Synthesis, Spectroscopic and Theoretical Studies of Some New Transition Metal Complexes with Mixed ligands Schiff Base and Bipyridyl

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Abstract

The complexes Shiff base and mixed ligands complexes of bipyridyl and Schiff base 1,5-dimethyl-4-(5-oxohexan-2-ylideneamino)-2-phenyl-1H-pyrazol-3(2H)-one (L) with Cr(III), Mn(II), Fe(II) and Co(II) were prepared. The compounds have been characterized by FT-IR, UV-Vis, mass and ^{1}H and ^{13}C-NMR spectra, magnetic moment, elemental microanalyses (C.H.N.), chloride containing, atomic absorption and molar conductance. The studies made are indicating towards octahedral geometry for these complexes. Hyper Chem-8 program has been used to prediction structural geometries of compounds in gas state, the heat of formation, binding energy, total energy and electronic energy and dipole moment at 298^{o}K. The compounds were also screened for their bioactive to antibacterial and antifungal.

Key words: Complexes, Mixed ligands, Bipyrdayl, Bioactive.

Introduction

Schiff bases are a class of important compounds in medical and pharmaceutical field. They show biological activities including antibacterial, antifungal[1,2], anticancer and herbicidal activities[3].

The notion of mixed ligands complexes is always fascinating to the chemistry interest in synthesis because of their easiness of synthesis and generally less time requirement for using synthesized ligand and metal salt these reactions to happen than normal complex formation reaction. These formation have prompted many researchers to publish their research work in this wonderful and interesting area of study[4-6]. mixed ligand complexes play an important role in numerous biological and chemical systems such as water softening, ion exchange resin, drying, electroplating, photosynthesis in plants, antioxidant, removal of undesirable and harmful metals from living organisms. Much of these metal complexes exhibit good biological activity against pathogenic microorganisms[7-13]. bipyridyl and its derivatives are betwen the most more utilized class of ligands [14-51]. In report herein the synthesis and spectroscopic studies as well as the thermal realization of a new mixed ligands bipyridyl and Schiff base with some transition metals to Cr(III), Mn(II), Fe(II) and Co(II). The complexes were characterized by FT.IR, UV-Vis, mass spectra, magnetic moment, elemental microanalyses (C.H.N.), chloride containt, atomic absorption and molar conductance, were obtained to determine the structure of the complexes, theoretical and also studies of biological activeties.

Materials and Methods

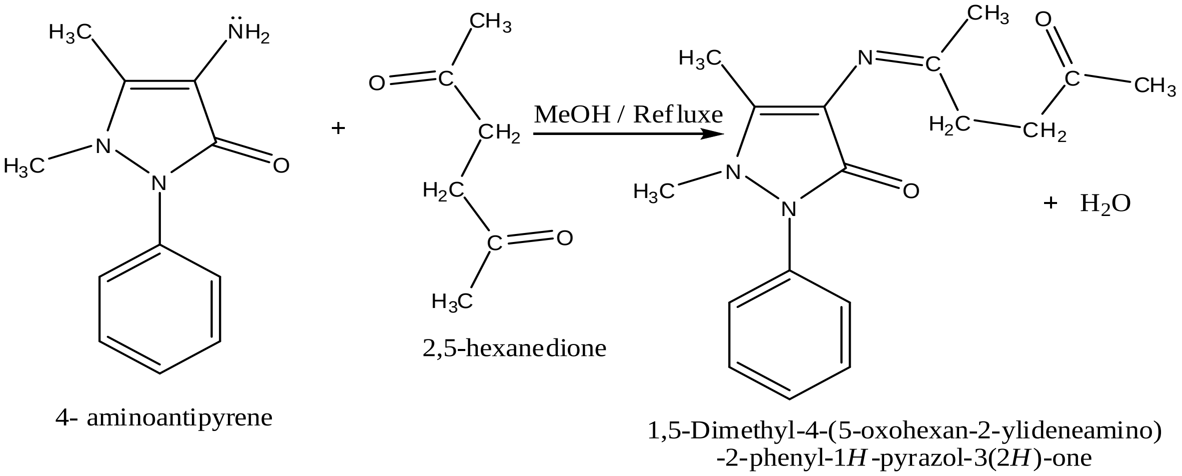
The following chemicals were commercially available and were used without further purification: (2,5-hexanedione, 4-aminoantpyrene, $FeCl_2.H_2O$, Aldrich)(diethyl ether, $CaCl_2$, bipyridyl, $CrCl_3.6H_2O$, BDH) (DMSO, pure ethanol, methanol, Fluka)($MnCl_2.4H_2O$ $CoCl_2.6H_2O$, Reedel).

FT-IR spectra were recorded in the range (4000-400) cm-1 on a Shimadzu 3800, spectrometer. Electronic absorption spectra were recorded in the range (200-900)nm for solution in Dimethyl sulfoxide (DMSO) (103-) on a Shimadzu 160 Spectrophotometer. 1H-13C NMR spectra were recorded using Bruker 400 MHz spectrometer Elemental (C.H.N) analyses were carried out on a Perkin-Elmer automatic equipment model 240.B. Mass spectra were obtained by using LC-Mass 100P Shimadzu. Melting points obtained on a Buchi SMP - 20 capillary melting point apparatus and are uncorrected. Metal ratio were identified using a Shimadzu (A.A) 680G Atomic Absorption Spectrometer. Conductivity measurements were measured for solution in DMSO(103-) using a Jenway 4071 digital conductivity meter in room temperature, Chloride ion content is specified by using potentiometric titration method at a 686-Titro processor – 665 Dosimat Metrohm Swiss. Magnetic properties were measured using (Magnetic susceptibility balance model MSR- MKI).

Study of Bioactivity: All the metal complexes,ligands and metal salts were screened against *staphylococcus aureus* (gram positive) and *Pseudomonas aeruginosa* (gram negative) bacteria as well fungi like *Penicillium expansum*, *Fusarium graminearum*, *Macrophomina phasealina*, and *Candida albicans*, by using the wall agar diffusion method. using solvent (DMSO), the concentration of the compounds by this exposure was (10-3 M) by using disc sensitivity inspection. This method involves the exposure of the zone inhibition toward the diffusion from micro-organism on agar plate. The plates were incubated for 24 and 48 hurs of bacteria and fungi respectively at 37 OC.

Synthesis of Schiff base Ligand: 1,5-Dimethyl-4-(5-oxohexan-2-ylideneamino)-2-phenyl-1H-pyrazol-3 (2H) -one.(16)

A solution of 4-aminoantpyrene (1 g, 4.92 mmol) in methanol (25 ml) was mixed with a solution of 2,5-hexanedione (0.56g, 4.92mmol). The reaction was stirred and heated at (40-50)°C for four hrs. A colorless precipitated formed which was washed with diethyl ether and recrystallized from ethanol: water (1:1) mixture. The product was dried via anhydrous $CaCl_2$ in vacuum as shown in Scheme (1). The yield is (1.38g), 93.66%, mp.179°C.



Scheme (1)

Synthesis of Schiff base Complexes

A solution of Schiff base ligand (0.25g, 0.836 mmole) in methanol was added gradually with stirring to 0.105g, 0.222g, 0.165g 0.198g respectively, of $FeCl_2.H_2O$, $CrCl_3.6H_2O$, $MnCl_2.4H_2O$ and $CoCl_2.6H_2O$, respectively. The reaction mixture was allowed to reflux and the solid wase collected by filtration recrystallized from ethanol and dried in labortory temperature. Microelemental analysis data, yiled and color at the compounds are given in Table(1).

Synthesis of Mixed Ligands Complexes

A solution of the Schiff base ligand (0.25g, 0.836 mmole)in methanol was added gradually with stirring to the 0.105g, 0.222g, 0.165g 0.198g respectively, of $FeCl_2.H_2O$, $CrCl_3.6H_2O$, $MnCl_2.4H_2O$ and $CoCl_2.6H_2O$, respectively.It was added to the mixture gradually while stirring (0.13g,0.836mmol)of bipyrdayl dissolved in (10)cm^3 methanol, The reaction mixture was allowed to reflux and the solids were collected by filtration recrystallized from ethanol and dried in room temperature. Microelemental analysis data, color and yield for the compounds are given in Table (1).

Programs used in theoretical calculation

Hyper Chem-8 program is a sophisticated molecular modeler, editor and powerful computational pack that are known for its type, flexibility and ease of use. It is also uniting 3D visualization and animation with quantum chemical calculations, molecular mechanics and dynamics. at the present work, parameterization method (PM3) was used for the calculation of heat of binding energy and formation for all metal complexes. PM3 is more popular than last semi empirical method due to the availability of algorithms and it is more accurate than last method .PM3 / TM is an extension of the PM3 method to include orbital's with transition metals[17].

Results and Discussion

The LC-Mass for ligand (Schiff base) (299.3m/ z) with ($C_{17}H_{21}N_3O_2$), (244.2 m/ z) with ($C_{14}H_{18}N_3O$), (243.3m/ z) with ($C_{14}H_{17}N_3O$) and (144.2m/ z) with ($C_6H_{14}N_3O$). ^{1}H-NMR (DMSO-d_6, ppm): δ 2.044 (s,3H, N=C-CH_3), 2.147 (s,3H, O=C-CH_3), 3.11 (s, 3H, C=C-CH_3), 3.31 (s,3H, N-CH_3), 5.88 (tri, 4H, CH_2-CH_2), 7.282-7.513 (m, 5H, Ar-H). ^{13}C-NMR (100.622 MHz, DMSO-d_6): δ 162.22 (C_{16}), 153.25 (C_{12}), 134.67 (C_4), 129 ($C_{2,\ 6}$), 127 ($C_{8,\ 10}$), 124.31 (C_9), 109.83 (C_{11}), 105.95(C_7), 77.25($C_{5,\ 15}$), 76.93(C_3), 50.41(C_{17}), 36.09 (C_4), 12.5 (C_{13}), 10.62 (C_1), shown the Figure (1).

Molar conductance values in (DMSO) solution (10-3M) were found in the range (12-23) S. cm2 mol-1for all complexes Cr(III), Mn(II), Fe(II) and Co(II) which indicates that they are non-electrolytes, except that of Cr(III) mixed ligand complex with bipyrdyl (43) S. cm^2. mol^{-1} which refers to electrolyte nature (1:1) [18,19]. Physical properties and elemental microanalysis in are listed in Table(1).

Mass spectra for complexes

High resolution mass spectra of the [$Mn(L)Cl_2(H_2O)_2$], [$Co(L)Cl_2(H_2O)_2$] and mixed ligands [$Cr(L)(bipy)Cl_2$]Cl , [$MnL(bipy)Cl_2$] and [$FeL(bipy)Cl_2$] complexes, Shous parent ion peak m/z=461.3(M), 465.2(M), 614.3(M), 581.3(M), 571.4(M) respectively[19]. Further details for the fragmentation and their relative abunduance for each compound are given in Table(2).

IR spectra

1.Infrared Spectra from Free Ligands

The spectrum of ligands(L) and bipy exhibited weak bands at 3035 and 3055 cm^{-1}, this could be attributed to ν(C-H) aromatic respectively. Other strong bands belong to the ν(C=N) were found at 1640 and 1617 cm^{-1} respectively. The spectrum of ligand L, was noticed band at exhibited two bands 1740 and 1696 cm^{-1} which lwere attributed to ν(C=O)ring of pyrazol and ν(C=O) respectively.

2.Infrared Spectra Complexes

The infrared spectra from the prepared complexes exhibited ν(C=N) at the range from 1616-1626cm^{-1} which exhibited a shifting to the lower frequencies 16-18 cm^{-1} comparison with ligand (L), also appeared shifting to the higher frequencies among 9-7 cm^{-1} comparison with ligand (bipy), whose indicated the coordination from ligands with metal ions through the nitrogen atoms by their structures. The spectra of complexes showed bands in the range of 1670-1678cm-1 were differentiate for the carbonyl group which suffer a shift. So, it is suggested that the oxygen atom of the carbonyl group is coordinated with the metal ion [11]. the spectra of complexes showed bands at (487-548) cm^{-1} referred to the ν(M-N) and in the range of (412-490)cm^{-1} which was attributed to the of ν(M-O) [20-22]. This indicates that the ligand was coordinated with the metal ions through O carbonyl groups and N azomethine group. The IR-spectral data for the ligands and prepared complexes were listed in Table(3)

UV–Vis Spectra, Magnetic Moments

The electronic spectrum from the ligands of Schiff base and bipy exhibit intense absorption in (282,280)nm attributed to $\pi\rightarrow\pi^*$ respectively. Cr(III) Complexes [$Cr(L)Cl_3$ (H_2O)] and [$Cr(L)Cl_2(bipy)$]Cl gave two absorptions at (287, 299nm) assigned to ligand field respectively. The electronic spectrum of [$Cr(L)Cl_3(H_2O)$] complex showed three broad peaks at 493, 601 and 668 nm assigned to(d-d) transition type $^4A_{2g} \rightarrow {}^4T_{1g\ (p)}$, $^4A_{2g} \rightarrow {}^4T_{1g\ (F)}$, $^4A_{2g} \rightarrow {}^4T_{2g\ (f)}$ respectively and the given peak at 361 nm due for charge transfer (C.T). The electronic spectrum of [$Cr(L)Cl_2(bipy)$]Cl complex showed three broad peaks at 487,640 and 752nm assigned to(d-d) transition type $^{4}A_{2}g\rightarrow{}^{4}T_{1}g_{(P)}$,$^{4}A_{2}g\rightarrow{}^{4}T_{1}g_{(F)}$,$^{4}A_{2}g\rightarrow{}^{4}T_{2}g_{(F)}$ respectively and a peak at 414 nm due to charge transfer (C.T). Mn(II) Complexes [Mn(L)$Cl_2(H_2O)_2$] and[MnL(bipy)Cl_2] gave absorptions at (293, 293nm) assigned to ligand field respectively. The electronic spectrum of [MnL$Cl_2(H_2O)_2$] complex showed two broad peaks at 429 and 488 nm assigned to (d-d) transition type $^{6}A_{1g}\rightarrow{}^{4}A_{1g},{}^{4}E_{g(4G)}$, $^{6}A_{1g}\rightarrow{}^{4}T_{2g(4G)}$ respectively. The electronic spectrum of [MnL(bipy)Cl_2] complex showed two broad peaks at 498 and 632nm assigned to(d-d) transition type $^{6}A_{1g}\rightarrow{}^{4}A_{1g},{}^{4}E_{g(4G)}$, $^{6}A_{1g}\rightarrow{}^{4}T_{2g(4G)}$ respectively and apeak at 428 nm due to charge transfer(C.T). Fe(II) Complexes [Fe(L) $Cl_2(H_2O)_2$] and [Fe(L)Cl_2(bipy)] gave absorptions at (279, 282,348nm) assigned to ligand field respectively. the electronic spectrum of [Fe(L)$Cl_2(H_2O)_2$] complex showed one broad peak at 481 nm assigned to(d-d) transition type $^{5}T_{2}g_{(D)}\rightarrow{}^{5}E_{1}g_{(D)}$ and two peaks at (359, 438nm) due to charge transfer (C.T). [Fe(L)Cl_2(bipy)] complexes showed one broad peak at 489nm assigned to $^{5}T_{2}g_{(D)}\rightarrow{}^{5}E_{1}g_{(D)}$ and one peak at 436nm due to charge transfer (C.T). Co(II) complexes [Co(L)$Cl_2(H_2O)_2$] and [Co(L)Cl_2(bipy)] gave two absorptions at (280, 298nm) assigned to ligand field respectively. the spectrum of [Co(L)$Cl_2(H_2O)_2$] complex showed three broad peaks at 611, 652 and 664 nm assigned to(d-d) transition type $^{4}T_{1g(F)}\rightarrow{}^{4}T_{1g(p)}$,$^{4}T_{1g(F)}\rightarrow{}^{4}A_{2g(F)}$ to$^{4}T_{1}g_{(F)}\rightarrow{}^{4}T_{2}g_{(f)}$,transition respectively and two peaks at 414 and 488nm due to charge transfer (C.T). The spectrum of [Co(L)Cl_2(bipy)] complex showed three broad peaks at 621,669 and 760nm assigned to(d-d) transition type $^{4}T_{1g(F)}\rightarrow{}^{4}T_{1g(p)}$,$^{4}T_{1g(F)}\rightarrow{}^{4}A_{2g(F)}$, $^{4}T_{1g(F)}\rightarrow{}^{4}T_{2g(f)}$ transition respectively. The (d-d) electronic transition for all prepared complexes were in a good agreement for octahedral geometry around Cr(III), Mn(II), Fe(II) and Co(II) central ion. The magnetic moment value (3.78, 3.79), (5.93, 5.81), (4.91, 5.00) and (3.70, 3.65) B.M. of Cr(III) (d^3) Mn(II) (d^5), Fe(II) (d^6) and Co(II) (d^7) complexes respectively are typical for octahedral geometry [22-24]. All these electronic spectra data can be shown in Table (4).

Electrostatic Potentials

Electron distribution governs the electrostatic potential of the molecules. The electrostatic potential (E.P) term the interaction of energy from the molecular system with a positive point charge. (E.P) is helpful at finding sites of reaction in a molecule; positively charged species tend to attack a molecule where the electro static potential is strongly negative (electrophonic attack) [17]. The (E.P) of the free ligand was calculated and shape as 2D contour to investigate the reactive sites from the molecules show in Figure (3). Also one can interpret the stereo chemistry and rates of many reactions involving “soft” electrophiles and nucleophiles on terms from the properties of frontier orbital HOMO and LUMO. The results of calculations show that the LUMO of transition metal ions prefer to reaction with the HOMO of two-donor atoms of oxygen carbonyl and nitrogen from azomethen group at free ligands [25], Figure (2).

All theoretically probable structures of free ligand and their complexes have been calculated through (PM3) and (ZINDO/1) methods in gas state to search for the most probable model building stable structure. Calculation from parameters has been optimized bond lengths of the free ligand and metal complexes which to give excellent agreement with the experimental data as shown in Table (5).

Antimicrobial activity of ligands and all complexes

Bipyridyl, schiff base, metal salts and their complexes of transition metals were screened for antibacterial and antifungal activity. The entire tested compound exhibited variable activity antifungal and antibacterial as shown in figures (4 and 5).

Schiff base activity exhibited antibacterial against *S. aureus* and *P.aeruginosa* but activity was to be lower than the metal complexes and salts metals. bipy also exhibited activity antibacterial against *S. aureus* and *P.aeruginosa* but activity high in complexes and metal salts as shown in, Figure (4). schiff base which did not exhibit have antifungal activity but exhibited activity was in some metal complexes and salts metals as shown in, Figure (4). Where exhibited CrL and CoL Complex activity lower compared with salts of Cr and Co against *P.expansum* and *F. graminearum*. While the bipy and some salts metals exhibiting antifungal strong activity against *P.expansum* and *C. albicans*, by not exhibited antifungal activity against *F.graminearum* and *M. phaseolina* as compared with the antimicrobial activity with some mixed ligand metal complexes which exhibited antifungal activity top than ligands as shown in(5). exhibited some complexes Prepared antifungal activity strong against *F.graminearum* and *M. phaseolina* as compared with the ligands which did not exhibite antimicrobial activity. from the data shown in the Table (6) and Figures (6,7,8,9 and 10) alot of compounds exhibited bio activety againts 2 kinds of bacteria and 4 kinds of fungal.

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Table (1):Micro element of analysis and some physical properties of the ligands and its complexes

Sample Formula	M. wt. Yield%	Color m. p °C	Molar conductance S. cm^2. mol^{-1}	Element analysis % Calcu (Found)				
				C	H	N	M	Cl
L	299.37	Colorless	-	68.20	7.07	14.04	-	-
$C_{17}H_{21}N_3O_2$	89	179		68.95	6.68	14.44	-	-
bipy	156.18	White	-	-	-	-	-	-
$C_{10}H_8N_2$		70		-	-	-	-	-
CrL	475.74	reddish brown	19	(43.16)	(5.13)	(9.13)	(11.04)	(22.05)
$C_{17}H_{23}N_3O_3CrCl_3$	82	122		42.92	4.87	8.83	10.93	22.36
MnL	461.24	Yellow	12	(44.72)	(4.86)	(10.01)	(12.03)	(16.03)
$C_{17}H_{25}N_3O_4MnCl_2$	87	145		44.27	5.46	9.11	11.91	15.37
FeL	462.15	reddish brown	20	(43.92)	(4.87)	(9.13)	(12.87)	(16.04)
$C_{17}H_{25}N_3O_4FeCl_2$	75	228		44.18	5.45	9.09	12.08	15.34
CoL	465.24	Green	13	(44.05)	(4.98)	(9.16)	(13.13)	(15.24)
$C_{17}H_{25}N_3O4CoCl_2$	77	185d		43.89	5.42	9.03	12.67	15.54
CrL+bipy	613.91	Orange	43	(53.13)	(5.11)	(11.44)	(9.13)	(16.18)
$C_{27}H_{29}N_5O_2CrCl_3$	79	165		52.82	4.76	11.14	8.47	17.32
MnL+bipy	581.4	Yellow	23	(55.10)	(4.85)	(12.78)	(10.01)	(11.76)
$C_{27}H_{29}N_5O_2MnCl_2$	78	161d		55.78	5.03	12.05	9.45	12.20
FeL+bipy	582.30	Red	21	(56.03)	(4.93)	(11.75)	(10.18)	(12.88)
$C_{27}H_{29}N_5O_2FeCl_2$	79	159		55.69	5.02	12.03	9.59	12.18
CoL+bipy	585.39	Green	18	(55.11)	(5.15)	(12.24)	(10.28)	(11.95)
$C_{27}H_{29}N_5O_2CoCl_2$	76	163		55.87	5.03	11.96	10.07	12.11

Table (2) :The Fragmentation pattern data for complexes

complexes	Assignment	Peak m/z	Relative abundance%
[MnL Cl_2 $(H_2O)_2$]	M= ($C_{17}H_{25}N_3O_4MnCl_2$)	461.3	81%
	M- $C_6H_{10}O$ Mn = M_1	308.2	24%
	M_1- CH_{10}= M_2	287.2	17%
	M_2-H = M_3	286.2	57%
	M_3- C_2H_4N	244.2	16%
[$CoLCl_2(H_2O)_2$]	M= ($C_{17}H_{25}N_3O_4CoCl_2$)	465.2	83%
	M- $C_5H_6O_2$ Co = M_1	308.2	24%
	M_1- C_1H_9= M_2	287.2	14%
	M_2- H = M_3	286.2	56%
	M_3- C_3H_6	244.2	16%
[CrL(bipy)Cl_2]Cl	M= ($C_{27}H_{29}N_5O_2CrCl_3$)	614.3	82%
	M- $C_6H_3N_2$= M_1	511.3	9%
	M_1-$C_9H_{11}O_2Cr$ = M_2	308.2	24%
	M_2-CH_9 = M_3	287.2	17%
	M_3-H = M_4	286.2	57%
	M_4- C_2H_4N	244.2	16%
[MnL(bipy)Cl_2]	M= ($C_{27}H_{29}N_5O_2MnCl_2$)	581.3	82%
	M- $C_2H_4N_3$= M_1	511.3	9%
	M_1-$C_8H_6NO_2Mn$ = M_2	308.2	24%
	M_2-CH_9 = M_3	287.2	17%
	M_3-H = M_4	286.2	57%
	M_4-C_2H_4N = M_5	244.2	16%
	M_5-C_3H_3 = M_6	205.2	13%
	M_6-H	204.2	98%
[FeL(bipy)Cl_2]	M-C = M_1	571.4	14%
	M_1-CH_4N_2O = M_2	511.3	9%
	M_2-C_8H_4OFeCl = M_3	308.2	24%
	M_3-CH_9 = M_4	287.2	7%
	M_4-H = M_5	286.2	87%
	M_5-C_2H_4N = M_6	244.2	16%
	M_6-C_3H_3 = M_7	205.2	14%
	M_7- H	204.2	98%

Table (3): The Infrared spectra data of the free ligand and its metal complexes in(cm^{1})

Comp.	υC-H aliph.	υC-H arom.	υC=O ring	υC=O	υC=N	υC=N rang	υH_2O	υM-N	υM-O
L	-	3035	1740	1696	1640	-	-	-	-
bipy	-	3055	-	-	1617	-	-	-	-
CrL	2916	3063	1736	1670	1623	-	3422-867	548	470 455
MnL	2916	3036	1736	1674	1624	-	3429-887	532	490 416
FeL	2916	3063	1730	1670	1616	-	3422-867	548	455 470
CoL	2916	3033	1734	1672	1622	-	3422-887	487	422 412
CrL+bipy	2915	3076	1741	1675	1626	1582	-	544 489	476 420
MnL+bipy	2915	3076	1743	1675	1626	1578	-	544 498	476 420
FeL+bipy	2912	3070	1741	1678	1624	1581	-	544 498	471 420
CoL+bipy	2915	3073	1746	1673	1623	1580	-	544 594	474 425

Table (4): Electronic spectral data and magnetic moments of the prepared compounds.

Compound Geometry	μ_{eff} B.M	ύ (cm^{-1})	ABS	λ_{max} (nm)	ε_{max} L $mol^{-1}cm^{-1}$	Assignments
L	-	35460.99	2.48	282	24800	$\pi \rightarrow \pi^*$
bipy	-	35714.2	-	280	-	$\pi \rightarrow \pi^*$
$[Cr(L)Cl_3(H_2O)]$	3.78	34843.2	2.005	287	2005	L.F
Octahedral		27700.8	0.632	361	632	C.T
		20283.9	0.506	493	506	$^4A_{2g} \rightarrow {}^4T_{1g\ (P)}$
		16638.9	0.265	601	265	$^4A_{2g} \rightarrow {}^4T_{1g\ (F)}$
		14970.0	0.154	668	154	$^4A_{2g} \rightarrow {}^4T_{2g\ (F)}$
$[Mn (L)Cl_2(H_2O)_2]$	5.93	34129.6	2.114	293	2114	L.F
Octahedral		23310.0	0.138	429	138	$^6A_{1g} \rightarrow {}^4A_{1g}, {}^4E_{g(4G)}$
		20491.8	0,187	488	187	$^6A_{1g} \rightarrow {}^4T_{2g(4G)}$
$[Fe(L)Cl_2(H_2O)_2]$	4.91	35842.2	1.967	279	1967	L.F
Octahedral		27855.1	0.689	359	689	C.T
		228031.	0.333	438	333	C.T
		20790.0	0.373	481	373	$^5T_2g_{(D)} \rightarrow {}^5E_1g_{(D)}$
$[Co(L)Cl_2(H_2O)_2]$	3.70	35714.2	2.034	280	2034	L.F
Octahedral		24154.5	0.339	414	339	C.T
		20491.8	0.568	488	568	C.T
		16366.6	0.125	611	125	$^4T_{1g(F)} \rightarrow {}^4T_{1g(p)}$
		15337.4	0.106	652	106	$^4T_{1g(F)} \rightarrow {}^4A_{2g(F)}$
		15060.2	0.110	664	110	$^4T_{1g(F)} \rightarrow {}^4T_{2g(F)}$
$[Cr(L)Cl_2(bipy)]Cl$	3.79	33444.8	2.386	299	2386	L.F
Octahedral		24154.4	0.334	414	334	C.T
		20533.8	0.670	487	670	$^4A_{2g} \rightarrow {}^4T_{1g(p)}$
		15625.0	0.052	640	52	$^4A_2g \rightarrow {}^3T_1g_{(F)}$
		13297.8	0.043	752	43	$^4A_2g \rightarrow {}^3T_2g_{(F)}$
$[Mn(L)Cl_2(bipy)]$	5.81	34129.6	2.114	293	2114	L.F
Octahedral		23364.4	0.861	428	861	C.T
		20080.3	0.710	498	710	$^6A_{1g} \rightarrow {}^4A_{1g}, {}^4E_{g(4G)}$
		15822.7	0.072	632	72	$^6A_{1g} \rightarrow {}^4T_{2g(4G)}$
$[Fe(L)Cl_2(bipy)]$	5.00	34965.0	2.051	282	2051	L.F
Octahedral		28735.6	0.521	348	521	L.F
		22935.7	0.201	201	436	C.T
		20449.8	0.291	489	291	$^5T_2g_{(D)} \rightarrow {}^5E_1g_{(D)}$
$[Co(L)Cl_2(bipy)]$	3.65	33557.0	2.312	298	2312	L.F
Octahedral		16103.0	0.114	621	114	$^4T_{1g(F)} \rightarrow {}^4T_{1g(p)}$
		14947.6	0.147	669	147	$^4T_{1g(F)} \rightarrow {}^4A_{2g(F)}$
		13157.8	0.056	760	56	$^4T_{1g(F)} \rightarrow {}^4T_{2g(F)}$

Table (5): Conformation energetic in (K $J.Mol^{-1}$) for the ligands and complexes

Comp.	Total energy	Binding energy	Heat of formation	Electronic energy	Dipole Debyes
L	-78659.2647	-4472.7426	-15.35266	-600793.517	3.160
bipy	-37068.2314542	-1736.1966222	615.5193778	-201757.1026775	0.010
CrL	-113536.5548061	-4632.6657591	170.4572409	-962898.8007352	7.548
MnL	-116948.6270148	-4784.8350078	125.7609922	-1002483.2873625	9.225
FeL	-119947.9356997	-4672.8458167	269.3501833	-1038227.9787860	5.503
CoL	-126215.8958556	-5008.8710646	-63.5750646	-1059178.1703876	6.392
CrL+bipy	-136611.2137034	-6919.4704874	42.6155126	-1496731.4119088	2.401
MnL+bipy	-139955.0160289	-7010.1267259	-75.3407259	-1524685.6060488	2.163
FeL+bipy	-142965.9951884	-6909.8080094	56.5779906	-1547982.6779546	2.534
CoL+bipy	-148920.3131448	-6932.1910578	37.2949422	-1565519.7816116	3.661

Table (6): Antibacterial and antifungal activities for ligands, metal Salts and complexes.

no	Compound	*Staphylococcus aureus G(+)*		*Pseudomonas aeruginosa G(-)*		*Penicillium expansum*		*Fusarium graminearum*		*Macrophomina phaseolina*		*Candida albicans*	
		A	B	A	B	A	B	A	B	A	B	A	B
1	bipy	35	32	35	32	46	36	—	—	—	—	***	***
3	$CrCl_3.6H_2O$	15	12	16	15	38	28	38	33	—	—	—	—
4	$CoCl_2.6H_2O$	40	25	23	18	30	18	26	15	—	—	20	10
5	$MnCl_2.4H_2O$	40	18	20	14	—	—	—	—	—	—	—	—
6	$FeCl_2.\ H_2O$	30	12	15	—	—	—	—	—	—	—	—	—
7	L	12	—	12	—	—	—	—	—	—	—	—	—
8	MnL	20	—	12	—	—	—	—	—	—	—	—	—
9	CrL	16	—	15	—	20	18	28	22	24	16	—	—
10	CoL	20	—	15	—	13	—	—	—	25	16	—	—
11	FeL	12	—	10	—	—	—	—	—	—	—	—	—
12	FeL+bipy	24	—	14	10	—	—	—	—	20	15	—	—
13	CrL+bipy	18	—	20	18	23	20	—	—	25	15	—	—
14	CoL+bipy	20	12	14	12	—	—	—	—	25	14	—	—
15	MnL+bipy	24	—	20	15	12	—	12	—	24	20	12	8
20	Con.	0	0	0	0	0	0	0	0	0	0	0	0
***= highly active, A=conc., B=dilu.													

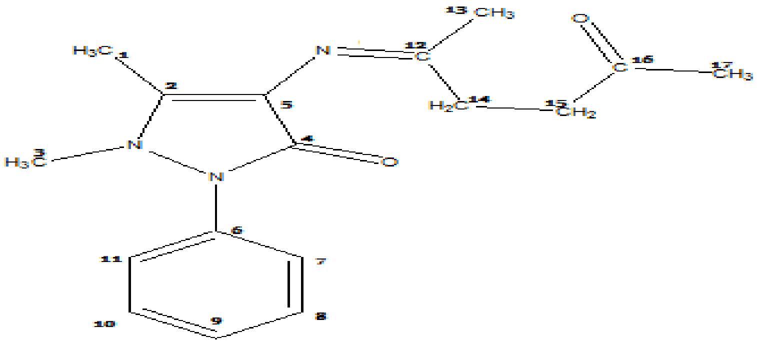
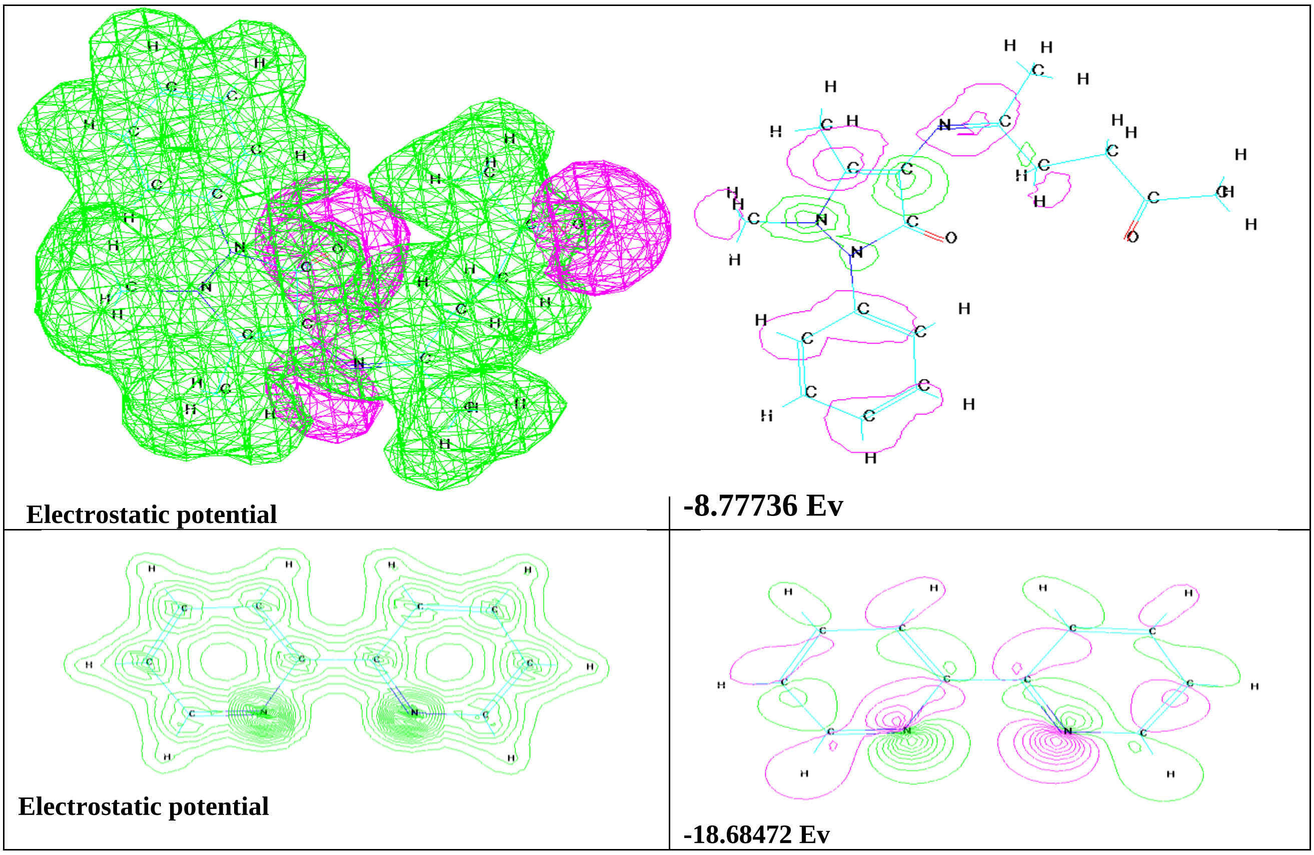


Figure (1): Structure of Schiff base Ligand



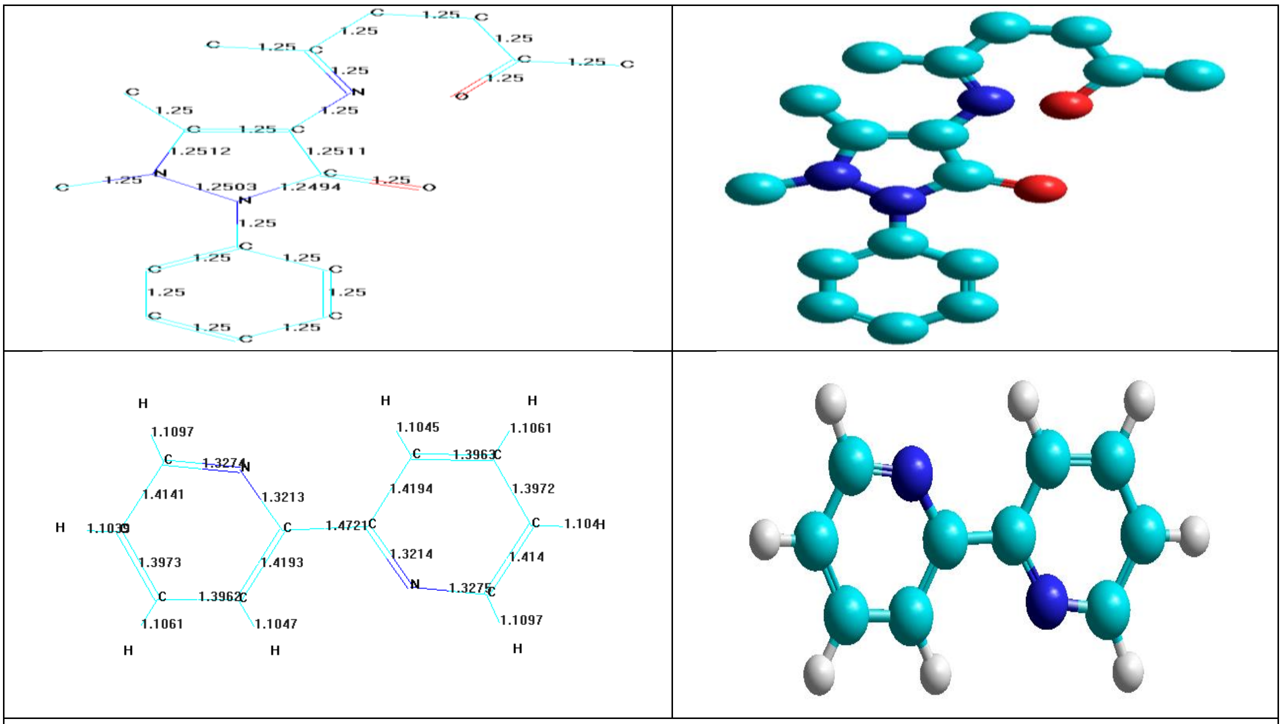
Electrostatic potential

-8.77736 Ev

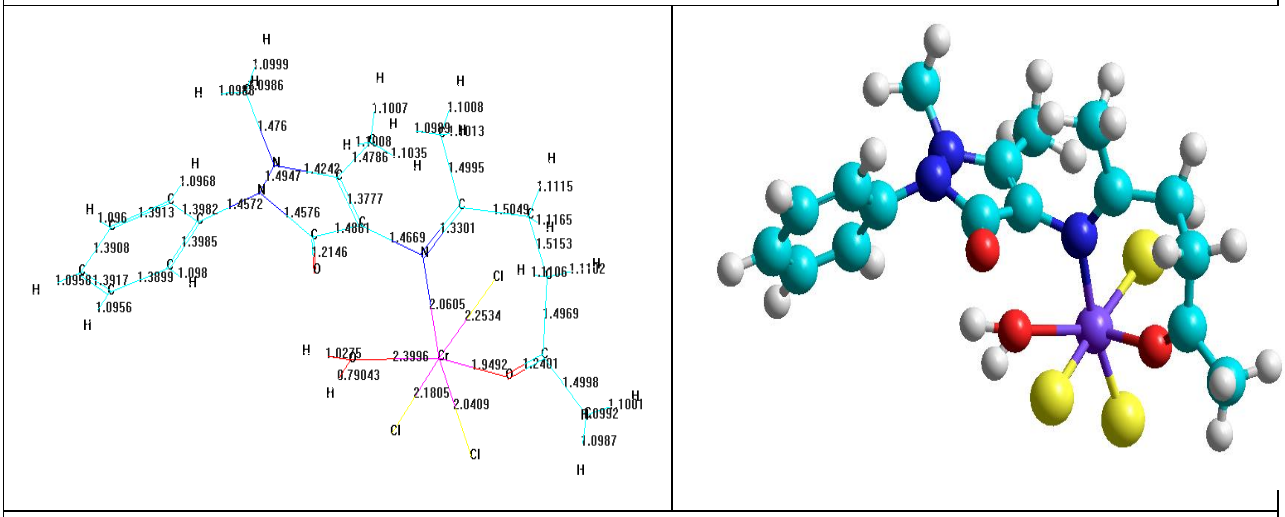
Electrostatic potential

-18.68472 Ev

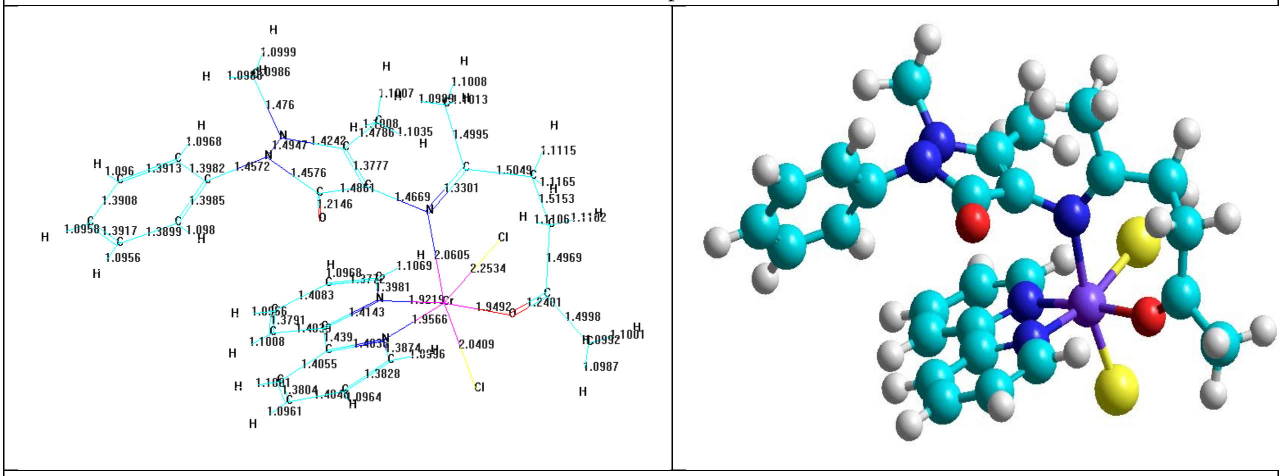
Figure (2): Electrostatic potential (HOMO and LUMO) contours for ligands



Schiff base and Bipy



CrL Complex



CrL+bipy

Figure (3):Bond length and 3D-structure for ligands and complexes

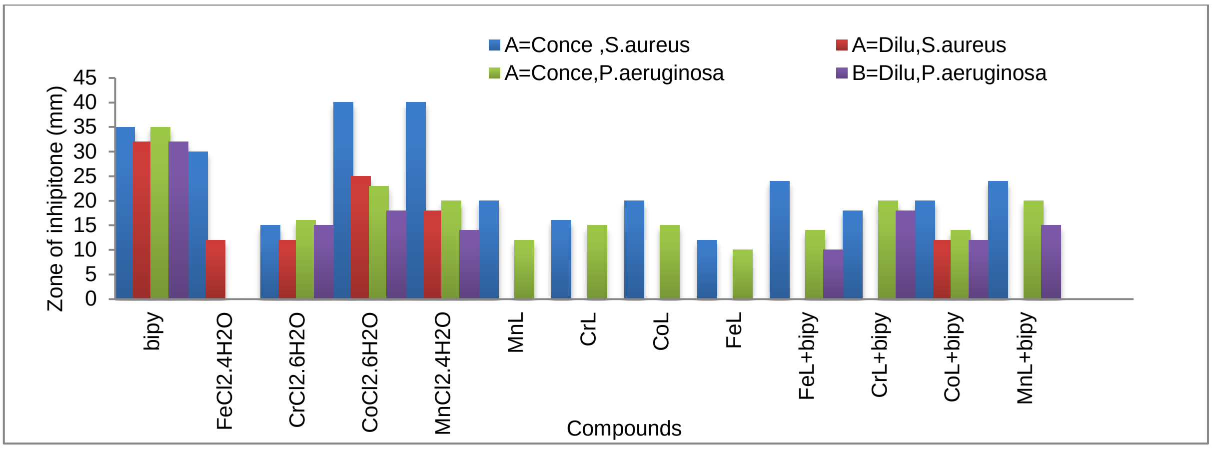


Figure (4):The antibacterial activity of compounds against *S. aureus* and *P.aeruginosa*

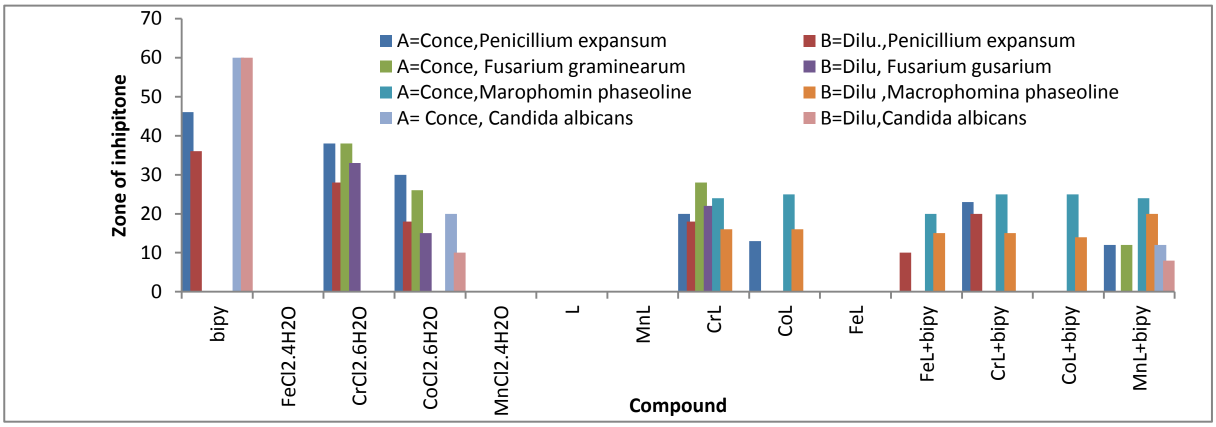


Figure (5):The antibacterial activity of compounds against *P.expansum, F.graminearum,*

Figure (6):Effect of the ligands complexes towards the *Staphylococcus aureus* and *Pseudomonas aeruginosa* .

Figure (7): Effect of the ligands and complexes towards the *Penicillium expansum*

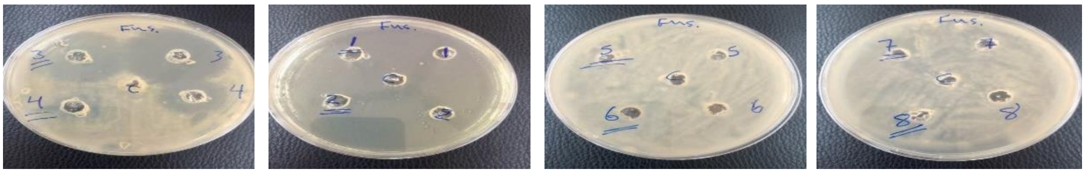


Figure (8): Effect of the ligands and complexes towards the *Fusarium graminearum*

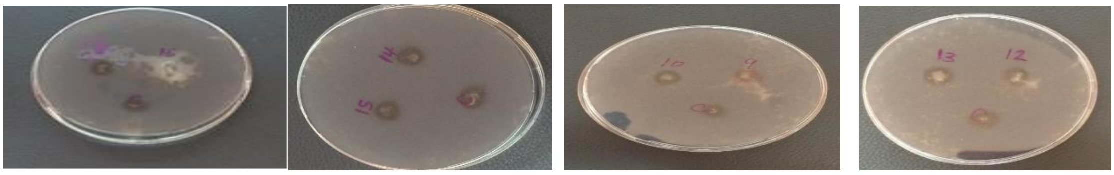


Figure (9): Effect of the ligands and complexes towards the *Macrophomina phaseolina*

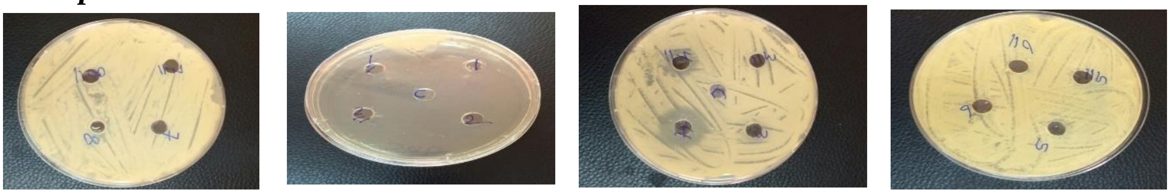


Figure (10):Effect of the ligands and complexes towards the *Candida albican*.