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Preparation, Diagnosis, Thermodynamic and Biological Studies of New Complexes Derived from Heterocyclic Ligand

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ABSTRACT
The ligand Schiff base [(E)-3-(2-hydroxy-5-methylbenzylideneamino)- 1-phenyl-1H-pyrazol-5(4H) –one] with some metals ion as Mn(II); Co(II); Ni(II); Cu(II); Cd(II) and Hg(II) complexes have been preparation and characterized on the basic of mass spectrum for L, elemental analyses, FTIR, electronic spectral, magnetic susceptibility, molar conductivity measurement and functions thermodynamic data study (ΔH°, ΔS° and ΔG°). Results of conductivity indicated that all complexes were non electrolytes. Spectroscopy and other analytical studies reveal distorted octahedral geometry for all complexes. The antibacterial activity of the ligand and preparers metal complexes was also studied against gram and negative bacteria.

Keyword: Elemental Analyses, Antibacterial, Schiff Base, Thermodynamic Data.

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INTRODUCTION

The ligand (Schiff base) prepared from carboxylic compounds and primary amines were first reported by chemist Hugo Schiff [1-3]. Element ions have played an important role in the biological system for the past years. Metal ions can be introduced into a biological system for therapeutic or diagnostic purposes, although these purposes may overlap in many cases. Minerals not only provide a way to synthesize, but also introduce functions that enhance drug action [4-6]. Salicylaldehyde has an important role; it is considered a substance that has multiple commercial and chelating uses in addition to being considered as a precursor to the preparation of other chemicals [7]. Tin(IV) complexes were prepared from 2-hydroxy-5-methylbenzaldehyde, diagnosed by X-ray technique to find out their crystalline structure in addition to toxicological activity [8]. The Ga(III) complexes were prepared from the derivative of N-Salicylidene- o- aminophenol. The three complexes were diagnosed by infrared and X-ray, where the results showed that it is the octahedral shape of the [9]. Metal-Schiff base complexes Ni (II), Pd(II) and Zn(II) with ligands Schiff bases derived from 2-hydroxyl-5-methylbenzaldehyde [10]. In this study, six complexes were prepared from the interaction of some metallic ions with a ligand derived from a heterogeneous cycle, and the study of new compounds by spectral methods and biological activity, and then a study of the thermodynamic functions for them.

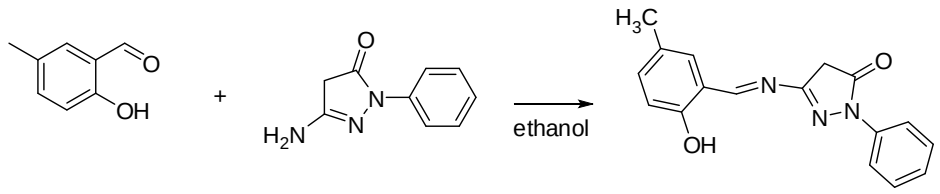
EXPERIMENTAL

Materials and Methods

Chemicals used in the laboratory, are the highest purity that does not need any further purity, and they have been purchased from distinguished sources. The device used to measure the melting point is by Stuart Melting Point Kit; the CHN for all compounds is measured by Euro (EA 3000); ultra Violet-Visible spectra are performed on a Shimadzu UV- 160A; the FTIR spectra are verified via FTIR - 8400S Spectrophotometer on 4000-400 cm^{-1}in KBr discs; atomic absorption method by means of AA 620G Shimadzu spectrophotometer; magnetic sensitivity was measured using a Faraday's method using Bruker BM6 instrument.

Synthesis of Ligand

A solution of 2-hydroxy-5-methylbenzaldehyde (0.136g ,1mol) in 10 ml ethanol has been inserted to a mixture solution of [3-amino-1-phenyl-1H-pyrazol-5(4H)-one] (0.175g, 1 mol) in 5ml ethanol and three drops of glacial acetic acid, the product combination has been refluxed for 4h. The resulted orange solid is composed by filtration, recrystallization from acetone absolute, and dried.



2-Hydroxy-5-methylbenzaldehyde **3-amino-1-phenyl-1*H*-pyrazol-5(4*H*)-one** **(*E*)-3-(2-hydroxy-5-methylbenzylideneamino)-1-phenyl-1*H*-pyrazol-5(4*H*)-one (L)**

Scheme 1: The preparation of ligand Schiff base

Preparation of Complexes

A solution of ligand (0.586g, 2mmol) in 10ml absolute ethanol, was added with stirred to a solution consisting of 10 ml ethanol and (0.126g Mn(II) chloride, 0.237g Co(II) chlorid.$6H_2O$, 0.237g Ni(II) chloride.$6H_2O$, 0.17Cu(II) chlorid.$2H_2O$, 0.201g Cd(II) chlorid.H_2O, and 0.272 g

Hg(II) chloride). The product mixture is stirred for sixty minutes and, then, the result is filtered and dried through anhydrous $CaCl_2$.

Biological Activity

The prepared compounds were tested against *Escharia coli* and *Staphylococcus aureus* by disc diffusion technique. The sample solution is prepared from the concentration of 0.001M in DMSO as a solvent. The dishes are incubated during 24 h at room temperature then the diameter of the inhibition is measured and this indicates the growth of bacteria.

RESULT AND DISCUSSION

The results of the solubility test showed in (DMF & DMSO) but insoluble in H_2O, molar absorptivity values of complexes were 33.31–38.33 Ω^{-1} cm^2 mol^{-1} in DMSO. The CHN analysis and the sensible features of the compounds are listed in table1. The suggested formula for the complexes is [M $(L)_2$ $(H_2O)_2$] when M; metal(II) ions and L; Schiff base ligand table 1, shows the physical and conductivity properties of prepared compounds[11].

Table 1: Physical properties and conductivity of prepared compounds

Compounds	code	M.wt g/mole	M.P °C	Color	Elemental analysis				Cond Ω^{-1}
					C	H	N	M	
$C_{17}H_{15}N_3O_2$	L	293.12	160	orange	60.45 59.53	5.15	14.33	-----	----
$[Mn(L)_2H_2O)_2]$	C1	675.59	230	Pail - brown	60.45 59.53	4.77 3.99	12.44 12.07	8.13 8.00	15.74
$[Co(L)_2H_2O)_2]$	C2	679.59	226	Brown	60.09 59.22	4.75 4.30	12.73 12.00	8.67 8.07	11.11
$[Ni(L)_2H_2O)_2]$	C3	679.35	238	Pail-brown	60.11 60.01	4.75 4.22	13.37 12.98	8.64 8.03	11.26
$[Cu(L)_2H_2O)_2]$	C4	684.20	250	Orange	59.68 59.42	4.71 4.52	12.28 12.11	9.29 9.15	11.90
$[Cd(L)_2H_2O)_2]$	C5	733.07	223	Pail-brown	55.71 54.97	4.40 4.39	11.46 11.33	15.33 15.12	10.82
$[Hg(L)_2H_2O)_2]$	C6	821.24	210	Dark brown	49.72 48.65	3.93 3.82	10.23 10.16	24.43 24.16	13.08

Mass spectrum of (L)

The mass spectrum of the heterocyclic compound was recorded. The spectrum showed a group of different fission peaks with molecular weights with variation in their relative abundance including the peak fractionation at (m / e 293) due to the partial ion of the prepared ligand $[C_{17}H_{15}N_3O_2]$. The spectrum also showed a split peak with a high relative abundance at (m / e) (171) Attributed to the molecular ion $[C_8H_6]^+$, there are many fractionation products that can be observed in the mass spectrum of the ligand base were shown in the figure 1[12,13].

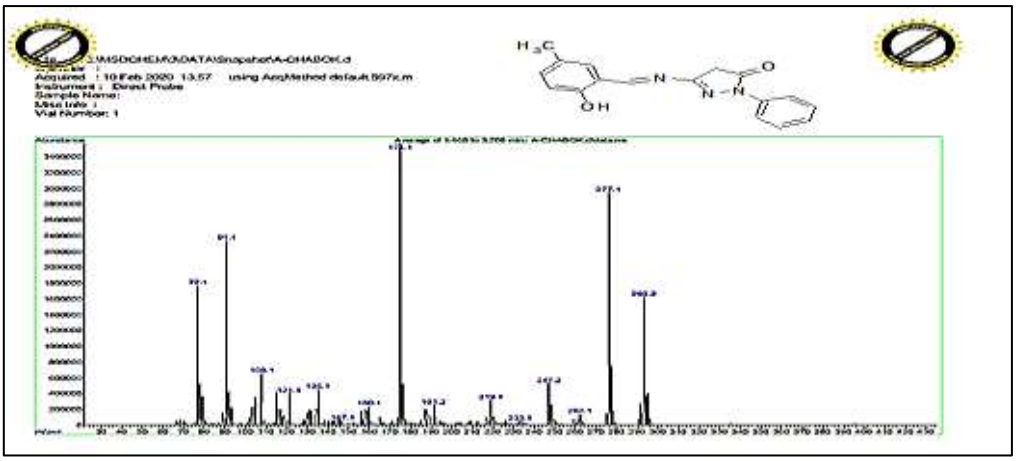


Figure 1: Mass spectrum of Schiff base ligand

FTIR and Electronic Spectra

The FTIR spectra of the free Schiff base (L) and their complexes provide information about the linked between metal and ligand bonding. The weak -broad band at 3342-3462 cm $^{-1}$ are assigned to the expansion vibrations of the O-H phenolic group of compounds [14,15]. Several ranges in the range of 2920-3020 cm $^{-1}$ have been assigned to the

distinct absorption of CH groups. The phenolic complex was purified at 1263 cm^{-1} due to the phenolic C-O group. The strong band at 1636 cm^{-1} is due to the (C=N azomethine) group, in which observed at wave number at range (1622-1624) cm^{-1} indicating the coordination of nitrogen atom for (imino group) to the metal ions. The newly observed bands in region (555-517) cm^{-1} and (451-413) cm^{-1} can be attributed to M-O and M-N bonds [16]. The Uv-vis spectrum of the ligand demonstrates one band at 295nm (33898 cm^{-1}) which due to $\pi \rightarrow \pi*$ transition [17,18]. Electronic spectra of complexes in table 3 reveal peaks to ligand and its complexes. Mn(II) complexes display one peaks for $^6A_1g \rightarrow {}^4T_2g(G)$ at 760nm [19]. Co(II) complex displays peaks in (756 and 907) nm which have been due to $^4T_1g \rightarrow {}^4A_2g$ and $^4T_1g \rightarrow {}^4T_2g$ respectively [20]. Ni(II) complex shows peaks at (401 and 774) nm attributed to the $^3A_2g \rightarrow {}^3T_1g$ and $^3A_2g(F) \rightarrow {}^3T_1g$ [21]. Cu(II) complex displays bands in the position 822nm due to $^2Eg \rightarrow {}^2T_2g$. the spectra of Cd(II) and Hg(II) complexes shows peaks at 435 and 359nm attributed to charge transfer [22]

Table 2: The FTIR spectra bands of compounds.

Compound	ν (O-H2)	C-H arom. C-H alph.	(HCN)Schiff	(CN)py	C=C	(MO) (ʁOH2)aq.	(M-N) Sch.
L	---	3075 2920	1636	1595	1574	---	--
C1	3410	3064 2920	1629	1591	1539	546 848	451
C2	3398	3050 2922	1624	1595	1545	555 855	432
C3	3402	3062 2920	1620	1595	1543	548 851	424
C4	3390	3064 2920	1622	1591	1533	552 862	444
C5	3438	3064 2972	1628	1597	1596	553 856	413
C6	3429	3062 2922	1641	1591	1493	517 858	451

Table 3: The Uv-visible peaks of ligand and their compounds.

Comp.	μeff B.M.	Peak snm	Wave number cm^{-1}	ϵ_{max}. Mol^{-1}. L. cm^{-1}	Transitions
L	----	295	33898	2298	$\pi^* \rightarrow \pi$
C1	24.6	359 760	27855 13157	1021 15	C.T. $^6A_1g \rightarrow {}^4T_2g(G)$
C2	7.95	416 756 907	24038 13227 11025	1841 18 4	C.T. $^4T_1g(F) \rightarrow {}^4A_2g(F)$ $^4T_1g(F) \rightarrow {}^4T_2g(F)$
C3	4.43	380 401 774	20833 24937 12919	1020 796 13	C.T. $^3A_2g(F) \rightarrow {}^3T_1g(P)$ $^3A_2g(F) \rightarrow {}^3T_1g(F)$
C4	1.14	412 822	24271 12165	36 31	C.T. $^2Eg \rightarrow {}^2T_2g$
C5	Diamagnetic	435	22988	2500	C.T.
C6	Diamagnetic	359	27855	1021	C.T.

Antibacterial Activities

Pathogenic microorganisms cause diverse kinds of ailments to both human as well as animals. The detection of chemotherapeutic agents has a very vital part in controlling and preventing such ailments. The microorganisms are able to grow resistance toward those chemotherapeutic agents and these strains which are resistant triggering an essential problem in the treatment of microbial infections. Searching for new antimicrobial agents gets to be very indispensable; therefore excessive efforts have been engaged to discover different antibiotics or novel compounds with worthy antimicrobial activity which could be proper to be utilized as chemotherapeutic agents. In this study, all prepared compounds have been evaluated *in vitro* as antimicrobial of one type Gram positive (*Staphylococcus aureus)* and Gram negative bacteria (*Echerchia coli).* However, all prepared

compounds have no inhibiting effect on bacteria, with the exception of Cd and Hg complexes and ligand, which show a good effect of inhibition on the bacteria, because According to "Tweedy's" chelation theory [23]. In the complexes, the polarity of the metal ion will be reduced to a greater extent leads to the overlap of the ligand orbital and partial sharing of the M^{+2} with donor groups[24], the delocalization of (π electrons) over the whole chelate ring and the large ring size of ligands moiety makes the complexes more lipophilic[25] table 4

Table 4: The Inhibiting Effect on Bacteria.

Comp.	*Staphylococcus aureus*	*Escherichia Coli*
L	12	17
C1	-	-
C2	-	-
C3	-	-
C4	-	-
C5	++	+++
C6	++	+++

Calculation of Thermodynamic Functions

Thermodynamic functions were extracted to decompose both systems through the following basic relationships [26].

$\Delta G = -RT \ln K_{eq}$ ------ (1)

$\ln K_{eq} = -\Delta H^\circ /RT + \Delta S^\circ/R$ ------(2)

were we get a linear relationship with a slope equal to -$\Delta H^\circ/R$ and $\Delta S^\circ/R$,from the slope and intersept values the ΔH° and ΔS° values table 6,are calculated in different temperatures.

Table 5: The Values of the Thermodynamic Constants for Both Systems.

ligand			Ni complex		
T(K)	1/T(K^{-1})	lnk	T(K)	1/T(K^{-1})	lnk
298	0.003356	-12.8390	298	0.003356	-16.21240
303	0.003300	-12.7548	303	0.003300	- 14.81244
308	0.003247	-12.6767	308	0.003247	-13.81245
313	0.003194	-12.6012	313	0.003194	-12.46480
318	0.003145	-12.5283	318	0.003145	-10.87105

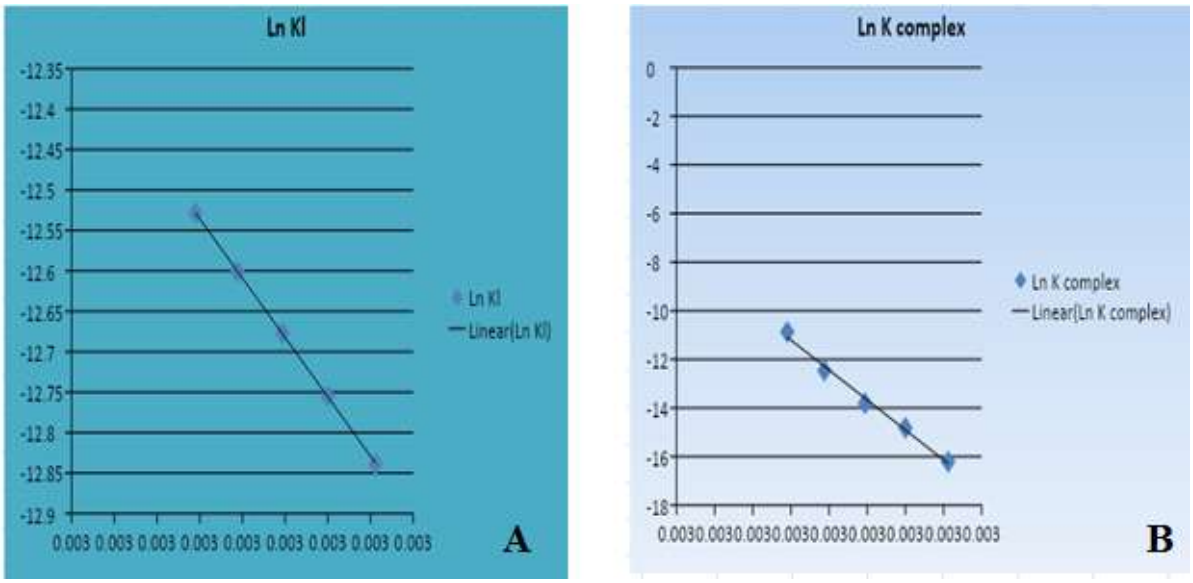


Figure 2: Plotting ln K_{eq} against 1/T for (A) Ligand and (B) Ni complex

Since plotting the graphical relationship between (lnK) verus (1/T) we get a straight line whose slope is equal to (-$\Delta H^\circ/R$ in J/mole) and an interrupt equal to ($\Delta S^\circ/R$ in J/mole.K) and (ΔG° (J/mole) as shown in table 6 for ligand and Ni complex.

Table 6: The values of enthalpy ΔH°, ΔS° and free energy ΔG°.

Ligand				Ni complex			
T(K)	ΔH°	ΔS°	ΔG°	T(K)	ΔH°	ΔS°	ΔG°
298	12204.1206	-65.7770	31809.5469	298	204856.96	552.0994	40167.3882
303	----------	----------	32131.1523	303	----------	----------	37314.6397
308	----------	----------	32461.3778	308	----------	----------	35369.7064
313	----------	----------	32791.8759	313	----------	----------	32440.8261
318	----------	----------	33122.9710	318	----------	----------	28741.4472

Where we notice from table 6 both processes of decomposition of the two systems are endothermic, however in the case of Ni complex they are much higher than the case of the ligand that it was due to the fact that the stability of the complex is high because it was ring-shaped claw structures with high stability. As for the values of entropy ΔS° we notice that it is negative for the process of decomposition the ligand while it is positive in the decomposition of the complex and high value, this is due to the decomposition of ligand includes its transformation into ionic species that tend to increase the regularity of the solvent molecules around the ions resulting from the decomposition and thus the entropy ΔS° of the total system at decomposition [27]. As for Ni complex, the number of ions released is greater as the opening of the cyclic structures (more regular) and its transformation into free spinning and random chains by turning gives the entropy a very large over all process as shown in table 7. As for the ΔG° to press for the decomposition process of both systems, we notice that its value is positive and this means that the decomposition process is an spontonuse process and this is normal due to the low values of the decomposition constants [28]

CONCLUSIONS

The new Schiff base derived from primary amine with 2-hydroxy-5-methylbenzaldehyde was preparation and diagnosed. The results indicated that the ligand is coordinated with the metal ions via nitrogen (imine group) and oxygen (phenolic group), The proposed form of complexes is octahedral geometry. The compounds were studied as antimicrobial and the values of thermodynamic functions (ΔH°, ΔS° and ΔG°) obtained indicated that the endothermic process for both system and an spontaneous and randomness increasing for Ni complex.

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