RESEARCH ARTICLE

Synthesis, Characterization and Study of the Biological Activity of New Metal Complexes of Ligand[2-(3-benzoylthioureido)-3-(-4-hydroxyphenyl) Propanoic Acid (BHP)

Enass Jasim Waheed[1*], Ban Zaidan Neema[2], Basima Mohsen Serhan[1]

[1.] *Department of Chemistry, College of Education for Pure Sciences, Ibn -Al-Haitham, University of Baghdad, Adhamiyah, Baghdad, Iraq.*

[2.] *Ministry of Education/General Directorate for the Education of Rusafa.*

*Corresponding Author: Enass Jasim Waheed

Abstract

In this paper, series of new complexes of Manganese(II), Cobalt(II), Nickel (II) Cupper(II) Zinc(II), Cadmium(II) and Mercury (II) are prepared from the new ligand [2-(3-benzoylthioureido)-3-(-4-hydroxyphenyl) propanoic acid (BHP) derived from tyrosine and benzoylisothiocyanate .Chemical structures are obtained from their ^{1} H, ^{13}CNMR spectra (for BHP), elemental microanalyses, molar conductance, FTIR, UV–Vis, magnetic susceptibility in addition to TGA/DTG and DSC analysis, the suggested geometry for all complexes was tetrahedral. The biological activity of BHP and its complexes has been extensively studied against two bacterial species *Staphylococcus aurous* (G+) and *Escherichia coli* (G-) by agar-well diffusion technique, where Mn(II), Co(II), Ni (II) complexes showed greater biological activity compared to ligand.

 Keywords: *Tyrosine, Metal complexes, Biological activity.*

Introduction

The main role in building blocks of proteins and intermediates in metabolism is played by amino acids. One of the 20 standard amino acids that are used by cells to synthesize proteins is tyrosine [1, 2]. Chelating ligands based on N, S and O donor atoms exhibit wide-ranging organic performance. Metal ions have significant roles in organic activities and in the fields related with inorganic chemistry application to diagnosis or for therapy of disease that stands for therapeutic lifeless chemistry [3, 4].

Some of the metal ions complex with amino acid derivatives are very important in biological fields and in the study of the effects of pharmaceutical drugs used as models or to increase biological compatibility and to reduce the toxicity of some metals. The tyrosine complexes showed important properties such as antibacterial, antifungal, anticancer, antiradical, antioxidant and inhibitors corrosion for metallic alloys materials [5, 7]. New complexes [MLaLbX], (where M= Copper(II), Nickel(II), Zinc(II) and Cobalt(II); La = ligand derived from L-tyrosine; Lb = $(CH_3)_2NCH_2CH_2N(CH_3)_2$; X = H_2O) were synthesis and characterization as a result of spectra studies such as Ultra violet–visible and Fourier-transform infrared [8]. Correspondingly, ligand derived of Vanillaldehyde and (A.A) (L-tyrosine and L-phenylalanine) and its complexes with iron (iii) were synthase and determined using various physicochemical such as FT-IR and UV-Vis [9].

The aim of this work to prepare new ligand [2-(3-benzoyl thioureido)-3-(-4-hydroxyphenyl) propionic acid (BHP) in addition to its metal complexes with Manganese (II), Cobalt (II), Nickel (II) Cupper(II) Zinc(II), Cadmium(II) and Mercury(II).

Experimental

All solvents, reagents, chemicals and metal chloride salts from BDH, Merck and Fluka are commercially available and used as received without purification.

Physical Measurements

The Acrlo Erba 1106 elemental analyze was used to measure Element Microanalysis for C.H.N.S. .NMR spectra (^{1}H- and ^{13}C–NMR) were acquired in $(CD_3)_2SO$ using Ultra Shield 300 MHz Switzerland with tetramethylsilane (TMS). Fourier-trans form infrared spectra have been registered at (4000-400) cm^{-1}range and (4000-200) cm^{-1} range of ligand and metal complexes on a Shimadzu IR-470 spectrum used KBr and CsI pellets. UV160 Shimadzu spectrophotometer at 25 Degrees Celsius for 10^{-3}mol.L^{-1} solution Dimethyl sulfoxide with1.000+0.001cm matched quartz cell was used to obtain Ultra violet –visible spectra.

Melting point has been documented as a result of Stuart SMP10 is a digital melting point apparatus. Conductivity measurements were performed using Philips PW 9529 conductivity meter with DMSO solutions at room temperature. Magnetic moments of complexes have been gotten by Magnetic Susceptibility Balances model MSB Mk1. A Shimadzu (A.A) 680 G atomic absorption spectrophotometer was implemented to determine metal content in complexes. TGA was obtained using apparatus type a STA PT-1000 Linseis as the temperature range of 30-600℃ and used argon gas.

Preparation of ligand (BHP)

The ligand has been prepared by two steps [10], Scheme (1)

Preparation of the (benzoylisothiocyanate)

Mixture of C_6H_5COCl (3.05ml, 26 mmol) and NH_4SCN (2g, 26mmol) in (25ml) of CH_3COCH_3, for 3 hours the mixture was stirred under reflex and then filtered, the filtrate was used in the subsequent step.

Preparation of [2-(3-benzoylthioureido)-3-(-4-hydroxyphenyl) propanoic acid (BHP)

About (4.71g, 26mmol) of $C_9H_{11}NO_3$ in 20 ml CH3COCH3 was quickly added to C_6H_5CONCS and left under reflux for 6 hours, after which the solid precipitate was collected, washed with CH_3COCH_3 and re-crystallized with C_2H_5OH. Yield(85%), (m.p =102-104)°C, C% actual (60.02) calc. (59.29), H% actual (4.50), calc. (4.68),N% actual (8.32), calc. (8.13),S% actual (10.15), calc. (9.31).
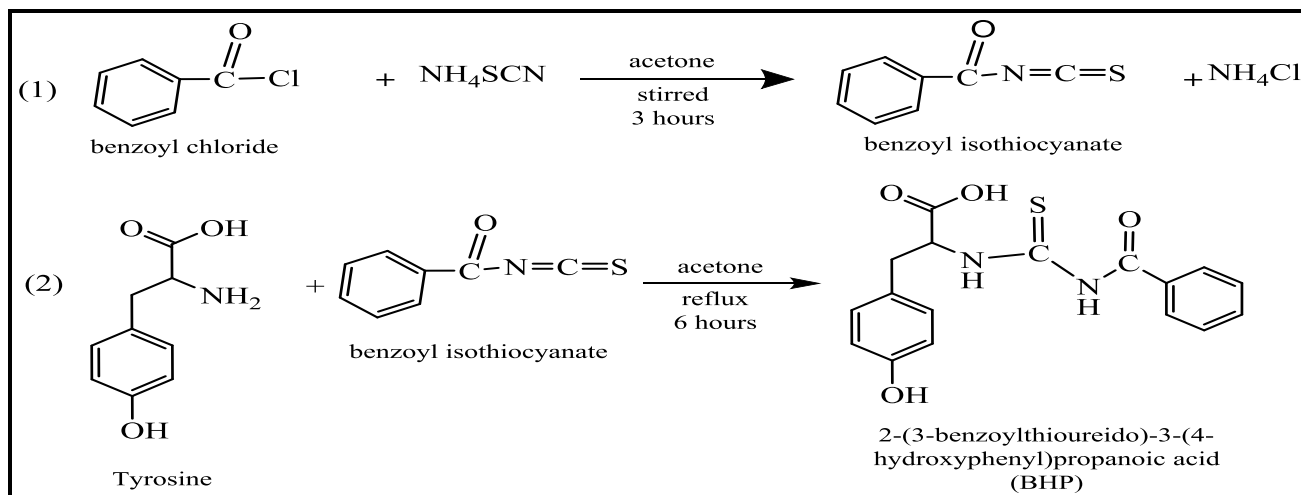
Scheme 1: preparation route of BHP

Preparation of Complexes

Preparation of [Ni$_2$ (BHP) Cl$_3$ H$_2$O]

Add the ethanol solution (10ml) of NiCl$_2$.6H$_2$O (0.475g, 2mmol) to the ethanol solution (10ml) of the ligand salt (BHP$^-$K$^+$) that prepared from (0.34g, 1mmol) BHP in 10 ml ethanol containing (0.056g, 1mmol) of KOH. For 6 hours at room temperature, the mixture was stirred. The precipitate back was collected, washed with mixture of H$_2$O: CH$_3$CH$_2$OH then dried under vacuum to give the pure product. Yield (79%), (m.p=290-292) °C.

Preparation of Manganese (II), Cobalt (II), Cupper (II) Zinc (II), Cadmium (II) and Mercury (II) Complexes

The complexes of [Mn^{+2}, Co^{+2}, Cu^{+2}, Zn^{+2}, Cd^{+2}and Hg^{+2}] ions with (BHP) were prepared in the same way as the nickel complex; Most of the physical data of all complexes are listed in the Table (1).

Table 1: Most physical data of the (BHP) and their complexes

Compound	M.wt (gm/mole)	Colour	m.p(°C) or Decom.	M% Calc. (actual)	Conductance ohm^{-1}cm^{2}mol^{-1} in DMSO	μ_{eff} (B.M)
(BHP) C$_{17}$H$_{16}$O$_4$N$_2$S	344.38	Yellow	102-104	----	----	----
[Mn$_2$(BHP)Cl$_3$H$_2$O]	578.76	Brown	395 dec.	18.98 (19.05)	13.9	4.22
[Co$_2$(BHP)Cl$_3$H$_2$O]	586.74	Green	200-202	20.08 (20.19)	13.5	3.50
[Ni$_2$(BHP)Cl$_3$H$_2$O]	586.26	Green	290-292	20.02 (20.39)	11	2.31
[Cu$_2$(BHP)Cl$_3$H$_2$O]	595.98	Green	195-197	21.32 (21.39)	5	1.85
[Zn$_2$(BHP)Cl$_3$H$_2$O]	599.66	Yellow	275-277	21.80 (21.94)	15.2	0
[Cd$_2$(BHP)Cl$_3$H$_2$O]	693.7	Yellow	210-212	32.40 (32.47)	13.8	0
[Hg$_2$(BHP)Cl$_3$H$_2$O]	870.06	Yellow	289-291	46.10 (46.18)	12.2	0

dec. =decomposition

Results and Discussion

Ligand BHP

The ligand has been prepared in two steps (1) by reaction benzoyl chloride and ammonium thiocyanate in a 1:1 mole ratio in acetone solvent gave benzoylisothiocyanate. (2) By reaction of the resulting compound with tyrosine in a 1:1 mole ratio in same solvent gave ligand BHP, Scheme 1. By 2: 1 (M: L) the complexes was prepared, Fig.1. A range of analytical and spectroscopic techniques were used to confirm the entity of compounds including; ^{1}H, ^{13}C-NMR, FT-IR, UV-Vis, C.H.N.S, magnetic susceptibility and conductance.
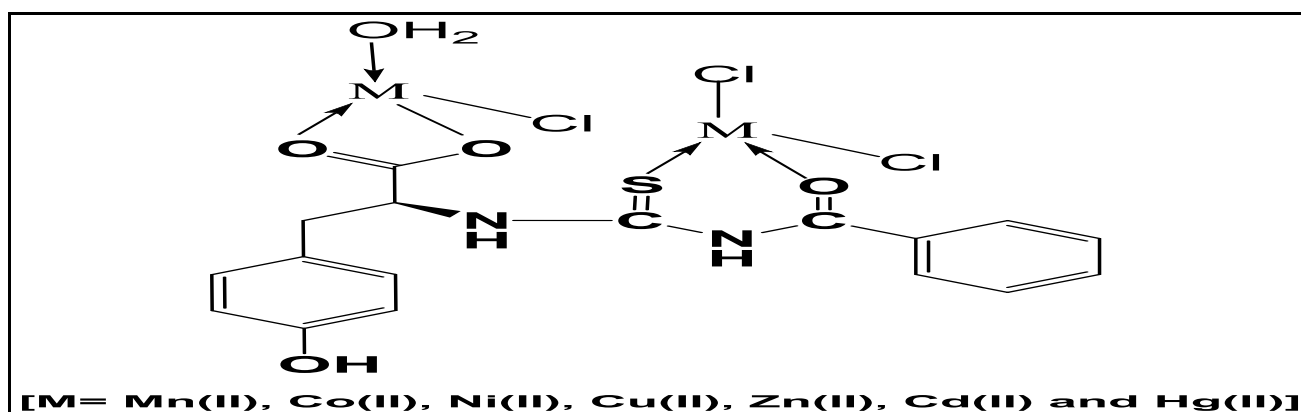

[M= Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II)]

Fig. 1: The proposed chemical structure of the complexes

Proton-1,Nuclear magnetic resonance spectra of (BHP), Fig.2 in (CD$_3$)$_2$SO have the following signals: doublet peak at δ(2.2)ppm of (1H,N-H Sec ,NH$_2$), doublet peaks at δ(3.10 – 3.11)ppm of (2H,CH$_2$),quartet peaks at δ (3.23–3.48)ppm of (1H, CH), singlet peak at δ(5.08-5.10) ppm of (1H ,OH phenolic), doublet peaks at δ(6.15-7.03) ppm of (4H, protons of aromatic), multiplet peaks at δ(7.25-8.45)ppm of (5H, protons of aromatic), singlet peak at δ(9.31) ppm of (1H,N-H sec, CONH$_2$), and singlet peak at δ(11.20- 11.22) ppm of (1H, COOH) [11-12].
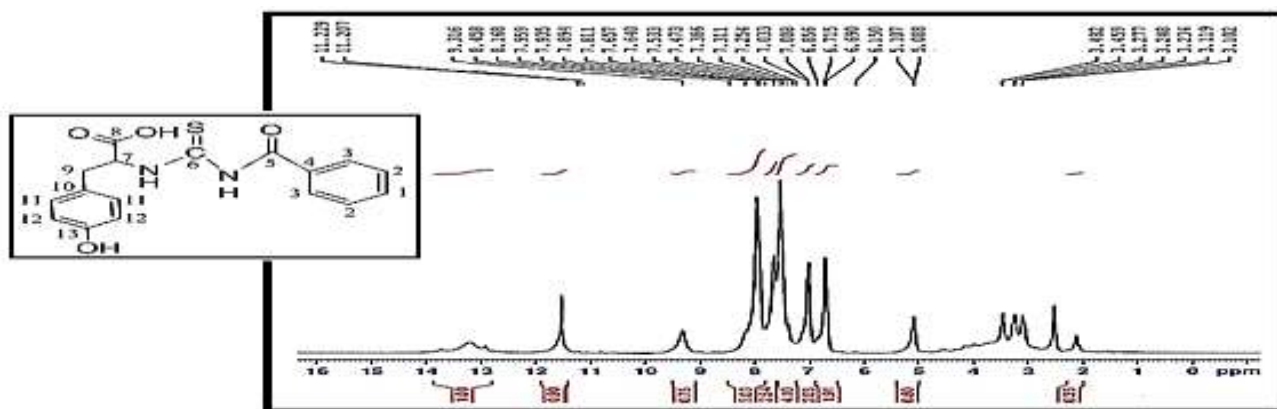

Fig. 2: Proton-1, Nuclear magnetic resonance spectra of (BHP)

Carbon -13 Nuclear magnetic resonance spectrum of (BHP), Fig.3, in $(CD_3)_2SO$ have the following signals: signal at δ (35.27) ppm of (C_9,CH_2) , signal at δ (58.87) ppm of (C_7,CH),signal at δ (115.17) ppm of (C_{12},CH), meltiplate at δ (126.04-133.04) ppm

of (C_1-C_4,C_{10},C_{11}) carbons of aromatic , signal at δ (156.22) ppm of $(C_{13},C-OH)$, signal at δ (168.33)ppm of $(C_5,C=O$ sec. ,$CONH_2)$, signal at δ (171.44) ppm of $(C_8,C=O$,$COOH)$, and signal at δ (180.16)ppm of (C_6,CS) [13-14].
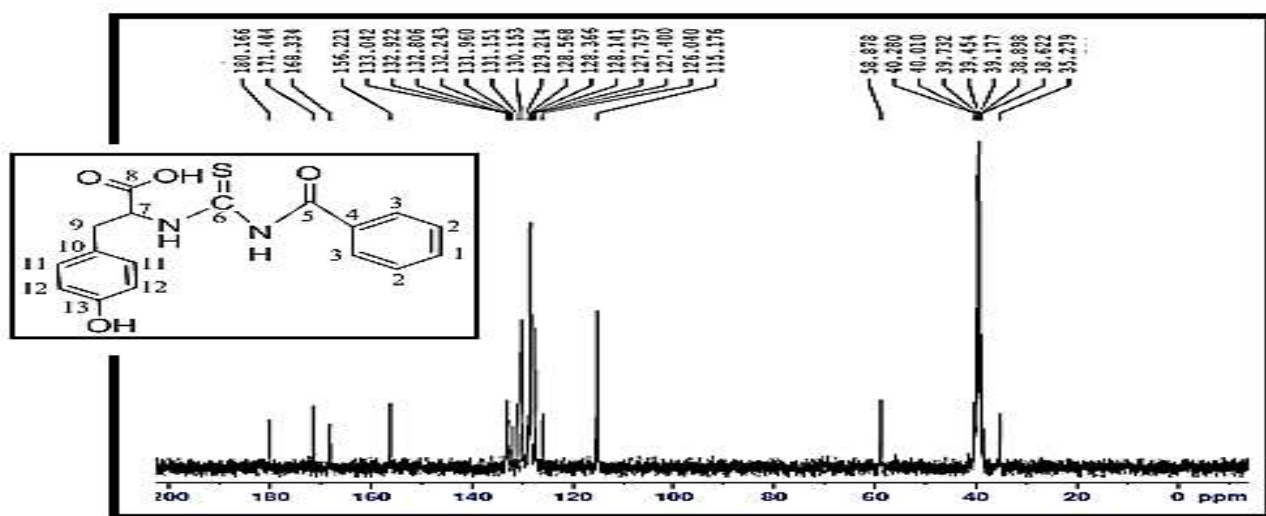

Fig. 3: Carbon -13 Nuclear magnetic resonance spectrum of (BHP)

The FT-IR spectrum of BHP has broad band at (3380,3230) cm^{-1} due to υ(OH, NH) While another absorbance bands at 1448 cm^{-1}, 1677 cm^{-1} ,1650 cm^{-1} ,1365 cm^{-1}due to υ COO $_{sym}$, υCOO_{asym}, υ C=O amidic and υ C=S respectively [15-16]. The Fourier-trans form infrared spectra results of BHP were recorded in Table 2. The UV-Vis spectrum of BHP exhibits two peaks in 36231 and 28169 cm^{-1} which are attributable to electronic transition types ($\pi\rightarrow\pi^*$) and ($n\rightarrow\pi^*$) [17-18].The data of electronic spectrum of BHP were listed in Table (3).

FTIR Spectra, Molar Conductivity and Magnetic Moment for complexes

By studying the prepared complexes, it was found to be thermally stable and dissolve in some solvents such as DMF, DMSO. Their atomic absorbance measured results for all complexes have shown approximated magnitudes as compared them with theoretical values .From the data listed in the Table (1), each the prepared complexes have the non-electrolytic nature of DMSO solvent in 10^{-3} M at 25°C [19], it includes the physical properties for ligand and its complexes. The apparent difference between bands related to the υ C=O amido stretching vibration within 1516-1512 cm^{-1} range was shown in the FT-IR spectra. The BHP bond through the oxygen atom in the carbonyl group with the central ion in the complexes was confirmed by the displacement in the

frequencies of this group to the lower by 138-134 cm^{-1} [20], while the ligand bond through the sulfur atom in the thiol group with the central ion in the complexes was confirmed by the displacement in the frequencies of this group to the higher by 127-89 cm^{-1} [21]. The υ COO $_{sym}$ stretching group was designated at 1448 cm^{-1}. The frequencies of υ COO $_{asym}$ group were determined in the complexes between 1411-1381 cm^{-1}, which were shifted to frequencies less by 67-37 cm^{-1} than the frequency of this group in the ligand which appeared at 1677 cm^{-1}.

Which confirms the association of the carboxylic group in the ligand with the central ion is the displacement of the frequencies of this group, which was set at 1556-1543 cm^{-1} in the complexes at a frequency lower by 134-121 cm^{-1}[22]. The υ N-H in ligand was not correlated with the central ion and was confirmed by no changes in the frequencies of this group that were set at 3178-3150 cm^{-1} in the complexes. The appearance of stretching bands of υ M-O, υ M-S and υ M-Cl at 474-428, 432-397 and 340-270 cm^{-1} respectively confirms the occurrence of the metal bonding with the oxygen, sulfur and Chlorine. Which confirms the coordination of water with the central ion is the shower of bands in the range 887-860 cm^{-1} attributed to υ OH in the spectrum of complexes [23]. Table 2 recorded important bands for all prepared complexes.

Table 2: The characteristic infrared band for BHP and their complexes

Compound	υ N— H)	υ COO asym	υ COO sym	Δυ COO	υ C=O Amide	υ C=S	ρ O-H of H$_2$O	υ M-S	υ M-O	υ M-Cl
Ligand (BHP)	3380$_{(m)}$	1677$_{(S)}$	1448$_{(S)}$	229	1650$_{(S)}$	1365$_{(S)}$	---	---	---	---
[Mn$_2$(BHP)Cl$_3$H$_2$O]	3176$_{(b)}$	1556$_{(S)}$	1388$_{(S)}$	168	1510$_{(S)}$	1454$_{(b)}$	860$_{(m)}$	397$_{(m)}$	428$_{(m)}$	310$_{(m)}$
[Co$_2$(BHP)Cl$_3$H$_2$O]	3150$_{(b)}$	1554$_{(S)}$	1384$_{(S)}$	170	1516$_{(S)}$	1462$_{(S)}$	875$_{(m)}$	432$_{(m)}$	462$_{(m)}$	337$_{(m)}$
[Ni$_2$(BHP)Cl$_3$H$_2$O]	3160$_{(b)}$	1550$_{(b)}$	1411$_{(W)}$	139	1516$_{(m)}$	1492$_{(m)}$	887$_{(s)}$	430$_{(m)}$	451$_{(m)}$	270$_{(w)}$
[Cu$_2$(BHP)Cl$_3$H$_2$O]	3155$_{(b)}$	1543$_{(S)}$	1381$_{(m)}$	162	1516$_{(s)}$	1473$_{(S)}$	871$_{(m)}$	416$_{(m)}$	474$_{(m)}$	311$_{(m)}$
[Zn$_2$(BHP)Cl$_3$H$_2$O]	3178$_{(b)}$	1554$_{(S)}$	1381$_{(S)}$	173	1512$_{(S)}$	1485$_{(m)}$	879$_{(m)}$	416$_{(m)}$	443$_{(m)}$	332$_{(w)}$
[Cd$_2$(BHP)Cl$_3$H$_2$O]	3178$_{(b)}$	1554$_{(S)}$	1404$_{(W)}$	150	1516$_{(m)}$	1482$_{(S)}$	887$_{(m)}$	420$_{(m)}$	455$_{(m)}$	340$_{(m)}$
[Hg$_2$(BHP)Cl$_3$H$_2$O]	3174$_{(b)}$	1550$_{(m)}$	1388$_{(b)}$	162	1612$_{(S)}$	1489$_{(S)}$	883$_{(s)}$	401$_{(m)}$	447$_{(m)}$	316$_{(m)}$

The molar conductivities indicate that all complexes are non-electrolytes. Magnetic moment values show that there is a tetrahedral [24] arrangement around the metal (II) ions as revealed in Table 1.

UV-Vis Spectral for Complexes

Electronic transfer L.F , $^6A_1 \longrightarrow ^4T_{2(D)}$ and $^6A_1 \longrightarrow ^4T_{1\ (D)}$ caused the shower of bands (36496)cm^{-1}, 28901cm^{-1} and 11990cm^{-1} respectively in the spectrum of manganese complex . Based on magnetic moment value μeff of 4.22 B.M for the Mn(II)-complex, the complex has a tetrahedral geometry around Mn (II) ion [25]. Electronic transfer L.F, C.T with $^4A_{2\ (F)} \longrightarrow ^4T_{1(P)}$, $^4A_{1\ (F)} \longrightarrow ^4T_{1(F)}$ and $^4A_{2\ (F)} \longrightarrow ^4T_{2(F)}$ caused the shower of bands 36363, 28901, 22471 and 14388 cm^{-1} respectively in the spectrum of cobalt complex. Racah inter electronic repulsion parameter (B$^-$) has been 547.2 cm^{-1} from the relation (ß=B$^-$ / B^0) that equal to 0.563. Based on magnetic moment value μeff of 3.50 B.M for the Co(II)-complex, the complex has a tetrahedral geometry around Co(II) ion [26]. Electronic transfer L.F with $^3T_{1\ (F)} \longrightarrow ^3A_{1(P)}, ^3T_1 \longrightarrow ^3A_{2\ (F)}$, and $^3T_{1(F)} \longrightarrow ^3T_{2\ (F)}$ caused the shower of bands 35714 , 26666 , 20746 and 12820 cm^{-1} respectively in the spectrum of nickel complex. The (B$^-$) magnitude was 596.8 cm^{-1}, while ß was 0.57. Based on magnetic moment value μeff of 2.31 B.M for the Ni(II)-complex, the complex has a tetrahedral geometry around Ni (II) ion [27]. Electronic transfer L.F., $^2T_2 \longrightarrow ^2E$ caused the shower of bands 36496 and 11976 cm^{-1} respectively in the spectrum of copper complex. Based on magnetic moment value μeff of 1.85 B.M for the Cu (II)-complex, the complex has a tetrahedral geometry around Cu (II) ion[28]. The Zinc(II), Cadmium(II) and Mercury(II) complexes show only C.T and L.F of Metal →Ligand in range 36363-28098 cm^{-1}[29-30]. All transitions included in Table 3.

Table 3: Electronic transitions of BHP and its complexes in dimethylsulfoxide as solvent

Com.	λ(nm)	υ$^-$(cm^{-1})	ABC	ε$_{max}$ molar^{-1}cm^{-1}	Transitions
Ligand (BHP)	276	36231	2.318	2318	п→п*
	355	28169	0.488	488	n→п*
[Mn$_2$(BHP)Cl$_3$H$_2$O]	274	36496	2.227	2227	L.F
	346	28901	1.600	1600	$^6A_1 \rightarrow ^4T_2$ (D)
	834	11990	0.024	24	$^6A_1 \rightarrow ^4T_1$ (D)
[Co$_2$(BHP)Cl$_3$H$_2$O]	275	36363	2.292	2292	L.F
	346	28901	1.633	1633	C.T mix with $^4A_{2(F)} \rightarrow ^4T_1$ (P)
	445	22471	0.478	478	$^4A_{1(F)} \rightarrow ^4T_1$ (F)
	695	14388	0.112	112	$^4A_{2(F)} \rightarrow ^4T_2$ (F)
[Ni$_2$(BHP)Cl$_3$H$_2$O]	280	35714	2.406	2406	L.F
	375	26666	0.995	995	$^3T_1$ (F) $\rightarrow ^3A_1$ (P)
	482	20746	0.093	93	$^3T_1$ (F) $\rightarrow ^3A_2$ (F)
	780	12820	0.025	25	$^3T_1$ (F) $\rightarrow ^3T_2$ (F)
[Cu$_2$(BHP)Cl$_3$H$_2$O]	274	36496	2.231	2231	L.F
	835	11976	0.050	50	$^2T_2 \rightarrow ^2E$
[Zn$_2$(BHP)Cl$_3$H$_2$O]	275	36363	2.348	2348	L.F
	345	28985	2.244	2244	C.T
[Cd$_2$(BHP)Cl$_3$H$_2$O]	279	358422	2.436	2436	L.F
	356	28098	0.678	678	C.T
[Hg$_2$(BHP)Cl$_3$H$_2$O]	276	36231	0.838	838	L.F
	348	28735	2.322	2322	C.T

Biological Activity

Two types of bacteria *Staphylococcus aurous* (Gram-positive) and *Escherichia coli* (Gram-negative) were used to study antibacterial activity of BHP and its complexes. The size diameter of the inhibition against the growth of the various microorganisms was measured by the effect of the compounds prepared on the bacterial species. From the information collected, it is clear that, compared with BHP, it display a low antibacterial activity

against *Staphylococcus aurous* and *Escherichia coli*.

Thus, complex preparation increases the activities against bacteria selected. Increased complexes activity may be related to the chelation theory [31]. Therefore, the chelation decreases the polarity of the metal atom that resulted in the partial sharing of its positive charge with donor group and possible p-electron delocalization over the whole ring [32], Fig.4, Table 4.
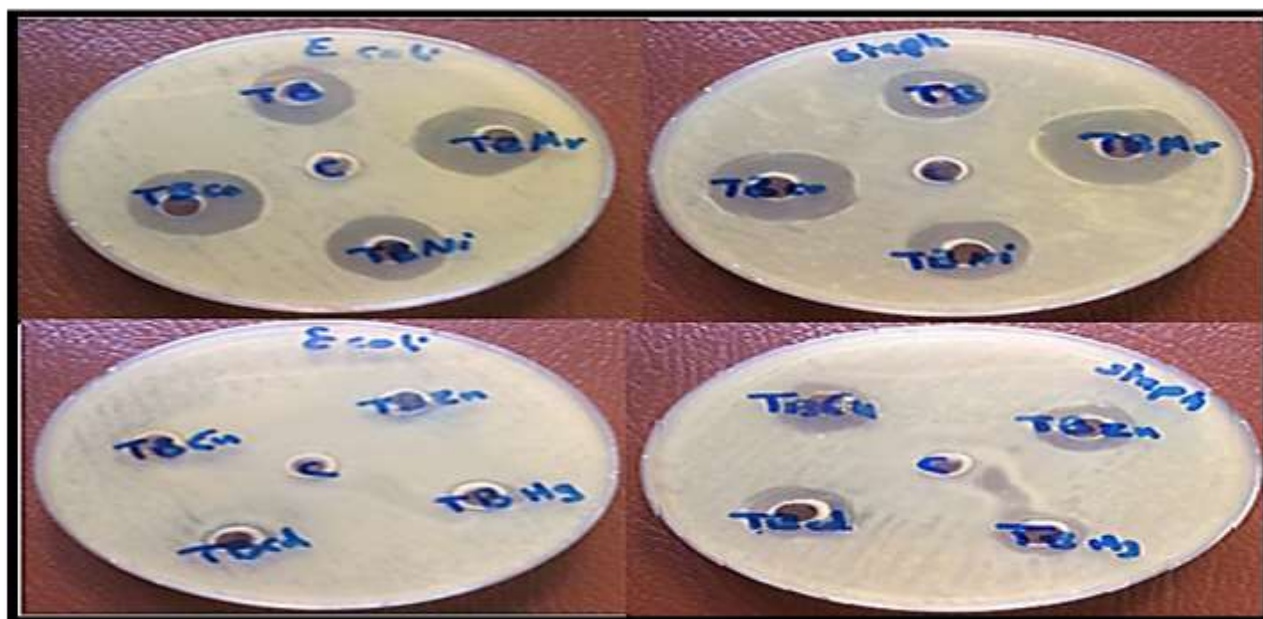

Fig.4: The effect of BHP and its complexes on Staphylococcus aurous and Escherichia coli

Table 4: Antibacterial activity of the BHP and its complexes

Compounds	*Staphylococcus aurous* gram (+)	*Escherichia coli* gram (-)
DMSO	Zero	Zero
Ligand (BHP)	17	18
$[Mn_2(BHP)Cl_3H_2O]$	23	21
$[Co_2(BHP)Cl_3H_2O]$	22	21
$[Ni_2(BHP)Cl_3H_2O]$	19	20
$[Cu_2(BHP)Cl_3H_2O]$	16	11
$[Zn_2(BHP)Cl_3H_2O]$	17	11
$[Cd_2(BHP)Cl_3H_2O]$	17	13
$[Hg_2(BHP)Cl_3H_2O]$	13	12

Thermal Analysis

The heating rates were suitably controlled at 10°C/min under the argon atmosphere and measure the mass change from ambient temperature to 600 °C for the simultaneous TGA / DTG and DSC study of BHP and the metal complexes. Table 5 shows the summary of TGA/DTG and DSC data and in Figs. 5 and 6 gives thermo gram of the ligand and the complex $[Cu_2 (BHP) Cl3H2O]$, [33].

The thermo gram of BHP indicates that the ligand is stable up to.135.9 °C and this temperature could be pointed out as the melting point of the ligand; see experimental part, Table 1. The TG curve of BHP display a total mass change of 83.3% which is observed in two steps within the temperature range of (135.9-594.5) °C which may attribute to the losing of organic part of BHP. The differences in the mass change may be related to a

sublimation process occurred at high temperature. The DSC curve recorded peaks at (135.9, 188.9 and 232.3) °C, which refer to an endothermic decomposition process. While the peak at 341.4 °C is indicate to an exothermic decomposition process. Both of the endothermic and exothermic peaks may refer pyrolysis of the organic ligand in an organ atmosphere [31]. As shown in the Fig.6, the $[Cu_2 (BHP) Cl3H2O]$ complex exhibit four decomposition steps.

The first step is in the temperature range (30-282) °C ,mass change = 54.9% which may a count for the loss of water molecules of hydration, the mass changes of the second and third decomposition steps amount to 20.66% and correspond to the removal of HCl ,H_2O and BHP molecules. The last step of decomposition with in the temperature range (460-595) °C with an estimated mass change

of 3.78%, this mass change corresponds to the pyrolysis of the BHP molecules leaving Cu_2S as a residue [34].
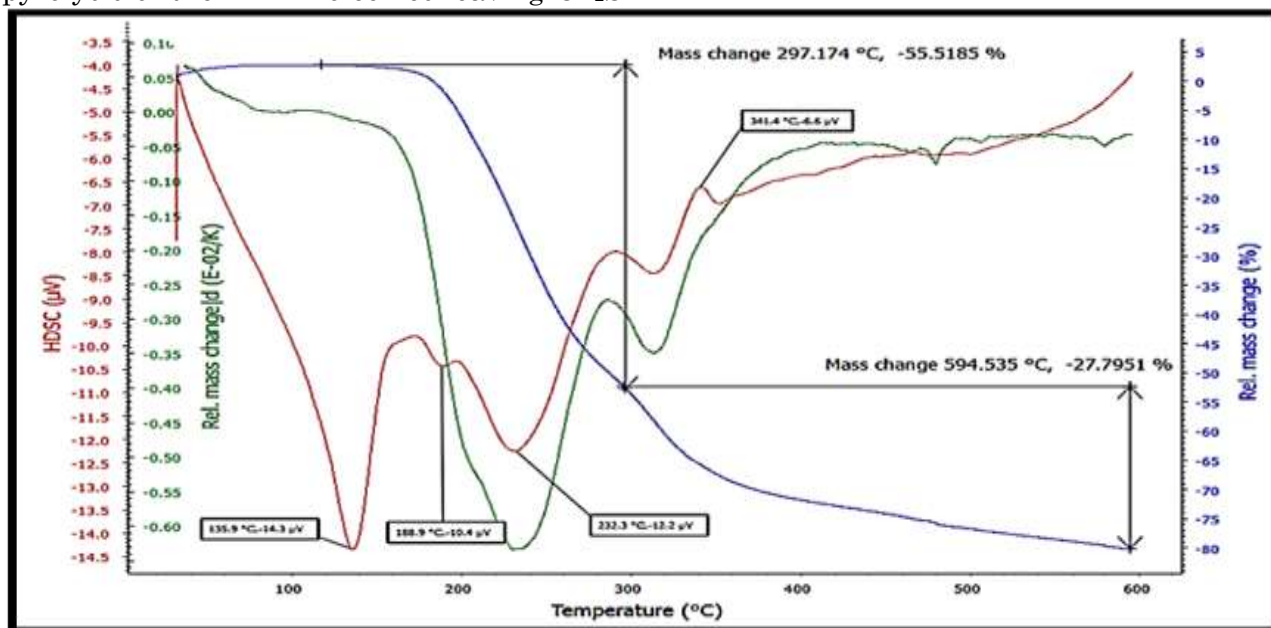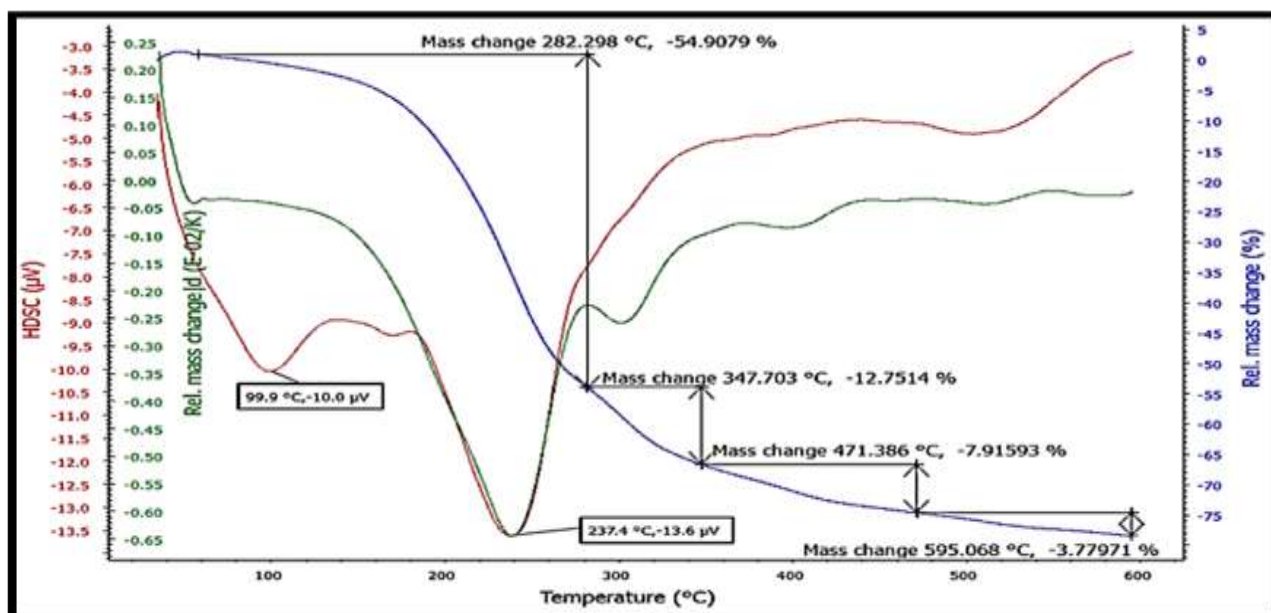

Fig.5: Thermal analysis of (BHP)

Fig.6: Thermal analysis of [Cu₂ (BHP) Cl₃ H₂O]

Table 5: Weight loss values correspond to temperature values for thermal analysis

Compound	Decomposition range (°C)	Peak temp. (°C)	Percentage weight loss %	Mass/mg change (Found)
Ligand (BHP)	135-600	297	55.51	11.10
		594	27.79	5.55
[Cu₂(BHP)Cl₃H₂O]	99-600	282	54.90	9.88
		347	12.75	2.29
		471	7.91	1.42
		595	3.77	0.68

Conclusions

Based on the results of the measurements 1H-13C NMR for (BHP only), conductance, magnetic moment, Fourier-trans form infrared, Ultraviolet –visible and atomic absorption for BHP and prepared complexes, we proposed BHP behaves as tetra dentate on coordination with metals ions M=

Manganese (II), Cobalt (II), Nickel (II) Cupper (II) Zinc (II), Cadmium(II) and Mercury (II) through two O atoms of COO (carboxylic group) , S atom of CS (thiol group) and O atom of CO (amide group) signifying tetrahedral geometry around metal ions for all prepared complexes as in Fig.1.

Acknowledgement

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