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SYNTHESIS AND NMR ASSIGNMENTS OF SOME Zn(II) AND Cd(II) COMPLEXES OF ACETYLENIC AMINES LIGANDS WITH THEIR BIOLOGICAL ACTIVITY

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Abstract: Acetylenic amines ligand N,N-diethyl Propargyl Amine, N-Propargyl Pyrrolidine and N-Propargyl-3-methyl Piperidine formed by reaction of Propargyl bromide and(N,N-diethyl amin , 3-methyl Piperidine and Pyrrolidine), and its Zn(II) and Cd(II) complexes were synthesized . their structure were elucidated on the basis of elemental analysis ,spectral (IR, NMR and UV-VIS). atomic absorption, Molar conductivity measurements, molar ratio studies and melting points. The complexes exhibit an octahedral geometry around the metal center. Conductance data of the complexes suggested them to be non-electrolytes. The bi dentate behavior of ligand was proposed on the basis of spectral studies. The free ligand and its complexes have been tested for their antibacterial activities against several human pathogenic bacteria: (Streptococcus paecalies, Staphylococcus aureus),(Escherichia coli, psedomonas aeruginosa) . the first group are Gram positive while the second group are Gram negative (by using agar well diffusion method). Finally, it was found that compounds show different activity of inhibition on growth of the bacteria.

1. Introduction :

Acetylenic amines are very important class of compounds for their pharmacological properties such as activity, low toxicity and easy to absorption from the body. Moreover these compounds are electron rich and easy to bond with receptor protein1. some of their pharmaceutical uses as anticancer 2 and hypotensives agent3.

Tremorine4 and oxotremorine5 have been widely used as compound of potential value in Parkinson's disease. Both compounds produce, in experimental animals, syndrome characterized by tremor, rigidity , hypokinesia and parasympathomitic effect, which are blocked by atropine and many agents of established effusiveness in treating Parkinson's disease. The importance of the acetlynic bond in oxotremorine and antagonists of oxotremorine has been the subject of so much discussion. It has been suggested that the triple bond represents a region of high electron density with is capable of binding to the muscarinic receptors at the same site as the furan oxygen of muscarine and ester oxygen of acetylcholine6. It has also been claimed that the acetylenic bond is not considered essential for activity but favors entry in the central nervous system (CNS) by reducing the base strength7.

The first stable acetylenic complexes were reported by Gelman et al8, who showed that the acetylenic glycol (HOCR2C≡COH) (ac)9. Forms complex, trans-[PtCl2(ac)Py] analogous to trans-[PtCl2(C2H4)Py]. Later work10 showed that olefins complexes of the types K[PtCl3(ac)] and cis-[Pt Cl2 (ac) (NH3)] by several methods. Alkyne Pt+2 complexe11 of the chloro-bridge type [Pt2Cl4(ac)2] and the mononuclear type M[Pt Cl3 (ac)] (M=Na,K). Recently, prepared complexes of acetylenic derivative with the metal Au, Pd, Pt, Cu and Ni have been prepared and their biological activity studies12,13.

2. Experimental Section :

2.1. INSTRUMENTATION:

A pye – Unicom sp3-100 infrared spectrophotometer was used to recorded the ir spectra as KBr and CsI disc , UV/VIS spectra were measured by a HITACHI U-2000 spectrophotometer, Elemental Analysis (C.H.N) founded on (Carlo Erloa microanalyizer type 1106),determination of all metals percentage by atomic absorption spectrophotometry on AA-680G (Shimadzu). H1-NMR spectra were recorded in DMSO-d6 as the solvent at Hitachi Perkin-Elmer 60 spectrophotometer (R-24B) using tetramethyl-silane (TMS) as an internal reference. Electrical conductance was measured on conductivity CDC304 (Jenway4070) Melting points determined by an electric heated block apparatus (Gallen Kamp), and were uncorrected.

2.2. MATERIALS:

All material were supplied by BDHchemicals , the solvents , Ethanol Absolute ,diethylether and DMSO were supplied by Aldrich .

2.3. Preparation of the ligands:

Preparation of N,N-diethyl Propargyl Amine, N-Propargyl Pyrrolidine and N-Propargyl-3-methyl Piperidine were prepared according to the literature[5]. The full name of the acetylenic amines will be replaced by a number (L_1,L_2, L_3) respectively as in shown in table (1) for the rest of this paper . The physical properties of these compounds (L_1, L_2, L_3) are listed in table (1). The characters ir bands and uv/vis spectrum in DMSO as shown in table (1).

2.4. General procedure for preparation of complexes :

All of complexes were prepared by the following methods; A solution of the ligand (2 mmole/l) in absolute ethanol we prepared and reacted with various metal chlorides in the required molar ratio.

To a solution of (L) (2 mmole/l) in absolute ethanol ,a hot ethanolic solution (96%) containing (1 mmole/l) of (Zn (II) was gradually added with sting the product .the color of the resultant mixture changed immediately , the mixture was left over night . a colored solid precipitate was separated and collected by filtration under vacuo, then it was washed successively with ethanol and recrystallized from absolute ethanol/ether to give colored complexes .

Analogous complexes were prepared in a similar manner to that described above by adding a hot solution of the Cd(II) chloride above (1 mmole/l) to a solution of ligand (2 mmole/l) . The physical properties of prepared complexes are listed in table (1).The molar ratio of the complexes was determined according to the methods [14].

2.5. Study of biological activity for ligands(L1,L2, L3) and their metal complexes :

The biological activity of the ligands and their metal complexes were studied against two selected type of bacteria which included pseudomonas aeuginosa , Escherichia coli as gram negative (-Ve) and Streptococcus paecalies, Staphylococcus aureus as gram positive (+Ve) to be cultivated and as control for the disc sensitivity test[15], this method involves the exposure of the zone of inhibition toward the diffusion of micro–organism on agar plat. The plates were incubated for (24 hours) , at 37C° , the zone of inhibition of bacteria growth around the disc was observed.

3.RESULTS AND DISCUSSION :

3.1. FT-IR spectra:

The spectra of all prepared complexes were prepared with ligand spectra in the region (4000-200) cm^{-1}. Stretching vibration of (C≡C) bonds for the prepared ligand appear near (2100) cm^{-1} [16]. This peak will shifted to lower frequency by (450) cm^{-1} (i.e. to 1750-1705) cm^{-1} the peak which belong to the frequency (C≡C) disappeared producing the change in ligand peak shape and appear intensity more than complex as shown in table (1).

υ^{M-N} frequency appears in the region (315-345) cm^{-1} which indicating the involving of nitrogen atoms in coordination with metallic ion .In addition, new bands appears attributed to the M- Cl stretching vibration table (2).

3.2. Electronic Spectra :

UV-Visible spectra for the prepared ligand show two bands, the first band at (319) nm and the second at (372) nm as shown in table (1). Comparing the UV-Vis for free ligand solution with metal complexes, clear sudden change have been made in bands spots weather increasing or decreasing in wavelength or by new absorbance band for all preparation complex which belong coordination complex formation ,the change in color were occurred after mix ligands solution with metal salt, the mixtures color differ free ligand and metal salt colors indicate occurring complexation , the data in table (1) clearly show that bands in all complexes appear shifted in λmax, compared to the same bands in the free ligand signs this band is due to (π-π*) and(n-π*) and this shifted in λmax can be to indicate the complexation between ligand and metal ions[17].

All the prepared complexes did not show any d-d bands and their spectra are dominated only by the charge transfer bands. The charge transfer band at 28550-28350 cm^{-1} and 2750 cm^{-1} for Zn and Cd complexes respectively assigned due to transition $^2Eg \rightarrow {}^2T_2g$ [18].

3.3. Magnetic Study :

Magnetic susceptibility measurements showed that the prepared complexes have diamagnetic properties . The magnetic moments of complexes were carried out at 25 ^OC[19].

3.4. Molar Conductance :

The measurements of the molar electrical conductivity of the complexes in DMSO solvent are prepared in 10^{-3} M at 25 ^OC are presented in table (1). The results clearly show the values for the molar conductivity of the complexes of metal ions are non-electrolyte[20].

3.5. Stochiometric Study :

Molar ratio (1:2) metal to ligand (ML_2) was also obtained for the complexes by Job's method of continuous variations as shown in fig.(1) that is agreement with the ratio found , according to elemental analysis table (2).

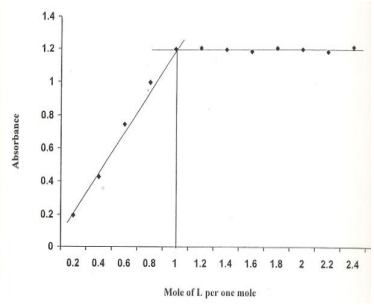


Fig.(1): Molar-ratio curve for some of prepared complexes

According to the results obtained from ir, uv/vis, molar ratio, molar conductivity and atomic absorption measurements for the prepared complexes, the proposed molecular structure of the complexes has an octahedral structure as shown below fig. (2).

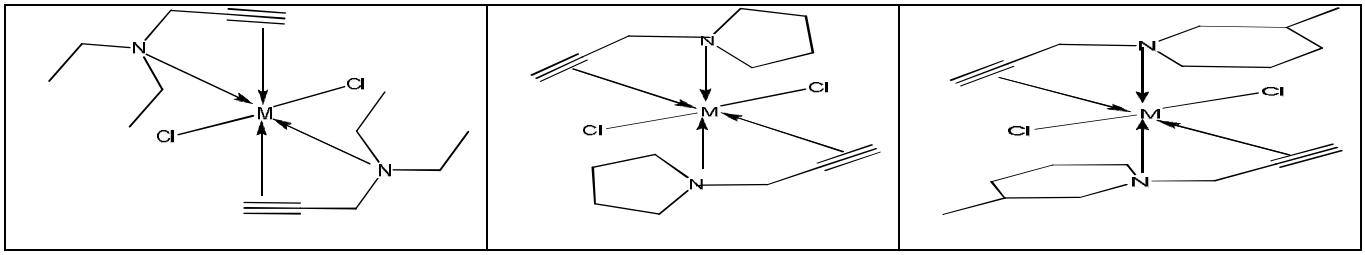


Fig (2): The proposed structure of complexes where M= Zn(II)and Cd(II)

3.6. 1H-NMR spectra:

The ^{1}H-NMR spectra of the free ligands and their complexes taken in DMSO-d_6 are listed in table (3). The numbering system of ligands is shown in fig.(3). The free ligands exhibited signals due to all the expected protons in their expected region and have been identified from the integration curve found to be equivalent to the total number of protons deduced from their proposed structure . there were compared with the reported[21] signals of the known identical compounds and gave further support for the composition of the ligands suggested by their ir and elemental analysis data.

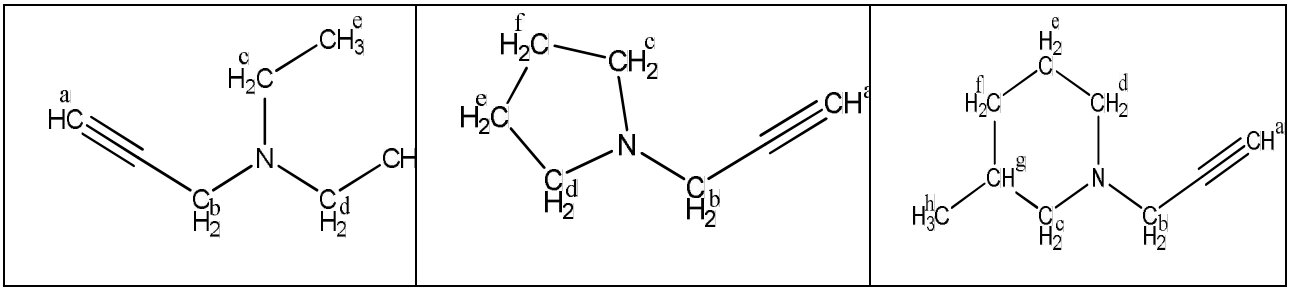


Fig (3): Numbering system of ligands L_1, L_2 ,L_3

In the spectra of the Zn(II) and Cd(II) complexes, the signals due to the Ha and Hb protons exhibit a downfield shift (0.01-0.12 ppm), suggesting the involvement of the nitrogen in the coordination to the metal ion. In the Zn (II) and Cd(II) complexes , the signals due to the Hc, Hd protons shift to downfield region by (0.05-0.11)ppm , indicating the coordination of the acetylenic group to the metal ion [22].

3.7. Antibacterial study:

The acetelynic amines ligands and their metal dictates were evaluated for their antibacterial activity against bacterial species Escherichia coli, staphylococcus aureas, psedomonas aeruginosa and Streptococcus paecalies. The compounds were tested at a concentration of 10^{-3} m in DMSO solution using the diffusion method. The susceptibility zone measured in diameter (mm) and the results are reproduced as shown in fig.(4). The susceptibility zone measured were the clear zones around the discs killing the bacteria degrees of inhibitory effects on the growth of the tested bacterial species. The antibacterial results evidently show that the activity of acetylenic amine ligands became more pronounced when coordinated to the metal ions. It is suggested that in the chelated atom present in the ligands and there is π -electron delocalization over the acetelynic group . This is permeation through the lipoid layers of the bacterial membranes may also the possible reasons for increasing this activity[23].

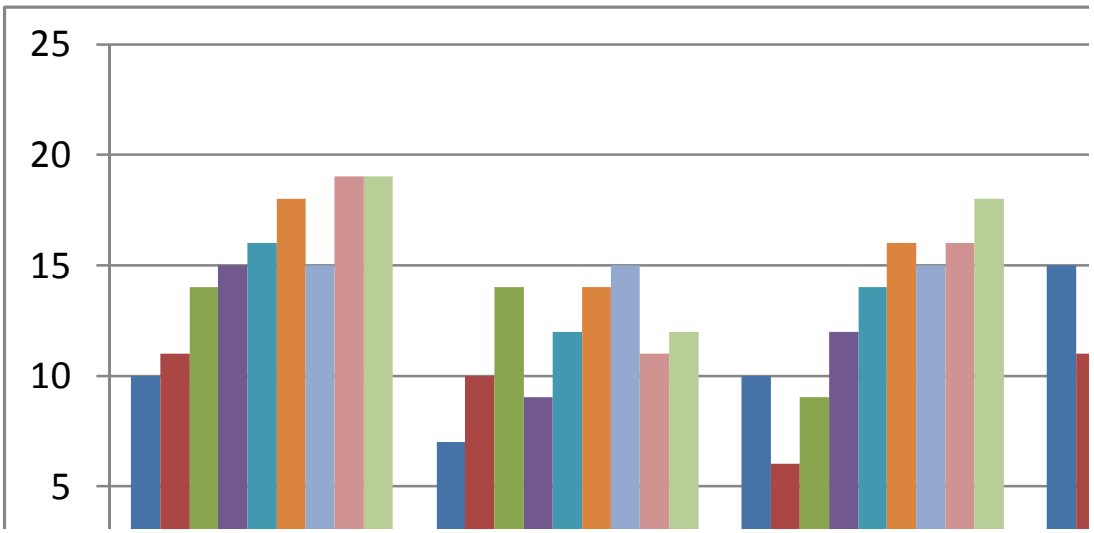


Fig (4): The effect of ligands and their metal complexes toward bacteria

Table (1): physical properties of the ligands (L_1,L_2, L_3)

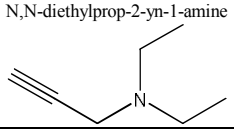
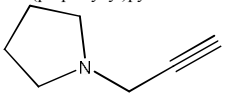
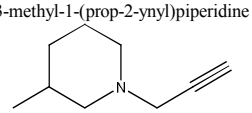
No.	Name and structure of compound	Yield %	Colour	M.P. °C picrate	Elemental analysis % found (% cal.)			Ir spectra cm^{-1}	Uv-Vis nm
					C	H	N		
L_1	N,N-diethylprop-2-yn-1-amine 	82	Pale yellow	109-111	40.70 (40.68)	3.70 (3.66)	17.28 (17.25)	υ(≡CH)3300, υ(C≡CH)2100, υ (CH)2950	311,382 In DMSO
L_2	1-(prop-2-ynyl)pyrrolidine 	70	Pale yellow	145-146	46.65 (46.75)	4.44 (4.52)	15.56 (16.21)	υ(≡CH)3300, υ(C≡CH)2100, υ (CH)2968	308,389 In DMSO
L_3	3-methyl-1-(prop-2-ynyl)piperidine 	90	Pale yellow	119-122	47.72 (47.69)	4.5 (4.45)	15.9 (15.87)	υ(≡CH)3310, υ(C≡CH)2110, υ (CH)2960	314,386 In DMSO

Table (2): Physical characterization ,analytical and Molar Conductance data of the compounds

Compound	Colour	ΔM/ S cm^2 mol^{-1}	M.P °C	Yield %	UV/VIS nm	Elemental analysis (% found) % cal	
						Cl	M
$[Zn(L_1)\ Cl_2]$	Pale yellow	19	181-183	50	299,374,386	(19.53) 19.55	(21.19) 21.23
$[Cd(L_1)\ Cl_2]$	creamy	17	175-177	55	286,373	(29.36) 29.39	(18.59) 18.63
$[Zn(L_2)\ Cl_2]$	Pale yellow	13	179-181	55	282,370,441	(19.77) 19.79	(21.46) 21.48
$[Cd(L_2)\ Cl_2]$	creamy	15	168-170	60	285,316,415	(29.67) 29.70	(18.79) 18.83
$[Zn(L_3)\ Cl_2]$	creamy	19	155-157	70	313,380,422	(17.25) 17.28	(18.74) 18.76
$[Cd(L_3)\ Cl_2]$	creamy	11	165-167	69	316,377,417	(26.31) 26.35	(16.67) 16.70

Table(3): IR and ^{1}H-NMR spectra data of the ligans and its complexes

Compound	^{1}H-NMR (DMSO-d_6) Chemical shifts in δ/ppm and (*J*=Hz)				IR spectra cm^{-1}
	(H) CH $^{a\ and\ g*}$	(2H) CH_2 ^{b}	(2H) CH_2 $^{c\ and\ d}$	(2H) CH_2 $^{e\ and\ f}$	

				(3H) CH_3 [h]	
L_1	2.65 (T,*J*=3.0)	3.87 (d,*J*=3.0)	2.41(q,*J*=8.0)	1.02 (T,*J*=8.0)	$\upsilon^{(C\equiv C)}$ 2100
L_2	2.65 (T,*J*=3.0)	3.87 (d,*J*=3.0)	2.51(q,*J*=7.1)	1.68 (q,*J*=7.1)	$\upsilon^{(C\equiv C)}$ 2100
L_3	2.65 (T,*J*=3.0) [1.67(m,*J*=6.8)]*	3.10 (d,*J*=3.0)	[2.41(q,*J*=7.0)]c [2.48(q,*J*=7.1)]d	[1.53 (m,*J*=7.0)]e [1.59 (m,*J*=7.1)]f [0.96 (d,*J*=6.8)]h	$\upsilon^{(C\equiv C)}$ 2110
$[Zn(L_1)\ Cl_2]$	2.72 (T,*J*=2.95)	3.88 (d,*J*=2.98)	2.45 (q,*J*=7.6)	1.02 (T,*J*=8.0)	$\upsilon^{(C\equiv C)}$ $1765_{(s)}$, $\upsilon^{(M-N)}$ $346_{(m)}$, $\upsilon^{(M-Cl)}$ $330_{(m)}$
$[Cd(L_1)\ Cl_2]$	2.75 (T,*J*=2.94)	3.90 (d,*J*=2.99)	2.47 (q,*J*=7.5)	1.02 (T,*J*=8.0)	$\upsilon^{(C\equiv C)}$ $1745_{(m)}$, $\upsilon^{(M-N)}$ $335_{(s)}$, $\upsilon^{(M-Cl)}$ $320_{(m)}$
$[Zn(L_2)\ Cl_2]$	2.73 (T,*J*=2.95)	3.91 (d,*J*=2.96)	2.60 (q,*J*=6.8)	1.68 (q,*J*=7.1)	$\upsilon^{(C\equiv C)}$ $1720_{(s)}$, $\upsilon^{(M-N)}$ $290_{(w)}$, $\upsilon^{(M-Cl)}$ $260_{(m)}$
$[Cd(L_2)\ Cl_2]$	2.70 (T,*J*=2.92)	3.92 (d,*J*=2.95)	2.59 (q,*J*=6.7)	1.68 (q,*J*=7.1)	$\upsilon^{(C\equiv C)}$ $1705_{(s)}$, $\upsilon^{(M-N)}$ $325_{(w)}$, $\upsilon^{(M-Cl)}$ $338_{(s)}$
$[Zn(L_3)\ Cl_2]$	2.77 (T,*J*=2.50) [1.67(m,*J*=6.8)]*	3.25(d,*J*=2.93)	[2.38(q,*J*=6.5)]c [2.58(q,*J*=6.6)]d	[1.53(m,*J*=7.0)]e [1.59(m,*J*=7.1)]f [0.96(d,*J*=6.8)]h	$\upsilon^{(C\equiv C)}$ $1725_{(s)}$, $\upsilon^{(M-N)}$ $300_{(w)}$, $\upsilon^{(M-Cl)}$ $295_{(s)}$
$[Cd(L_3)\ Cl_2]$	2.79(T,*J*=2.40) [1.67(m,*J*=6.8)]*	3.22(d,*J*=2.95)	[2.40(q,*J*=6.4)]c [2.60(q,*J*=6.5)]d	[1.53(m,*J*=7.0)]e [1.59(m,*J*=7.1)]f [0.96(d,*J*=6.8)]h	$\upsilon^{(C\equiv C)}$ $1720_{(s)}$, $\upsilon^{(M-N)}$ $349_{(s)}$, $\upsilon^{(M-Cl)}$ $330_{(w)}$

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