8.61)
$[Cu(H_2L^2)(N(Et)_3)Cl_2].H_2O$ **(12)** $CuC_{27}H_{34}N_2O_8Cl_2$ 649.125	Green	171	71	49.96 (50.00)	5.28 (5.30)	4.32 (4.35)	9.79 (9.80)
$[Zn(H_2L^2)(N(Et)_3)Cl_2]$ **(13)** $ZnC_{27}H_{32}N_2O_7Cl_2$ 632.940	Yellowish-white	146	51	51.24 (51.28)	5.10 (5.12)	4.43 (4.45)	10.33 (10.35)
$[Cd(H_2L^2)(N(Et)_3)Cl_2]$ **(14)** $CdC_{27}H_{32}N_2O_7Cl_2$ 679.96	Yellowish-white	187	71	47.69 (47.72)	4.74 (4.76)	4.12 (4.15)	16.53 (16.57)

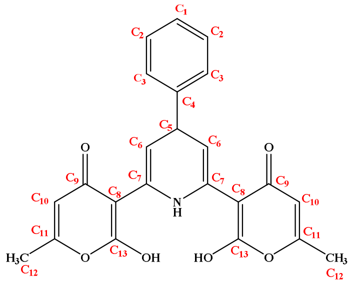
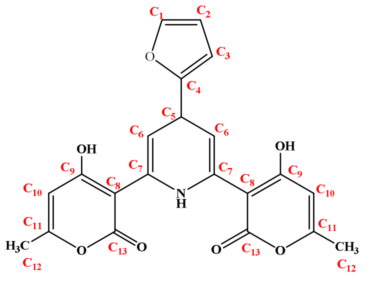
2.1. Nuclear magnetic resonance spectral studies

The ^1H and ^{13}C NMR spectra of H_2L^1, H_2L^2 and their Cd(II) and Zn(II) complexes were measured in DMSO. The ^1H NMR spectra of H_2L^1 and H_2L^2 in DMSO showed two signals at (12.07; 12.10) and (9.69; 9.71) ppm assignable to the (OH) and (NH) protons, respectively. The multiplet signals detected in the (7.35-7.61; 6.72-8.01) ppm regions, respectively were attributed to the aromatic protons. The sharp signal observed at 2.48; 2.54 ppm, respectively was attributed to methyl proton (CH_3).

The ^{13}C NMR spectra of H_2L^1 and H_2L^2 in DMSO showed significant signals at (160; 149), (183; 173), (162; 168) and (176; 163) attributed to C_7, C_9, C_{11} and C_{13}, respectively (Table 2) [15]. The data obtained confirmed the formation of 4,4'-(4-phenyl-1,4-dihydropyridine-2,6-diyl)bis(5-hydroxy-2-methyl-2H-pyran-3(6H)-one) and 3,3'-(4-(furan-2-yl)-1,4-dihydropyridine-2,6-diyl)bis(2-hydroxy-6-methyl-4H-pyran-4-one).

Moreover, the ^{1}H NMR spectra of the $[ZnL(N(Et)_3)(H_2O)_2].H_2O$ and $[CdL(N(Et)_3)(H_2O)_2].H_2O$ complexes showed the signal attributed to (NH) proton remained more or less at the same positions indicating that this group not deprotonated. But, the lack of signals due to (OH) protons in the ^{1}H NMR spectrum emphasized the deprotonating of the two hydroxyl groups.

Table 2. ^{13}C NMR Chemical shifts in (ppm) assignments for H_2L_1 and H_2L_2

Carbon atoms		
C_1	126	145
C_2	129	112
C_3	128	110
C_4	162	154
C_5	40	39
C_6	95	98
C_7	160	149
C_8	107	100
C_9	183	173
C_{10}	104	106
C_{11}	162	168
C_{12}	22	22
C_{13}	176	163

2.2. Infra-red spectral studies

In the IR spectra of H_2L^1 and H_2L^2, the bands observed at (1713; 1710), (3284; 3275) and (3350; 3355) were attributed to υ(C=O) [16], υ(NH) [17] and υ(OH) [18] vibrations, respectively (Table 3). The appearance of hydroxyl group as a broad band at lower wavenumber and the two weak broad bands at 1912–2075 and 2149–2237 cm^{-1} region proposed intramolecular hydrogen bonding.

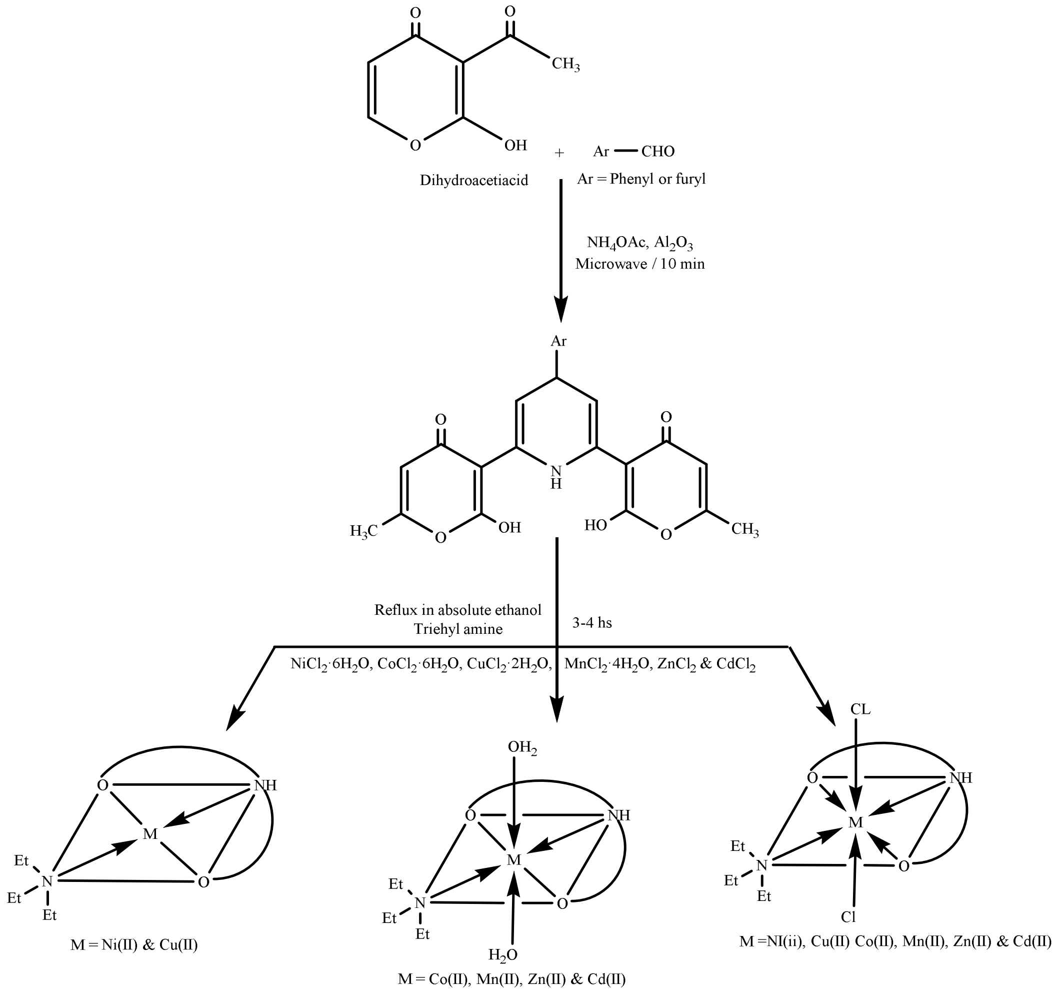
In Co(II), Ni(II), Mn(II), Cu(II), Zn(II) and Cd(II) complexes (Scheme 1), the H_2L^1 behaved as binegative tridentate ligand *via* υ(NH) and the two deprotonated hydroxyl groups υ(OH). This mode of chelation was maintained by the following observations: (i) the disappearance of two hydroxyl groups, (ii) the negative shift of (NH) group (iii) the appearance of two carbonyl groups at nearly the same frequencies, proposing that these groups did not participate in bonding and (iv) the appearance of new bands in 442–470 cm^{-1} and 527–562 cm^{-1} regions which may be attributed to (M-O) and υ(M-N) [19], respectively.

But, the IR spectra of H_2L^2 complexes revealed that the ligand acted as a neutral tridentate ligand *via* υ(NH) and the two carbonyl groups υ(C=O). This mode of chelation was confirmed by the following clarifications: (i) the negative shift of the υ(NH) and two carbonyl groups (iii) the appearance of hydroxyl groups at nearly the same frequencies, suggesting that these groups did not participate in bonding and (iv) the appearance of new bands in (449–467) cm^{-1} and (534–568) cm^{-1} regions which may be attributed to (M-O) and υ(M-N) [19], respectively.

The complexes which have coordinated water molecules have two sharp bands observed in 850–863 and 743–782 cm^{-1} attributed to $\rho r(H_2O)$ and $\rho w(H_2O)$ [20] vibrations, respectively.

Table 3. Most important IR spectral bands of H_2L^1, H_2L^2 and their metal complexes

Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
ν(OH)	3350	-	-	-	-	-	-	3355	3435	3475	3420	3356	3429	3421
ν(NH)	3284	3254	3263	3254	3261	3210	3257	3275	3260	3253	3259	3262	3225	3223
ν(C=O)	1713	1705	1710	1706	1707	1711	1708	1710	1685	1688	1686	1688	1680	1683



Scheme 1. The outline of the synthesis of ligands and their metal complexes

2.3. Magnetic moments and electronic spectra

The UV-visible spectral bands of the isolated compounds in DMSO besides the magnetic moments and the ligand field parameters were listed in table 4. The electronic spectra of the complexes were conquered by strong intra-ligand charge transfer bands. The ligand spectrum displayed an intense absorption band at 32679 cm^{-1} assignable to $\pi \rightarrow \pi^*$ transition of pyridine ring. A red shift was detected for this transition in the UV-visible spectra of isolated complexes due to the coordination of nitrogen atom of the pyridine ring [21]. The other intense band observed at 26316 cm^{-1} attributed to $n \rightarrow \pi^*$ transition of carbonyl group.

The electronic spectra of $[CoL(N(Et)_3)(H_2O)_2].H_2O$ and $[Co(H_2L^2)(N(Et)_3)Cl_2]$ complexes exhibited two bands at (14705, 14992) and (17313, 17857) cm^{-1} ascribed to ${}^4T_{1g}\rightarrow{}^4A_{2g}(F)$ and ${}^4T_{1g}\rightarrow{}^4T_{1g}(P)$ transitions, respectively in an octahedral configuration [22]. The value of υ_1 (6871, 6989 cm^{-1}) was intended theoretically. The values of magnetic moment (4.9 & 5.1 BM) were reliable with octahedral geometry around the Co(II) ion.

The diamagnetic behavior of $[NiL(N(Et)_3)].2H_2O$ complex indicated a square planar configuration. Further, the electronic spectrum showed a specific band at 18164 cm^{-1} attributed to ${}^1A_{1g}\rightarrow{}^1A_{2g}$ transition in a square planar geometry [23].

The electronic spectrum of $[Ni(H_2L^2)(N(Et)_3)Cl_2]$ complex displayed two bands at 17241 and 27778 cm^{-1} attributed to ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transitions, respectively, in an octahedral geometry [23]. The position of υ_1 (10843 cm^{-1}) was intended theoretically. The value of the magnetic moment (3.2 BM) confirmed the octahedral geometry around Ni(II) ion.

The two bands at (22222, 21505) and (28090, 26316) cm^{-1} in the spectra of $[MnL(N(Et)_3)(H_2O)_2].H_2O$ and $[Mn(H_2L^2)(N(Et)_3)Cl_2].H_2O$ complexes were attributed to $6A_{1g}\rightarrow4T_{1g}(G)$ and $6A_{1g}\rightarrow4T_{2g}(G)$, transitions, respectively, in an octahedral configuration. The values of magnetic moment (5.4 & 5.3 BM) were reliable with high spin d^5 system [23].

The Cu(II) complexes have magnetic moment values (2.0 & 1.9 BM) which stand for those stated for d^9-systems. The electronic spectrum of $[CuL(N(Et)_3)].2H_2O$ complex exhibited a broad band at 14428 attributed to $2B_{1g}\rightarrow2A_{1g}$ transition as specified for square planar Cu(II) configuration [24]. While, the electronic spectrum of $[Cu(H_2L^2)(N(Et)_3)Cl_2].H_2O$ complex showed a broad band at 16667 cm^{-1} with a shoulder at 14286 cm^{-1} which assignable to $2B_{1g}\rightarrow 2E_g$ and $2E_g\rightarrow 2A_{1g}$ transitions, respectively, in a tetragonally distorted octahedral geometry [24].

Table 4. Magnetic moments, electronic spectra and ligand field parameters of metal complexes

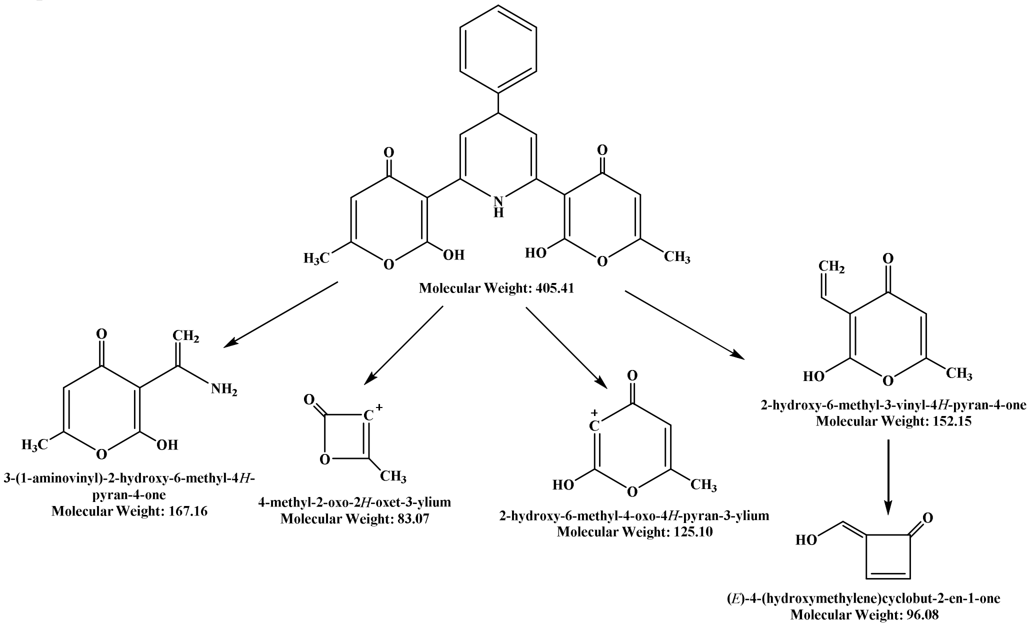
Compound	μ_{eff} (BM)	Band position (cm^{-1})	D_q (cm^{-1})	B (cm^{-1})	β	υ_2/υ_1
2	4.9	14705; 17313	770	770	0.79	2.14
3	Dia.	18164	-	-	-	-
4	5.4	22222; 28090	-	-	-	-
5	2.0	14428	-	-	-	-
9	5.1	14992; 17857	795	795	0.82	2.15
10	3.2	27778; 17241	1083	833	0.80	1.59
11	5.3	21505; 26316	-	-	-	-
12	1.9	14286; 16667	-	-	-	-

2.4. Mass spectra

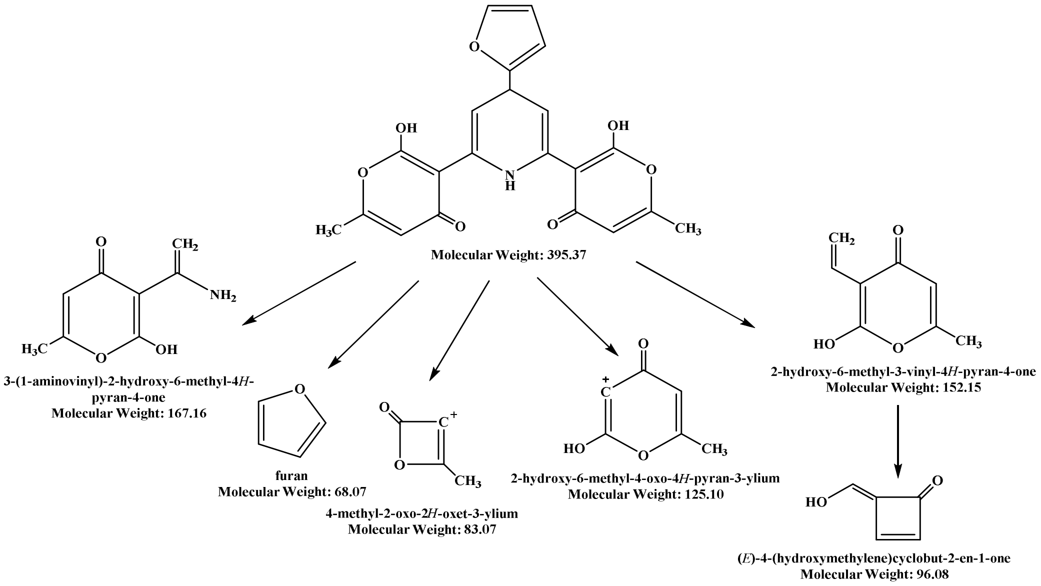
The ESI-MS of 1,4-dihydropyridines derivatives exhibited molecular ion peaks which were in covenant with their molecular formula. The molecular ion peak for the ligands (H_2L^1 = $C_{23}H_{19}NO_6$ & H_2L^2 = $C_{21}H_{17}NO_7$) corresponds to m/z 405.41 and 395.37, respectively. Also, a base peak was appeared at m/z =167 and m/z =168 which resemble the main fragmentation molecular weight of the respective compounds H_2L^1 and H_2L^2, respectively. These peaks confirmed the structure of the ligands. The different molecular ion peaks seemed in the mass spectra of ligands (abundance range 2-100%) was ascribed to the ligand fragmentation which obtained from the rupture of different bonds inside the molecule by successive degradation. The spectra of ligands displayed molecular ion peaks in good agreement with the proposed structure by elemental and spectral studies (Scheme 2, 3).

3. Antimicrobial activity

The antimicrobial activity of 1,4-dihydropyridines was encouraged us to assume systematic studies on their chelation affinity and test their efficiencies against economically essential bacteria [25, 26]. Whereas, various diseases initiated by microbial infections were a serious threat to the human health being and every so often have connection to some other diseases when the body system became weakened. The developing antimicrobial drugs to resistance various kinds of microorganisms such as a wide spectrum of antibacterial activity considered one of the most important fears of research in this zone.



Scheme 2. The mass spectroscopic fragmentation pathway of H_2L^1



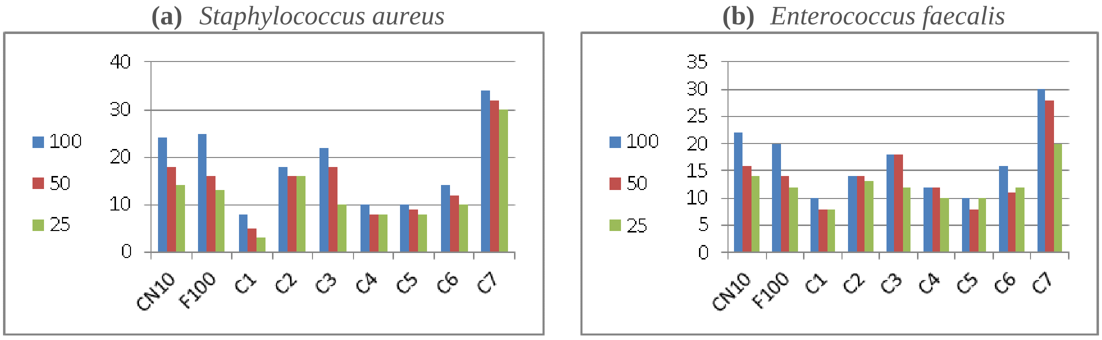
Scheme 3. The mass spectroscopic fragmentation pathway of H_2L^2

3.1. Antibacterial activity

The isolated ligands, chelates, standard drugs (Gentamicin; Nitrofurantoin) and DMSO solvent control were partitioned individually for their antibacterial activity against Gram-positive (*Staphylococcus aureus*; *Enterococcus faecalis*) and Gram negative bacterial strains (*Escherichia coli; Proteus*) [27, 28]. The antibacterial activity of isolated compounds was compared to the activity of Gentamicin (CN10) and Nitrofurantoin (F100) as standard antibiotics and then MIC of the tested compounds was evaluated. The antibacterial results suggested that the tested compounds (Figures 1, 2) have a modest activity against various kinds of bacteria. The MIC values showed the highest activity for Cd(II) complexes against all tested bacteria. We conclude that, the complexes were more effective against Gram-positive (*Staphylococcus aureus*; *Enterococcus faecalis*) than Gram negative bacterial strains (*Escherichia coli; Proteus*) and showed better antibacterial activity than the ligands alone.

The difference in antibacterial activity between ligands and their complexes may be due to the chelation properties wherever the metal complexes became more effective bactereostatic agents that stopping the microorganism growth. Furthermore, the chelation behavior compact the polarity of the metal ion mostly due to the partial sharing of positive charge with the donor groups as oxygen and nitrogen atoms within the chelate ring system. This manner raises the lipophilic nature of the metal ion, which preferred its penetration through the lipid layer of the microorganism, so destroying them more harmfully [29].

Gram positive


(a) *Staphylococcus aureus* **(b)** *Enterococcus faecalis*

Gram positive

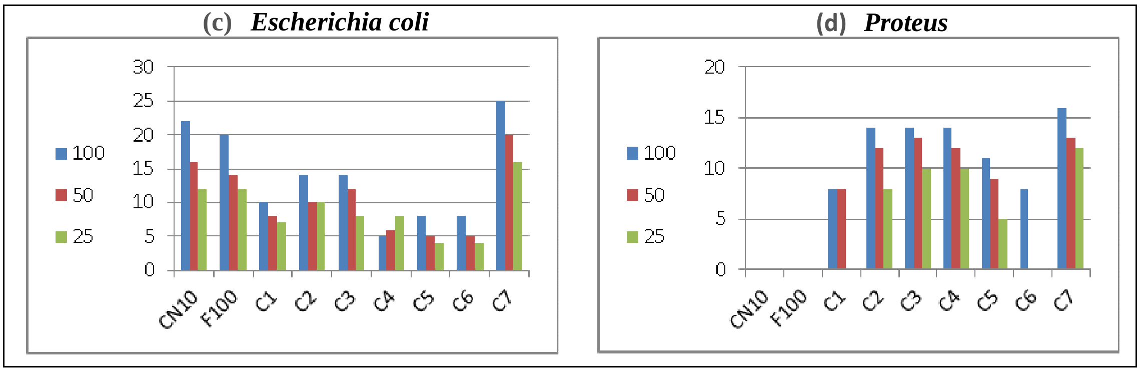


Fig.1. Effect of H_2L^1 and its metal complexes toward (a) *Staphylococcus aureus*, (b) *Enterococcus faecalis*, (c) *Escherichia coli* and (d) *Proteus*

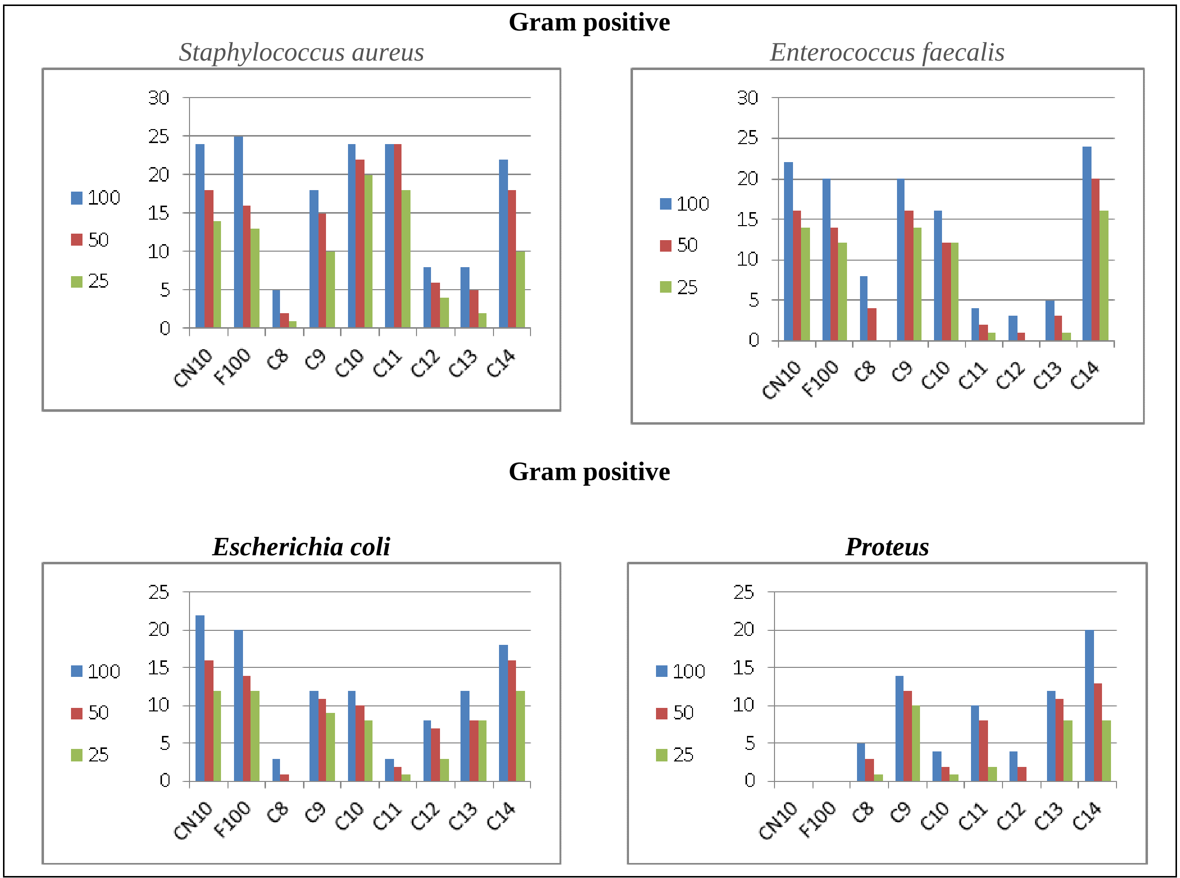


Fig.2. Effect of H_2L^2 and its metal complexes toward (a) *Staphylococcus aureus*, (b) *Enterococcus faecalis*, (c) *Escherichia coli* and (d) *Proteus*

4. Conclusions

In this paper, the derivative of 1,4-dihydropyridines were synthesized by a Hantzsch reaction of dehydroacetic acid with benzaldehyde or furfural by using microwave irradiation technique in basic alumina. A series of Co(II), Ni(II), Mn(II), Cu(II), Zn(II) and Cd(II) complexes were prepared. The isolated solid compounds were elucidated by using various spectroscopic techniques. Also, the synthesized compounds were tested against Gram-positive bacteria (*Staphylococcus aureus*, *Enterococcus faecalis*) and Gram-negative bacteria (*Escherichia coli*, *Proteus*) by disc diffusion method. The results of antibacterial test showed that Cd(II) complexes have the highest activity against all tested bacteria.

5. Experimental

5.1. Materials and reagents

The chemicals used were of the analytical reagent grade with high purity. They included benzaldehyde, furfural, ammonium acetate, dehydroacetic acid, basic alumina, $NiCl_2 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $MnCl_2 \cdot 4H_2O$, $ZnCl_2$ and $CdCl_2$ (Sigma-Aldrich). The solvent used involved absolute ethyl alcohol, diethyl ether and dimethylsulfoxid were spectroscopic pure from BDH.

5.2. Instrumentations

The reactions were made using Anton Paar's Monowave 300 microwave. The FTIR spectra were detailed on a Shimadzu FT-IR 8400s spectrophotometer using KBr discs. ^1H and ^{13}C-NMR spectra were determined on Burker DMX- 500 NMR Spectrophotometer on a 300 MHz, with TMS as standard and DMSO as solvent (Al albayt University-Jordan). The electronic spectra of the isolated solid compounds were recorded on a Shimadzu Uv-Vis spectrophotometer 1650 having wavelength range 190-1100 nm and spectral band width 2 nm. The spectra of the complexes were recorded at room temperature in the wavelength range 200-900 nm with a scanning rate 200 nm/minute. The Magnetic susceptibility measurements of the complexes were performed on a faraday balance at room temperature using $Hg[Co(SCN)_4]$ as a calibration MK-Magnetic balance. The molar conductance of complexes was measured on Philips 180 conductivity meter using 10^{-3} M solution in DMSO. Elemental analyses (C, H and N) were performed on Carlo-Erba1108 CHNS elemental analyzer. The metal contents of the complexes were determined by atomic absorption type Shimadzu (A.A-670). GC mass Spectrometer 200 Plus Shimadzu. Melting points were measured in an open capillary Stuart SMP30 melting point apparatus.

5.3. Procedures

5.3.1. Preparation of ligands

The 1,4-dihydropyridines (4,4'-(4-phenyl-1,4-dihydropyridine-2,6-diyl)bis(5-hydroxy-2-methyl-2H-pyran-3(6H)-one); H_2L^1 and 3,3'-(4-(furan-2-yl)-1,4-dihydropyridine-2,6-diyl)bis(2-hydroxy-6-methyl-4H-pyran-4-one); H_2L^2) (Fig. 3) were prepared by stirring a mixture of aryl aldehyde (benzaldehyde; furfural) (1 mmol), dehydroacetic acid (2 mmol), ammonium acetate (1 mmol) and basic alumina in ethanol (5 ml) at room temperature for 15 min. The mixture was transfer to the vial vessel and irradiated in microwave for 10 min at 400 W and 140 ºC. The completion of the reaction was monitored by TLC. The mixture was filtered to get rid of alumina layer and cooled to room temperature then water 10 mL was added to the reaction mixture. The prepared ligands were filtered and recrystallized from ethanol (Scheme 1).

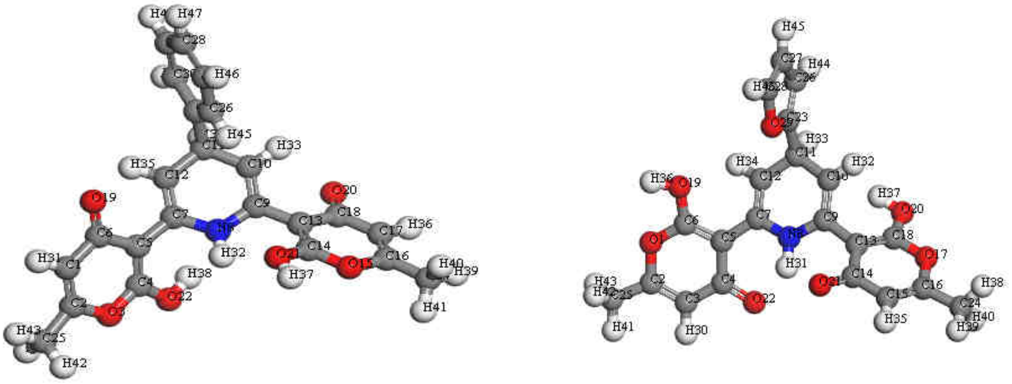


Fig.3. The molecular modelling of H_2L^1 and H_2L^2

5.3.2. Preparation of Complexes

To a stirred solution of ligands (1.22 mmol) and triethylamine (2.44 mmol) in ethanol (15 mL), metal chloride $M(Cl)_2.XH_2O$ (1.22 mmol) was added drop by drop. The contents were allowed to string for 30 minutes then refluxed on water bath for 3-4 h depending on the type of metal salt used. The yellow precipitates were filtered off, washed with hot absolute ethanol and finally well-kept in a vacuum desiccator over anhydrous $CaCl_2$.

5.3.3. Preparation of Cd(II) and Ni(II) complexes by microwave technique

The $[CdL(N(Et)_3)(H_2O)_2].H_2O$ and $[Ni(H_2L^2)(N(Et)_3)Cl_2]$ complexes were prepared by stirring a mixture of aryl aldehyde (benzaldehyde; furfural) (1 mmol), dehydroacetic acid (2 mmol), ammonium acetate (1 mmol) and basic alumina in ethanol (5 ml) at room temperature for 15 min. To a stirred solution of ligands (1.22 mmol) and triethylamine (2.44 mmol) in ethanol (15 mL), metal chloride $M(Cl)_2.XH_2O$ (1.22 mmol) was added drop wise and allowed to string for 30 minutes. The mixture was transfer to the vial vessel and irradiated in microwave for 10 min at 400 W and 140 ºC. The reaction progress was monitored by TLC. After completion of the reaction, the mixture was filtered and cooled to room temperature then water (10 mL) was added to the reaction mixture. The resulting solid product was filtered and washed with hot EtOH and/or H_2O successfully and finally preserved in a vacuum desiccator over anhydrous $CaCl_2$.

5.3.4. Biological activity

Antibacterial activity of the isolated solid compounds was tested against Gram-positive (*Staphylococcus aureus* and *Enterococcus faecalis*) and Gram negative bacterial strains (*Escherichia coli* and *Proteus*) by disc diffusion method [30]. Each investigated compound was dissolved in DMSO and a solution of the concentration 1 mg/ml was prepared. The sterile medium (Nutrient Agar medium, 15 mL) in each petri plates was consistently muddy with cultures of Gram positive and Gram negative bacteria. Each treatment was replicated three times. Also, the antibacterial activity of a standard antibiotic Gentamicin (CN10) and Nitrofurantoin (F100) was measured using the same procedure as above. The dishes were incubated at 25 ± 2ºC for 24 h and the size of the resulting inhibition zone was determined.

Reference

K. Sharma, R. Singh, N. Fahmi, R. V. Singh, (2010). *Spectrochim. Acta*, *75A*, 422. doi: 10.1016/j.saa.2009.10.052

A. K. Sharma, A. K. Mishra, (2010). *Adv. Mat. Lett.*, *1*, 59. doi: 10.5185/amlett.2011.9307

K. Mahajan, N. Fahmi, R. V. Singh, (2007). *Indian J. Chem.*, *46A*, 1221.

R. Garg, M. K. Saini, N. Fahmi, R. V. Singh, (2006). *Trans. Met. Chem.*, *31*, 362. doi: 10.1007/s11243-005-0001-1

K. Mahajan, M. Swami, R. V. Singh, (2009). *Russ. J. Coord. Chem.*, *35*, 179. doi: 10.1134/S1070328409030038

A. P. Mishra, A. Tiwari, R. K. Jain, (2012). *Adv. Mat. Lett.*, *3*, 213.

R. S. Verma, (1999). *Green Chem.*, *1*, 43. doi.org/10.1039/a808223e

M. M. Mojtahed, M. R. Saidi, M. Bolourtchian, (1999). *J. Chem. Res.*, *12*, 710.

R. Kurtaran, L. T. Yıldırım, A. D. Azaz, H. Namli, O. Atakol, (2005). *J. Inorg. Biochem.*, *99*, 1937. doi:10.1016/j.jinorgbio.2005.05.016

A. Hantzsch, *Jusfus Liebigs Ann. Chem.* 1882, *215*, 1. doi: 10.1002/jlac.18822150102

F. Bossert, H. Meyer, E. Wehinger, (1981). *Angew. Chem. Int. Ed. Engl.*, *20*, 762. doi: 10.1002/anie.198107621

B. Love, M. M. Goodman, K. M. Snader, R. Tedeschi, E. Macko, (1974). *J. Med. Chem.*, *17*, 956. doi: 10.1021/jm00255a010

A. Kumar, S. Sharma, (2011). *Green. Chem.*, *13*, 2017. doi: 10.1039/c1gc15223h

S. Cosconati, L. Marinelli, A. Lavecchia, E. Novellino, (2007). *J. Med. Chem.*, *50*, 1504. doi: 10.1021/jm061245a

R. R. Zaky, T. A. Yousef, K. M. Ibrahim, (2012). *Spectrochim. Acta.*, *97*, 683. doi.org/10.1016/j.saa.2012.05.086

K. M. Ibrahim, I. M. Gabr, G. M. Abu El-Reash, R. R. Zaky, (2009). *Monatsh. Fur. Chem.*, *140*, 625. doi: 10.1007/s00706-009-0106-x

K. M. Ibrahim, R. R. Zaky, E. A. Gomaa, M. N. Abd El-Hady, (2013). *Spectrochim. Acta Part A*, *107*, 133. doi.org/10.1016/j.saa.2013.01.031

A. Fekri, R. R. Zaky, (2014). *Spectrochim. Acta Part A*, *132*, 846. doi.org/10.1016/j.saa.2014.05.062

R. R. Zaky, A. Fekri, (2015). *J. Mol. Struct.*, *1079*, 203. doi.org/10.1016/j.molstruc.2014.09.033

K. M. Ibrahim, R. R. Zaky, H. M. Abou-El-Nadar, S.M. Abo-Zeid, (2014). *J. Mol. Struct.*, *1075*, 71. doi.org/10.1016/j.molstruc.2014.06.059

E. B. Seena, M. R. P. Kurup, (2007). *Polyhedron*, *26*, 829. doi:10.1016/j.poly.2006.09.040

M. N. Abd El-Hady, R. R. Zaky, K. M. Ibrahim, E. A. Gomaa, (2012). *Mol. Struct.*, *1016*, 169. doi:10.1016/j.molstruc.2012.02.006

F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, (2003). *Advanced Inorganic Chemistry*, 6th ed., John Wiley & Sons Inc.

A. B. P. Lever, (1984). *Inorganic Electronic Spectroscopy*, 2nd edn., New York: Elsevier.

R. Nagar, (1990). *J. Inorg. Biochem.*, *40*, 349. doi:10.1016/0162-0134(90)80069-A

P. Jigna, R. Nairi, S. Baluja, S. Chandai, (2005). *J. Serb. Chem. Soc.*, *70*, 1115. doi:10.2298/JSC0510155P

Z. H. Abd El-Wahab, M. R. El-Sarrag, (2004). *Spectrochim. Acta*, *60*, 271. doi:10.1016/j.saa.2004.01.021

M. N. Patel, (2010). *Polyhedron*, *29*, 1918. doi: 10.1016/j.poly.2010.03.007

N. Raman, V. Muthuraj, S. Ravichandran, A. Kulandaisamy, (2003). *Proc. Indian Acad. Sci.*, *115*, 161.

R. Kurtaran, L. T. Yıldırım, A. D. Azaz, H. Namli, O. Atakol, (2005). *J. Inorg. Biochem.* *99*, 1937. doi:10.1016/j.jinorgbio.2005.05.016