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Preparation, Spectral Characterization, DFT and Antibacterial Study of New Azo Ligand Derived From 2-aminoanthracene-9,10-dione With Antipyrine Mixed Ligand Complexes Involving 1,10-phenanthroline Ligand

Faris Subhi Al alsultan*, Rana A.S. Al Quaba*
Department of Chemistry/ College of Sciences, University of Mousel. Iraq.

Abstract

A new heterocyclicligand 2-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)diazenyl)anthracene-9,10-dione. was synthesized by the diazotization of 2-Aminonthracene 9,10-dione coupling with Antipyrine in alkaline alcoholic solution under suitable optimized experimental conditions to yield a new azo dye(Azo-Anthq-Ap) . Then React mixed(Azo dye ligand with 1,10-phenanthroline complexes has been Prepared Fe(II), Co(II) Ni(II), Cu(II) , Zn(II), and, Hg(II) ions. They confirmed by[1]H-NMR,UV-visb,XRD, thermal analysis (TG, DSC).FT-IR spectroscopic methods, magnetic susceptibility, elemental analysis, atomic absorption, and molar conductance. The isolated solid complexes are found to have the general formula [M (L)(phen) Cl]. And [Fe (L)(phen)(H$_2$O)Cl] Cl,conductivity measurements for prepared complexes showed [1:1] electrolyte for Fe(II), and non-electrolyte for the Co(II) Ni(II), Cu(II), Zn(II), and, Hg(II) complexes. The spectral and analytical data revealed that this ligand behaves as a Bidentate chelating agent and coordination number of all metal ions were found to be Six Shape.. Finally The synthesized Ligand and metal complexes were screened for their Antibacterial activity against bacterial species, one Gram positive bacteria *(Staphylococcus aureus)* and three Gram negative bacteria *Escherichia coli, Pseudomonas aereuguinosa and Klebsiellapneumoniaea.*, it was found that these compounds show different activity of inhibition on the growth of the bacteria.
  Key Words: Azo 2-aminoanthracene-9,10-dione, Mixed ligand , 1,10-phenanthroline, Antipyrine.

Introduction

Azo dyes are known for extended applications in different fields and have been attracting the attention of synthetic and theoretical chemists [1]. Also, textile dyes, due to containing azo group -N=N- and the conjugated bonds, appear colored by the absorption of light in the visible region [2]. Azo compound derived from hemicyclic amines containing their metal complexes, particularly fused
with anthrequinone have been drawing the interest of many studies due to their biological activities [3,4]. compounds show biological activities such as antifungal, antibacterial, anti-inflammatory and anthelmintic [6], antitubercular [7], antiblood pressures, antiallergic, antiasthma [8] and anticancer [9]. The study of azo dyes of pyrazoline-2-one and pyran-2-one derivatives has been of much interest in recent years due to theirantibacterial, antiviral, anticancer, antifungal, antihelminthes and insecticidal activities [1]. In particular, the tautomerism of pyran-2-one ligands show a dramatic increase in the diversity of biological properties.[2,4] .Depending on these results, we reported her the preparation and characterization of the new azo dye ligand2-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)diazeny lanthracene-9,10-dione (Azo-Anthq-Ap) ligand .And Mixed with 1,10-phenanthroline ligand and Fe (II), Co(II), Ni(II), Cu(II), Zn(II), and Hg(II) ions. The ligand and their metal complexes were screened for antibacterial activity against *Klebsiellapneumoniae, Staphyolococ usaureus P.aeruginosa, and E.coli*.

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Experimental

Materials

All chemicals used in this study were of the highest purity available. 2-amino anthracene-9,10-dione, Antipyrine , 1,10-phenanthroline, hydro chloride acid , Sodium hydroxide and Sodium Nitrite, were purchased from Sigma Aldrich The C.H.N. EA (300) was used to analyze the elements of the ligand (Azo-Anthq-Ap) and its complexes. (element Analyses system GmbH). Absorption spectra in absolute ethanol (10^{-3}M) solution were recorded using U.V.-visb. Shimadzu UV-1800 UV Spectrophotometers),(^{1}H- NMR spectra of ligand recorded in DMSO-d^6 The internal reference standard was TMS, (Varian Agillent 500 MHz) spectrometer. FT-IR alpha was used to record infrared spectra .FT-IR-ATR platinum reflective)(Bruker (400-4000 cm^{-1})is the range. Analytic Jena Model Nova (AA-350) used the atomic absorption technique to calculate the metal percentages. At room temperature, on a balance magnetic MSB, magnetic susceptibility measure ments of metal complexes were performed -MK (That's the Gouy method.) Electrical conductivity was measured in DMF at room temperature and use a digital conductivity meter (Conductivity Meter-Model-Eutech pc700) with a solute concentration of (10^{-3}M). Electro thermal 9300 was used to determine the melting point in an open capillary tube. A Philips pw 9421 Ph meter has been used to start taking the measurements. DiffractogramX,pert Phillips Holland. Has been used to scan XRD patterns.. TGA analysis was recorded with Matluer Touldo.

Preparation of azo ligand (Azo-Anthq-Ap)

The 2-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)diazenyl)anthracene-9,10-dione azo dye ligand (Azo-Anthq-Ap) has been synthesized by the diazotization coupling reaction by using the flwoing methods by KhalidJ.AL-Adilee*et al*. [3,12].with some modifications (Scheme1) by dissolving (3.839gm) ,(0.0172mol) of 2-aminoanthracene-9,10-dione in mixture of (5.5ml) ml distilled water and 5ml concentration hydrochloric acid with continuously cooling and stirring until reach the temperature at (0-5)℃ and then added solution of Sodium nitrite prepared from the dissolved 1.18gm (0.0172mol) in 5 ml distilled water   dropwise   to   solution   of   2-aminoanthracene-9,10-dione at (0℃) in ice e bath, The resulting diazonium chloride solution was added drop by drop with constant stirring
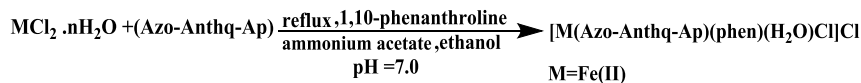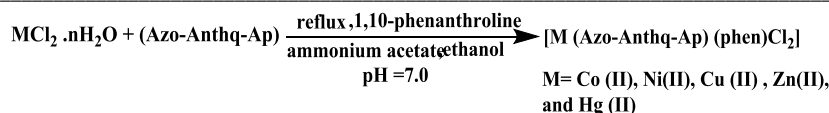
to solution consisting of (3.237gm) (0.0172mol) Antipyrine(solved in 18 ml ethanol and (18 ml 6%) NaOH mixture of cooled without a degree high more than (0℃) observed mixture color light Red Brawn, solution was obtained and after the complete of added left the mixture to stable for 2 h followed by addition (200ml) of distilled water modifying the Ph of solution to (pH = 6) leaving the precipitate for overnight and then filtered and washed several times with distilled water and (10 ml) ethanol solution to remove the excess of unreacted substances .The yield was (78 %) of Red Brawn crystals and m.p (162C). The structure of azo dye ligand was confirmed by IR,^{1}H- NMR, C.H N , UV-Visb.
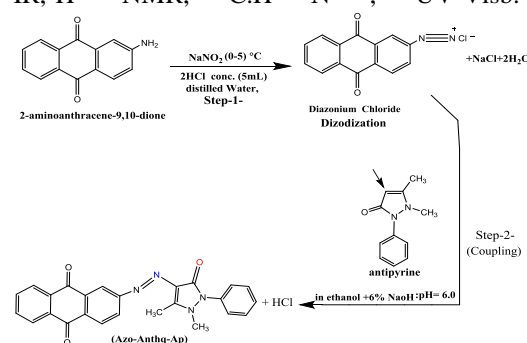
Scheme 1.The synthesis of Azo dye ligand (Azo-Anthq-Ap).

Synthesis of metal complexes

The metal chelate complexes were synthesized at (pH =7.0) value in buffer solution (ammonium acetate) by dissolving (0.882gm)(0.003mol) in (30 ml) ethanol and then added dropwise with stirring a stoichiometric amount of [1M:1L] mole ratio to (0.003 mol) of metal chloride M=Fe(II), Co (II), Ni(II), Cu (II) , Zn(II), and Hg (II) ligand dissolved in 25 ml buffer solution. The reaction mixture was refluxed for (45-60 min) .After refluxing for 1 h, (0.003 mol) of 1,10-phenanthrolinewas added to the solution. The reaction was heated for an additional (2h)until solid complexes precipitated and covered with shiny stratum then left over night, then the solid chelate complexes are filtered off washed with distilled water, until the solution become colorless .Table(1) shows the collects of some physical properties and analytical data for ligand and its metal 6636helate complexes[13,14].

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MCl$_2$ .nH$_2$O + (Azo-Anthq-Ap) $\xrightarrow[\text{pH =7.0}]{\text{reflux ,1,10-phenanthroline ammonium acetate,ethanol}}$ [M (Azo-Anthq-Ap) (phen)Cl$_2$]

M= Co (II), Ni(II), Cu (II) , Zn(II), and Hg (II)

MCl$_2$ .nH$_2$O +(Azo-Anthq-Ap) $\xrightarrow[\text{pH =7.0}]{\text{reflux ,1,10-phenanthroline ammonium acetate ,ethanol}}$ [M(Azo-Anthq-Ap)(phen)(H$_2$O)Cl]Cl

M=Fe(II)

Scheme 2

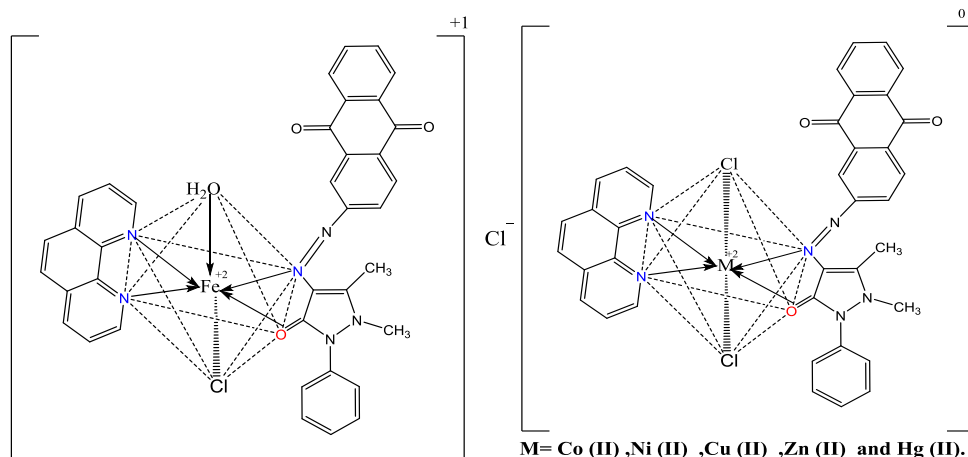M= Co (II) ,Ni (II) ,Cu (II) ,Zn (II) and Hg (II).

Fig. 1. The proposed structural formula of the metal chelate complexes .

Results and discussion

The heterocyclic azo dye ligand (Azo-Anthq-Ap) developed Red Brawn crystals, but the Depending on the metal ion, the metal chelate complexes obtained were of different colors. The ligand and its complexes are stable in air at room temperature and insoluble in water. Some organic solvents, such as ethanol, methanol, acetone, CHCl$_3$, DMF, DMSO, alkaline solutions, and strongly acidic solutions, are soluble in it .

Molar conductivity measurements

The molar conductivity of the prepared metal complexes was measured at room temperature in DMF as a solvent with a concentration of (10^{-3}M).

The conductivity values are described in the below Table3. The molar conductivity of the Fe(II) complex indicates that it was an electrolyte with a [1:1] ratio. The ionic nature of the Co(II), Ni(II), Cu(II), Zn(II), and Hg (II) complexes was demonstrated Used a silver nitrate (AgNO$_3$) solution, which resulted in a white silver chloride precipitate (AgCl) [10]. However, because of the low molar conductivity of these complexes indicated their nonionic structure and nonelectrolyte nature [15-16].

TABLE.1. Elemental analysis of (Azo-Anthq-Ap) and its complexes and some physical properties.

| compound	Color	M.p (°C)	Yeild %	Mol. formula (mol. Wt)	Found (calc)%			
					C	H	N	M
L=Azo-Anthq-Ap	Red Brown	162	78	C$_{25}$H$_{18}$N$_4$O$_3$ (422.14)	71.08 (71.20)(	4.30 (4.10)	13.26 (13.35)	--
[Fe (L)(phen)(H$_2$O)Cl]Cl	Dark Brown	290	75	C^{37}H$_{28}$Cl$_2$FeN$_6$O$_4$ (747.41)	59.46 (59.62)	3.78 (3.52)	11.24 (11.16)	7.47 (7.30)
[Co (L)(phen) Cl$_2$]	Bluish Brown greenish	210	70	C$_{37}$H$_{26}$Cl$_2$CoN$_6$O$_3$ (731.08)	60.67 (60.85)	3.58 (3.45)	11.47 (11.39)	8.05 (7.90)
[Ni (L) (phen) Cl$_2$]	Brown bluish	294	67	C$_{37}$H$_{26}$Cl$_2$N$_6$NiO$_3$ (730.08)	60.69 (60.80)	3.58 (3.49)	11.48 (11.36)	8.02 (7.92)
[Cu (L) (phen) Cl$_2$]	Dark Brown	280	69	C$_{37}$H$_{26}$Cl$_2$CuN$_6$O$_3$ (737.10)	60.29 (60.50)	3.56 (3.38)	11.40 (11.29)	8.62 (8.40)
[Zn (L) (phen)Cl$_2$]	Dark Brown	275	71	C$_{37}$H$_{26}$Cl$_2$N$_6$O$_3$Zn (736.07)	60.14 (60.18)	3.55 (3.57)	11.37 (11.40)	8.85 (8.80)
[Hg (L) (phen)Cl$_2$]	Dark Brown	230	78	C$_{37}$H$_{26}$Cl$_2$HgN$_6$O$_3$ (874.14)	50.84 (50.66)	3.00 (3.10)	9.61 (15.38)	22.95 (22.25)

Infrared spectra

The infrared spectra of azo dye ligand (Azo-Anthq-Ap)and its metal complexes with Fe(II), Co(II), Ni (II),Cu(II), Zn(II), and Hg(II). ions are studied by using KBr disc in the range (400-4000 cm^{-1}) and given in Table(3) The strong absorptions at (1490 cm^{-1}) for –N=N– of ligand, and 1412-1430 cm^{-1} . Its complexes the band in the region 1630-1652 cm^{-1} gives a clear indication of chelated C=O group suggesting involvement of carbonyl oxygen of pyrazolone ring in the coordination with metal ions [17,18].

TABLE.2. :The Key IR absorption bands (cm^{-1}) of the azo dye ligand (Azo-Anth) and the perpend complexes.

| Group	Ligand	Fe(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Hg(II)
ν OH	--	3378	--	--	--	--	--
ν C=O	1677	1652	1652	1530	1536	1537	1632
νC=N	1583	1576	1576	1576	1580	1582	1578
ν C-H Aromatic	3045	3041	3097	3097	3070	3049	3070
νN=N	1490	1430	1429	1429	1422	1412	1422
ν (C-N=N-C)	1378	1364	1378	1366	1326	1321	1328
ν(M-O)	--	522	505	526	570	589	540
ν(M-N)	--	438	447	431	438	492	438
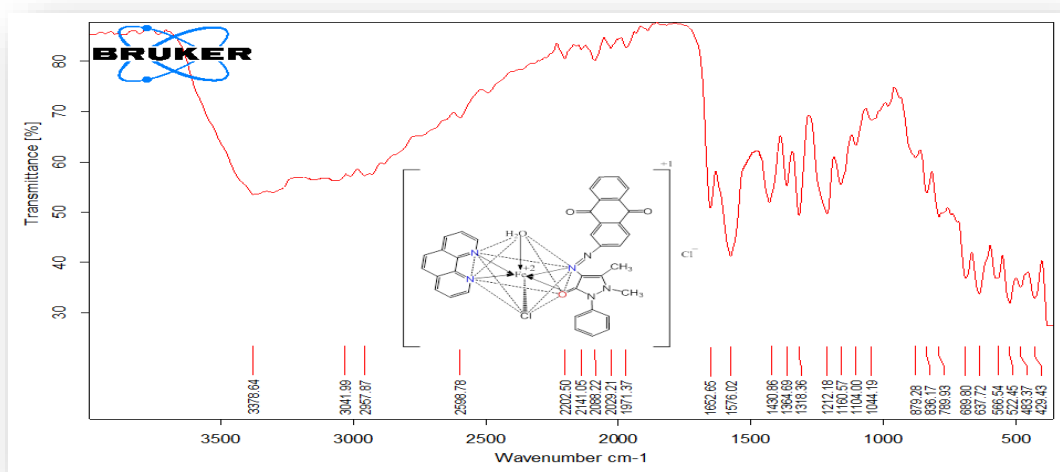
Fig. 2. IR Spectrum of the free ligand (Azo-Anthq-Ap) **and Fe(II),Zn(II) complexes .**
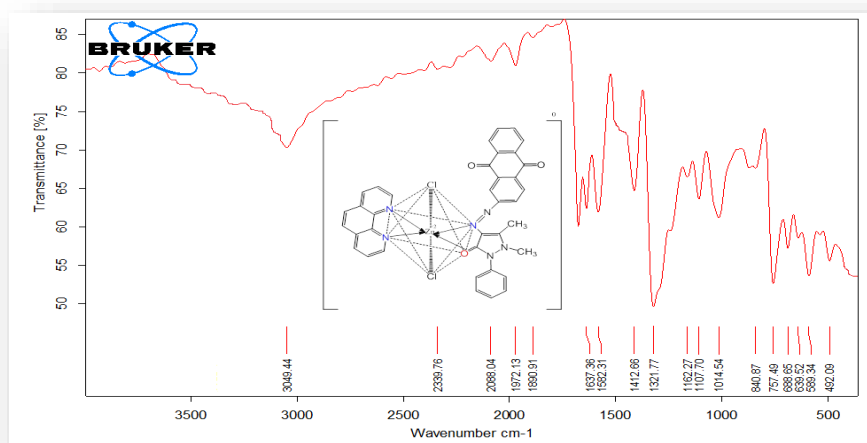
^{1}H-NMR spectra

The ^{1}HNMR spectrum of ligand (Azo-Anthq-Ap)was recorded in (DMSO-d^6) and Spectrum was shown in (Fig.5). ^{1}HNMR spectrum of the Azo dye ligand shows peak at (7.01-8.22 10H) δ ppm, multiplet aromaticThe ligand also shows the following signals(3H singlet,2.81−3.04 δppm)N-CH$_3$ and , (3H singlet, 2.31−2.81δppm) C-CH$_3$ of Antipyrine group [17,18]. All the protons were found to be in their expected region. The conclusions drawn from these studies offer additional support to the mode of bonding discussed in the (C.H.N) and IR spectra. And agreement with The number of protons .
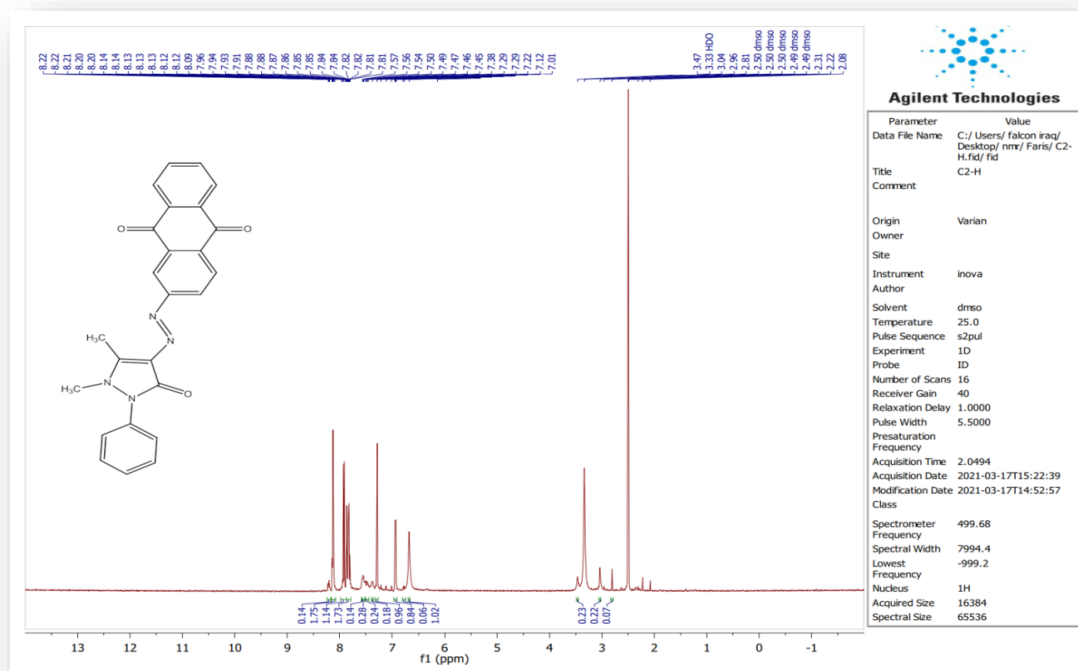
Fig.3.^{1}HNMR spectrum of Ligand .

Magnetic measurements

The Magnetic moment of the complexes at room temperature are listed in Table (3). Fe(II)., complex has a magnetic moment of (5.17 BM) which is in agreement with the reported value high spain for octahedral[10-18] . Co(II).complex has a magnetic moment of (4.59BM) due to orbital contribution then, which is in agreement with the reported value high spain for octahedral Co(II) complexes The present Ni(II) complex shows a magnetic moment value of 3.108BMwithin the range of (2.9–3.3 BM) suggesting an octahedral environment around Ni (II) ion . The Cu(II) complex shows a magnetic moment value of (2.06BM) higher than the spin-only value (1.73BM) expected for one unpaired electron, monomeric and consistent with a distorted octahedral geometry, The Zn(II)and Hg(II) complexes were diamagnetic and according to the empirical formulae of these complexes, they have an octahedral geometry [12-19] .
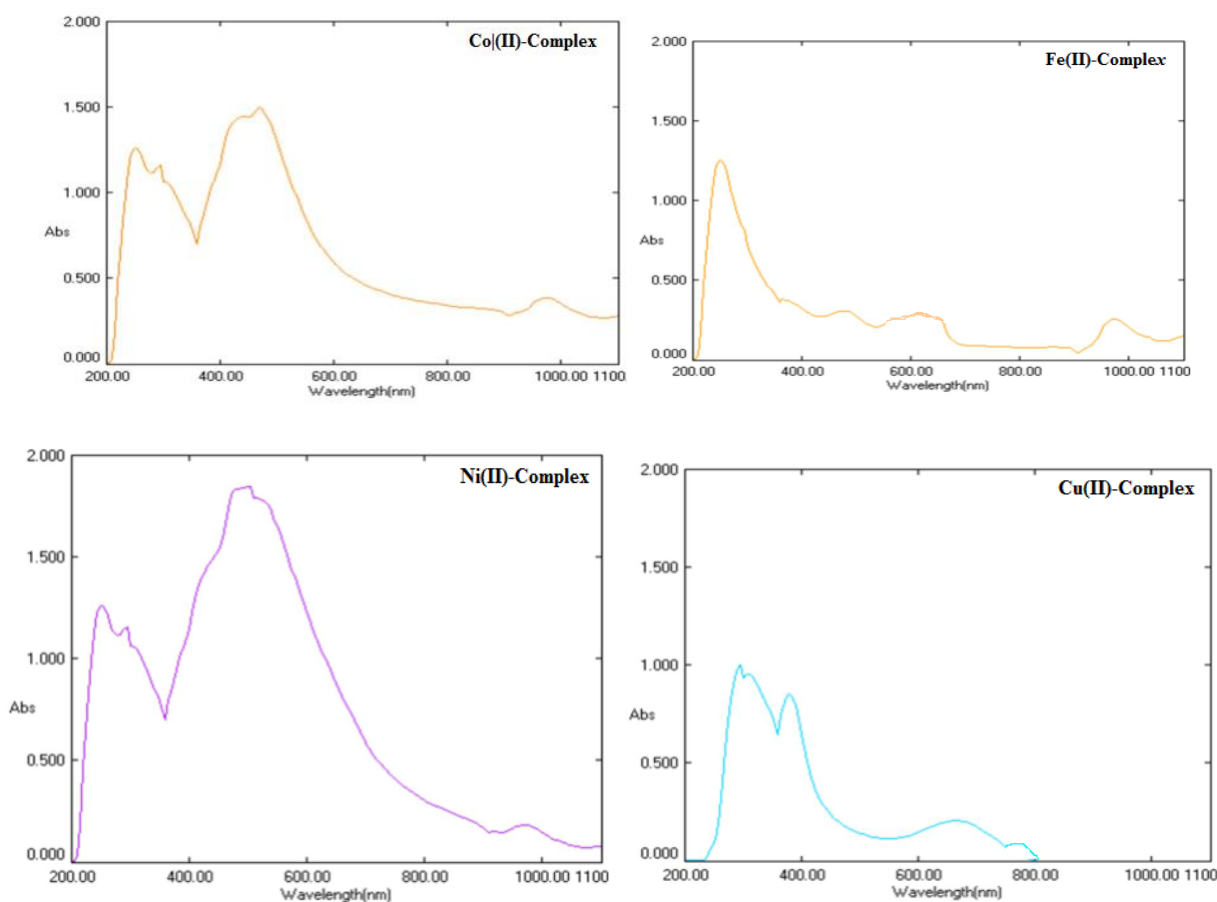
Electronic spectra

Spectrums of ligand (Azo-Anthq-Ap) and its complexes. Fe(II),Co(II),Ni(II) Cu (II), Zn(II) and Hg(II) in DMF   [10^{-3}M] The electronic spectra and magnetic measurements are taken in to account to establish the geometric structures of the complexes Table(3). The electronic spectrum of Fe(II) complex displays weak absorption band at 11904cm^{-1} corresponding to^{5}T$_2$g → ^{5}Eg transition and could be assigned to octahedral structure   . The electronic spectrum of Co(II) complex displays weak absorption bands at (10890cm^{-1})(12787cm^{-1}) and (22727 cm^{-1}) characteristic of octahedral geometry corresponding to ^{4}T$_1$g(F) →^{4}T$_2$g(F)(ν$_1$) ,^{4}T$_1$g(F) → ^{4}A$_2$g (P)(F) (ν$_2$), ^{4}T$_1$g→^{4}T$_1$g (P) (ν$_3$) transitions respectively. The Co(II) complex which supports octahedral geometry. The Ni(II) complex also exhibits three weak absorption bands at (11235 cm^{-1}) , (13440 cm^{-1}) and (22727cm^{-1}) assignable to ^{3}A$_2$g(F)(ν$_1$) →^{3}T$_2$g(F), ^{3}A$_2$g(F) (ν$_2$) →^{3}T$_1$g(F) , ^{3}A$_2$g(F) (ν$_3$) →^{3}T$_1$g(P) which are characteristic of octahedral geometry around Ni(II) ion . The Cu(II) complex depicts a broad band in the region (13560cm$^{-1)}$ to (17760 cm^{-1}) with maximum at 15625 cm^{-1} assignable to^{2}Eg → ^{2}T$_2$g in its spectrum, the broadness of the band may be due to distorted octahedral geometry [3-12].

**TABLE. 3 . The electronic spectrums of ligand and its complexes , magnetic
Susceptibility and values of molar conductance of complexes**

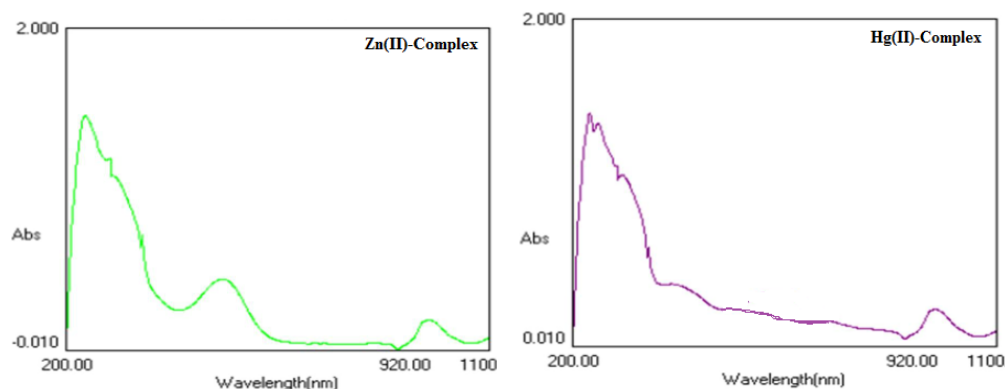| Compounds	Band position, cm^{-1}	Transition	Ω^{-1} cm^{2}mol^{-1}	Suggested geometry	μeff (BM)
L=Azo-Anthq-Ap	32258	$\pi \rightarrow \pi^*$	--	--	--
	26954	$n \rightarrow \pi^*$			
	37037	Center ligand			
	28571	Center ligand			
[Fe (L)(phen)(H$_2$O)Cl]Cl	11904	$^5T_2g \rightarrow {}^5Eg$	71.6	octahedral	5.17
		$^4T_1g(F) \rightarrow {}^4T_2g(F)$			
[Co (L) (phen)Cl$_2$]	16328	$^4T_1g(F) \rightarrow {}^4A_2g$ (F)		octahedral	4.59
	22727	$^4T_1g \rightarrow {}^4T_1g$ (P)			
			12.5		
[Ni(L) (phen) Cl$_2$]	11235	$^3A_2g \rightarrow {}^3T_2g(F)$		octahedral	3.10
	134402272 7	$^3A_2g \rightarrow {}^3T_1g(F)$			
		$^3A_2g \rightarrow {}^3T_1g(P)$	13.1		
[Cu (L) (phen) Cl$_2$]	15625	$^2Eg \rightarrow {}^2T_2g$	10.0		2.06
[Zn (L) (phen)Cl$_2$]	30687	C-T	19.4	octahedral	Di
[Hg (L) (phen)Cl$_2$]	30488	C-T	18.5	octahedral	Di

Fig. 4. Absorption spectra of complexes in DMF solution (10 $^{-3}$ M).

XRD analysis

The XRD powder pattern is processed in X'pert high score software package(Fig.5). The search matching procedure is adopted for the PXRD pattern for the [Co(Azo-Anthq-Ap) (phen) Cl₂] and revealed a match with a copper compound corresponding JCPDS powder diffraction file with PDF (No991218). Table (4)The pattern can be indexed to be a monoclinic crystal system with (a = 8.088133), (b =19.286010)(c =6.268824)(α= γ = 90) (β =103) , Unit volume cell (950.13 x10^{-3}°A) , K is a constant (0.94 for Cu grid), is the X-ray wavelength (1.5406 A) , is the Bragg diffraction angle, and is the full-width at half-maximum

(FWHM) of prominent intensity peak, intensity (%), and integrated intensity[19,20] The crystallite sizes were calculated using Debye-Scherrer's formula as given in equation (1)

$$D = 0.9\frac{\lambda}{\beta\cos\theta} \quad \text{------ (1)}$$

Where θ is the Bragg diffraction angle at the peak position in degrees: β is the Full width at Half Maximum of the peak position in radian ; λ and is the CuK wavelength Co(II) complex crystallite size is (0.16-0.74nm) [21,22].

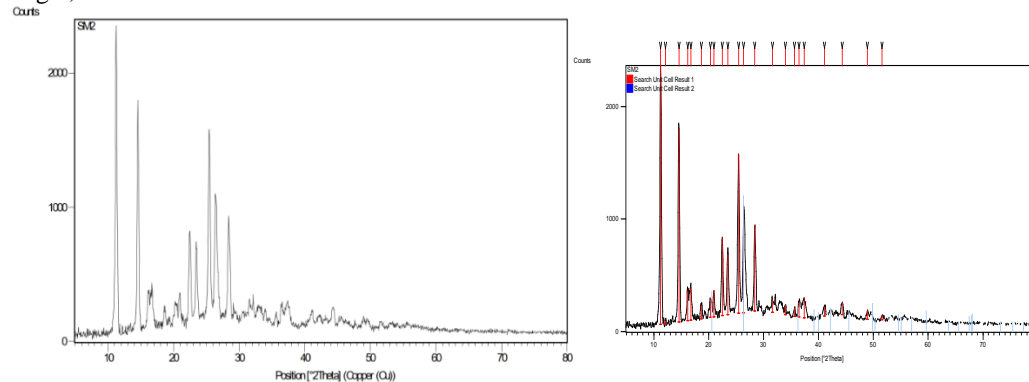**TABLE 4. Inter planar distances,2θ value and FWHM relative intensity for Co(II)complex.**

Strongest peak no	2θ (deg)	Height [cts]	FWHM [°2Th.]	d (Å)	Rel. Int. [%]	Crystallite Size	Lattice Strain
1	11.2426					0.74	0.713
2	14.5619	1711.00	0.2952	6.08306	74.42	0.57	1.195
3	20.9324	232.85	0.1968	4.24395	10.13	0.40	2.465
4	22.4579	696.34	0.2952	3.95901	30.29	0.37	2.835
5	23.5044	542.00	0.2952	3.78505	23.58	0.35	3.058
6	25.4458	1417.00	0.2952	3.50050	61.64	0.329	3.103
7	26.3556	951.00	0.2952	3.38169	41.37	0.320	3.633
8	28.3810	761.00	0.3444	3.14480	33.10	0.29	3.895
9	51.5615	41.00	0.7200	1.77109	1.78	0.160	14.555

Fig. 5. X-ray diffraction patterns for Co (II.)

Thermal studies

Details thermal study of (Azo-Anthq-Ap) ligand and its complexes. Fe(II) and Co(II)

complexes are listed in Table (5) .The decomposition occurs in at least Six major

detectable steps, each step does not referred in generally to single process

but rather is reflects of three data thermal stability of Ligand and Its complexes Fe(II) and Co(II) undergo [17,18] .

TABLE. 5. Date (T.G, DSC) of ligand and its complex Fe(II) ,and Co(II).

Compound	TG Range (°C)	Mass loss%	Assignment	Residue	DSC (°C)
Azo-Anthq-Ap	28-300	10	Evolution of CO_2 and moisture	--	50(+)
	-350300	30	-Loss Azo group -N=N-		230(+)
	350-400	50	-Loss $-CH_3$ $-CH_2$ group		
	400-450	70	-Loss $-CH_3$ $-C_6H_6$ group		560(+)
	450-500	80	-Loss $-C6H5-$, C=O group		
	500-600		-Loss of a part of the ligand		
	28-300	10	Evolution of CO_2 and moisture	Fe_2O_3+2C	290 (+)
	300-350	30	-Loss $-H_2O$ Coordination		
	350-380	50	-Loss $-CH_3$ $-CH_2$ group		430 (+)
[Fe (L)(phen)(H$_2$O)Cl]Cl	380-480	70	-Loss $-CH_3$ $-C_6H_6$ group		
	480-580	80	-Loss $-C6H5-$, C=O group		
	580-600		-Loss of a part of the ligand		
[Co (L) (phen)Cl$_2$]	28-240	10	-Evolution of CO_2 and moisture	$CoO+2C$	45 (+)
	240-300	30	-Loss Azo group -N=N-		300(+)
	300-350	50	-Loss $-CH_3$ $-CH_2$ group		380(+)
	350-400	70	-Loss phenyl Ring		
	400-450	80	-Loss $-C_5H_5-$, C=O group		580(+)
	450-530		-Lose all part of the ligand		
	530-60				

L = ligand (Azo-Anthq-Ap)

DFT Study

A computational study of the investigating compounds is made to examine their reactivates and to evaluate geometrical parameters. Gauss view 4.1[23] is used to draw the structures. The structures of the ligand and Its all metal complexes are optimized at B3LYP[24] level of theory using 6-311++G(d,p) basis set. 6-311++G(d,p) is a large basis set which include diffused and polarized wave functions to take in to account the characteristics associated with ionic species having heavy atoms like N. Chemcraft software[25] is used to visualize the optimized geometry of the investigating compounds. The harmonic frequency calculation is also carried out at the same level of theory to ensure that the structures are true minima. Optimization was performed without any symmetry constraint using the default convergence criteria provided in the software. The molecular calculations in this work are done using the Gaussian 09 routine. This computational strategy is used successfully on coordination compounds and organic molecules. Conceptual DFT defines chemical potential (μ) as the first derivative of energy with respect to number of electrons

$$\mu = \left(\frac{\partial E}{\partial N}\right) \vartheta(r)$$

where *E*= energy, *N*= number of electrons of the system at constant external pressure and chemical hardness (η) as the half of the second derivative of energy with respect to number of electrons, so chemical hardness will the first derivative of energy with respect to number of electrons[25].

$$n = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right) \vartheta(r)$$

But chemical potential(μ) and chemical hardness(n) are also calculated in most cases in terms ionization potential(IP) and electron affinity(EA) and therefore [26].

$$\mu = -\left(\frac{IP+EA}{2}\right) \text{ and } n = \left(\frac{IP-EA}{2}\right)$$

According Koopman's theorem, *IP* and *EA* are related to energies of the Highest occupied molecular orbital (EHOMO) and Lowest occupied molecular orbital (ELUMO) in this way - IP = - E HOMO and EA = - E LOMO

$$\mu = \left(\frac{ELUMO-EHOMO}{2}\right) \text{ and } n = \left(\frac{ELUMO+EHOMO}{2}\right)$$

and Parr and co-workers proposed electrophilicity, as a measure of electrophilic power of a compound the electrophilicity can be represented as

$$ш = \frac{\mu2}{2n}$$

The chemical potential(μ) and chemical hardness(η), electrophilicity of the ligand and complexes are given in the Table (6) . The reactivity of the ligand and its metal complexes

can be predicted by considering the minimum electrophilicity principle. According to minimum electrophilicity principle, compound having minimum electrophilicity will have maximum stability. The chemical potential(μ), chemical hardness(η), electrophilicity (ω) are calculated from the HOMO and LUMO value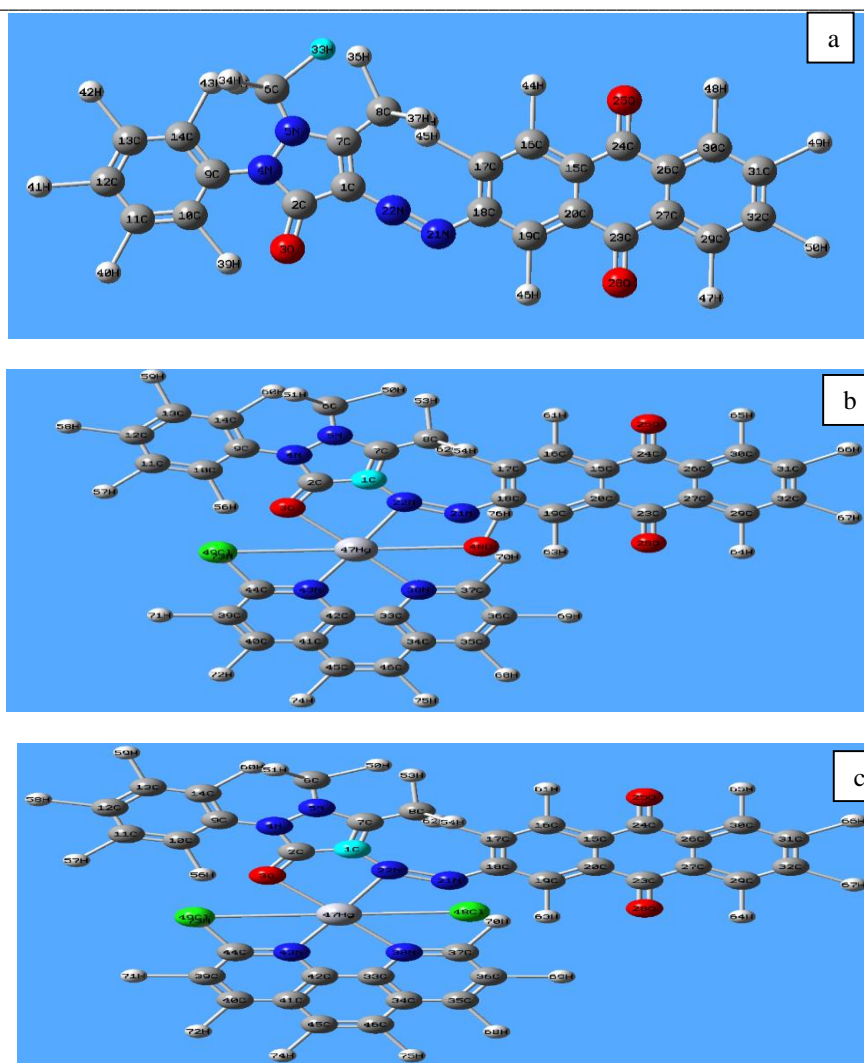 of the ligand (Fig7-15) and its complexes(Fig8-16) and presented in the Table(6). The metal complexes are more reactive than the ligand and the order of reactivity of the complexes is Fe(II) > Zn > Co(II) > Cu(II) >Ni(II) > Ligand >Hg(II) .

TABLE .6. HOMO and LOMO ,η , $\mu(eV)$, and ω of compounds.

/ Complexes Ligand	HOMO	LUMO	η	$\mu(eV)$	ω
(Azo-Anthq-Ap) L=	-11.61	-10.644	0.483	-11.127	29.90015
[Fe(L)(phen)(H$_2$O)Cl] Cl	-11.334	-8.791	1.2715	-10.0625	64.37217
[Co(L)(phen) Cl$_2$]	-10.307	-8.813	0.747	-9.56	34.13551
[Ni(L)(phen) Cl$_2$]	-8.819	-6.574	1.1225	-7.6965	33.24627
[Cu(L)(phen) Cl$_2$]	-8.826	-6.570	1.128	-7.70	33.38027
[Zn(L)(phen) Cl$_2$]	-8.831	-6.431	1.2	-7.631	34.9393
[Hg(L)(phen) Cl$_2$]	-0.267	0.439	0.353	0.08625	0.001314

-2- LOMO Ligand -2-   **HOMO Ligand**

LOMO of Fe(II)-Complex   **HOMO of Fe(II)-Complex**
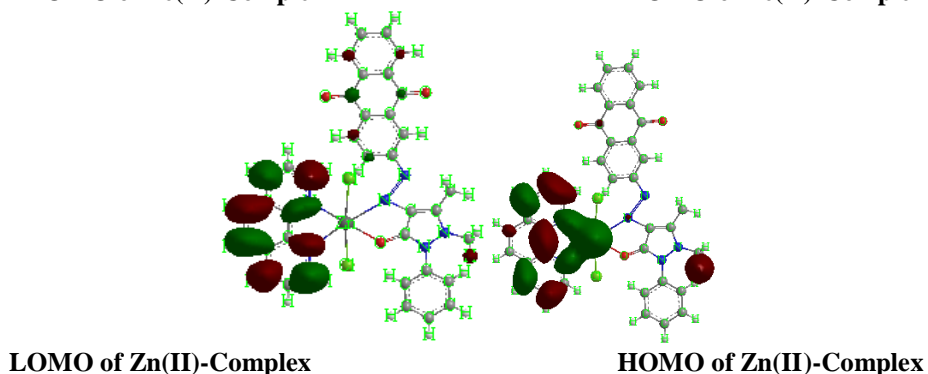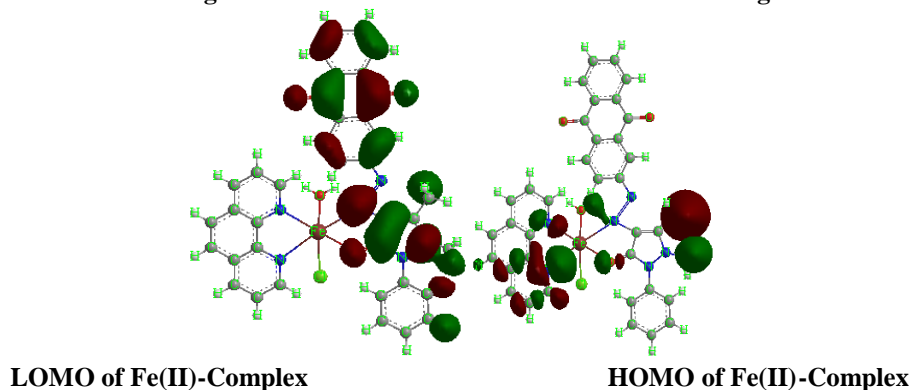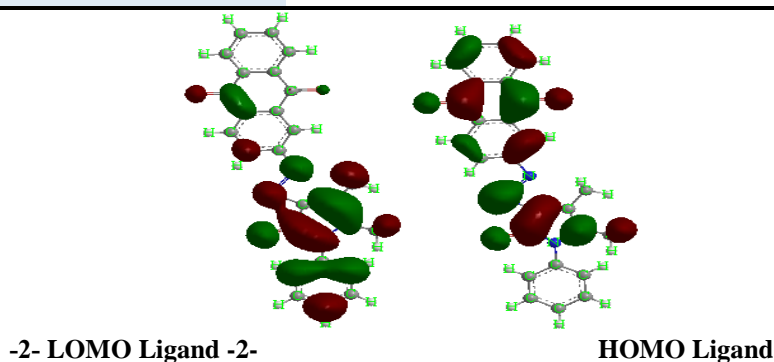
LOMO of Zn(II)-Complex   **HOMO of Zn(II)-Complex**
Fig 6. HOMO and LOMO of Ligand and Fe(II) and Zn(II) Complexes.

Fig 7. Optimized geometry(a) of the Ligand (b)Fe(II) and (c)Hg (II) complexes

Antibacterial study

The investigated compounds' *in-vitro* biological screening effects were checked against bacteria using the experiment was repeated three times under identical conditions using the disc diffusion method and nutrients agar as the medium. Table (6) summarizes the results, with DMSO serving as a negative control and Amoxicillin acting as a positive normal . .

. **TABLE.7. The synthesized compounds' minimum inhibitory concentrations against the growth of four bacteria (MIC in µg/mL).**

Compound	*Escherichia coli*	*Pseudomonas aeruginosa*	*Staphylococcus aureus*	*Klebsiella pneumonia*
(Azo-Anthq-Ap)L=	12	6	21	16
[Fe(L) (phen)(H$_2$O)Cl] Cl	18	12	22	18
[Co(L) (phen) Cl$_2$]	14	10	22	15
[Ni(L) (phen) Cl$_2$]	16	8	23	16
[Cu(L) (phen) Cl$_2$]	14	10	18	12
[Zn(L) (phen) Cl$_2$]	12	10	16	14
[Hg(L) (phen) Cl$_2$]	26	18	28	24
Amoxicillin	8.8	6.8	12	10
DMSO	0	0	0	0

The zone of inhibition region for metal chelates is much greater than the ligand, as shown in Table(6). Chelation theory may describe the increased activity of metal chelates in this way. Due to the overlap of the ligand orbitals, the polarity of the metal ion would be decreased to a greater degree during chelation.

It also promotes the delocalization of π - electrons. over the entire chelate ring and increases the complexes' lipophilicity [27,28] This increased lipophilicity causes the cell's permeability barrier to break down, slowing down normal cell processes.
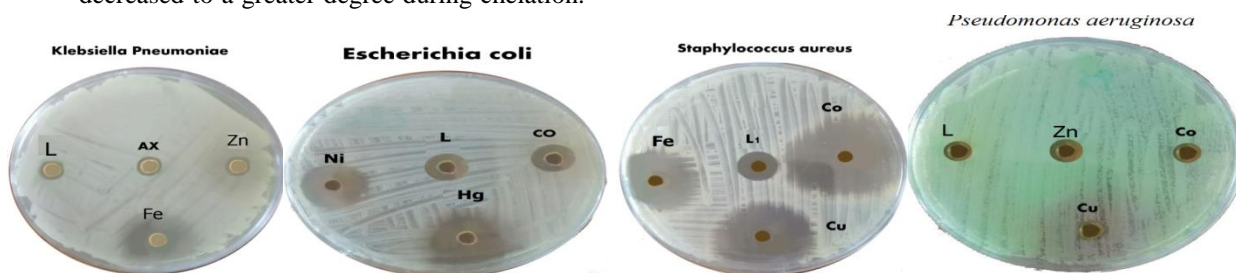

Fig . 8. Results of antibacterial screening.

Conclusions

In this paper authors reported the synthesis and spectral characterization of new Azo dye ligand derived from 2-aminoanthracene-9,10-dione with Anti pyrine (Azo-Anthq-Ap) and its metal complexes with Fe(II),Co(II) ,Ni(II), Cu(II), Zn(II), and Hg(II) ions. Analytical , Physical and Spectral data such as IR,^{1}H-NMR,UV-Visb.and XRD of the complex Co(II) the ligand(Azo-Anthq-Ap), showed behaves as Bidentate coordination involving one of the azo nitrogen which is the farthest of Azo group between pyrazole ring and anthracene-9,10-dione ring , and the oxygen of Carbonyl group of pyrazole ring,

Mixed ligand with(N,N) from free ligand 1,10-phenanthroline. The octa hedral geometry has been suggested to all complexes. The Fe(II) complex is ionic character to give [1:1] electrolyte but non ion character with Co(II), Ni(II) ,Cu(II),Zn(II), and Hg(II) complexes . The thermal stability of ligand and Some of complexes were studied by TG-DSC diagrams and it was found that the complexes had good thermal stability and theoretical Calculation (HOMO, LOMO)Orbitals. The prepared complexes showed important applications in medicinal fields such as pharmacology, toxicology and biochemistry.

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