

Article

Synthesis , Characterization of New Poly Dentate Schiff Base ligand With Cu(II) ,Ag(I),Cd(II) ,and Pd(II) Complexes And Studying Their Biological Activity As Antioxidants And Anticancer

¹Amer Saeed Jasim Ashour and ²Tariq Hussein Mgheer

1. Department of Chemistry, College of Education, University of Al-Qadisiyah, Al-Diwaniyah, Iraq

2. Department of Chemistry, and Biochemistry- College of Medicine-Babylon University

Corresponding author:

1. Email: edu-chem6.post@qu.edu.iq
2. Email: almgheer.tariq@uobabylon.edu.iq

Abstract:

The Schiff base ligand was prepared by reacting Diacetyl monoxime with O-phenylene diamine. Then react the resulting compound from the first step with 4-aminoantipyrine to produce the ligand [(2E,3E)-3-(((Z)-4-amino-1,5-dimethyl-2-phenyl-1,2-dihydro-3h-pyrazol-3-ylidene)amino)phenyl)imino)butan-2-one oxime]. Then the step of preparing the complexes is by reacting with metal salts of the elements CuCl₂.2H₂O, CdCl₂.2H₂O, PdCl₂ and AgNO₃. The complexes exhibited a metal ion-to-ligand ratio (M:L) of 1:1. The Cu(II) complex displayed an octahedral geometric shape, while the Ag(I) and Cd(II) complexes displayed tetrahedral geometric shapes. On the other hand, the Pd(II) complex displayed a square planar geometric shape. The structure of the compounds was confirmed through a series of spectroscopic measurements, including FTIR, ¹H-NMR, ¹³C-NMR, UV-Vis, C. H. N, FESEM, magnetic susceptibility, molar conductivity, and melting point. Assessing the biological efficacy of ligand and Ag(I)- complex through antioxidant testing and anticancer testing is a multifaceted process and complex. It was found that it has good effectiveness against HL-60 leukemia and MCF-7 breast cancer cells, and it can be used as a medicine after being well studied.

Keywords:

anticancer; antioxidant; 4-aminoantipyrine ; Diacetyl monoxime ; O-phenylene diamine; Schiff base.

1.Introduction

Schiff bases are important intermediate compounds in the preparation of some biologically active compounds such as (β-Lactams) [1]. In addition to its importance in the biological field, it has been used as antibacterial, antifungal[2], anti-cancer[3],

and others. The biological effectiveness of these compounds is attributed to the formation of stable aggregates in these molecules with the metal ions present in the cell, and the presence of the azomethine group ($C=N$) is an effective and appropriate factor for the formation of stable complexes with metal ions [4]. Therefore, a large number of Schiff bases were prepared and were produced. Study of their biological effectiveness. A recent study conducted by Rajavel and Sakthilatha [5] indicated that Schiff bases derived from the condensation of nitrobenzaldehyde-2-amino-5 with p-Phenylenediamine possess bio-logical effectiveness with many types of bacteria [6]. Schiff bases have good abilities to coordinate with metal ions to form their corresponding complexes while improving their properties even with the heavy elements actinides and lanthanides[7], as well as in bioorganic and medicinal chemistry[8], as well as in biological activities (such as antiviral, anti-inflammatory, antibacterial, etc.) Fungi and bacteria[9], nuclear medicine[10] and pharmaceutically active crystal components[11]. Oxime is an organic compound that belongs to the imines. This term dates back to the nineteenth century, and it is a combination of the words oxygen and imine[12]. Diacetyl monoxime (2,3-Butanedione monoxime) is a chemical compound known with the chemical formula ($C_4H_7NO_2$) This chemical compound has special properties and is a white solid [13]. Oximes are usually generated by the reaction of hydroxylamine with aldehydes or ketones [14]. This substance is widely used at millimole concentrations in cellular biological experiments[15]. Diacetyl monoxime can be used with thiosemicarbazide to detect small amounts of urea in the presence of other nitrogen-containing compounds[16]. O-phenyldiamine is an aromatic organic chemical compound, formula $C_6H_4(NH_2)_2$ with three isomerisms (ortho, para, meta). It is considered an aniline and has a yellowish-brown color. It is slightly soluble in water and is well soluble in ether [17]. It reacts with ketones and aldehydes through a condensation process to produce a range of useful products. It reacts with carboxylic acids and their derivatives called benzimidazoles. The herbicide Benomyl is manufactured. Quinoxalinedione can also be prepared by condensing Orthophenyldiamine with dimethyl oxalate [18]. The condensation reaction of O-phenyldiamine with diketone compounds is used in the preparation of a group of pharmaceutical preparations. Because the compound contains groups (amine, carbonyl, amine) as well as the presence of different derivatives of these groups, it has given great importance to entering into various fields, including pharmaceutical industries [19]. It is used as a medicinal substance that relieves pain, reduces fever, and is an anti-inflammatory for the pharynx and all infections [20]. In addition to analytical, biological and therapeutic applications, it also has anti-fungal, anti-bacterial and sedative properties [21].

2.Experimental

Materials and reagent

The materials used are Diacetyl monoxime, O-phenylenedi-amine, 4-aminoantipyrine, GAA, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, AgNO_3 , $\text{Cd(II)} \cdot 2\text{H}_2\text{O}$, Pd(II)Cl_2 , DMSO, DMF, MeOH, EtOH, NaOH, KBr, were of high purity and were supplied by (Sigma-Alderic, Merck). Diphenyltetrazolium bromide MTT. For antioxidant screening, MCF-7 breast cancer cell lines and HL-60 leukemia cell lines were obtained from the University of Tehran, Iran.

Physical Measurements

Measurements used include UV spectra in the region from 200 to 800 nm, ^1H -NMR and ^{13}C -NMR spectroscopy at 400 MHz with TMS as a reference internal standard in the solvent as for the DMSO- d_6 device. FTIR spectrophotometer in the range of $4000\text{--}400\text{ cm}^{-1}$, Melting point, Magnetic susceptibility measurements, Atomic flame absorption spectrometry, elemental analysis, FESEM images to clarify the nanoscopic shape and size of the crystals, and to demonstrate some of the properties of the prepared materials, XRD spectroscopy was used.

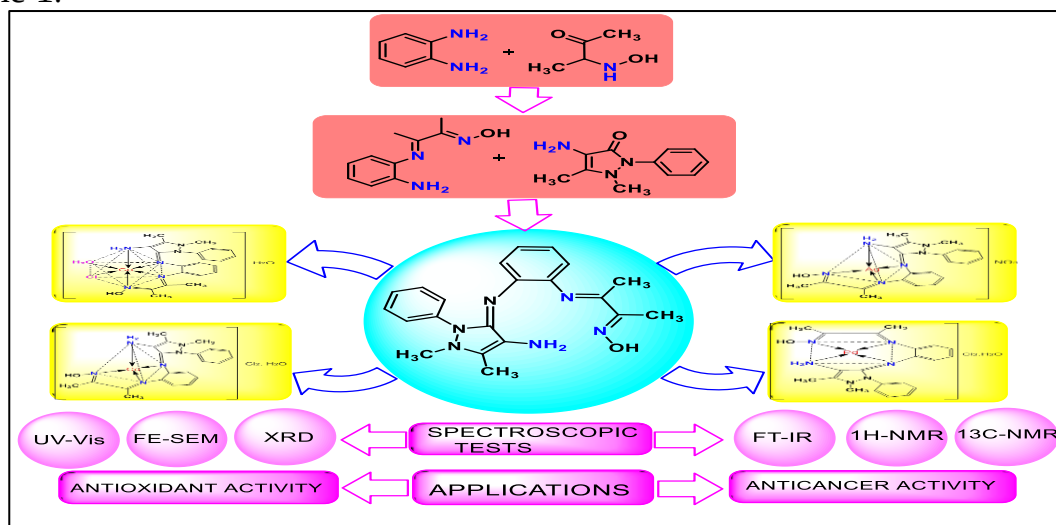
Preparation of the ligand

First, prepare the compound [(2E)-3- ((2-aminophenyl)imino)butan-2-one oxime]. From taking (0.05 mol) of Diacetyl monoxime dissolved in 30 mL of ethanol, add 8-6 drops of GAA. Another cup is taken (0.01 mol) O-phenyldiamine in 30 mL of ethanol. The two solutions are mixed and the reflux process is carried out for 8-6 hours. The resultant product is subjected to a drying process, The resulting precipitate is dried and purified by recrystallization using absolute ethanol as a solvent, followed by further drying. Second: The same amount of Schiff base from the first stage is taken and dissolved in 30 mL of ethanol and 8-6 drops of glacial acetic acid are added to it. Another cup (0.01 mol) of 4-aminoantipyrine is dissolved in 30mL of ethanol. The two compounds are combined. The reflux procedure is conducted for a duration of 6 to 8 hours. The substance is obtained as a precipitate through a process of drying, purification through recrystallization, and subsequent drying. It was found that its color is brown, the percentage of pure product is 90%, and its melting point is 141°C [22].

Synthesis of Metal Complexes

Prepare complexes at a ratio of M:L (1:1) by dissolving 0.5 mmol of ligand in 10 mL of ethanol, adding 0.5 mmol of transition metal salts Cl or NO_3 solution and dissolving it in 10 mL of ethanol ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, AgNO_3 , $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$, PdCl_2). The reaction was carried out in a basic medium of NaOH 10 mmol. The reflux process is carried out, then the mixture is cooled, filtered and dried, and then recrystallized,

to obtain a pure colored precipitate of metal ion complexes [23], as shown in Scheme 1.



Scheme(1): Graphical abstract

Measuring antioxidant Activity

To determine the effectiveness of these compounds as antioxidants and to measure the antioxidant activity by means of free radicals stabilized on the body's cells, the antioxidant Activity of the ligand and silver complex was measured. Concentrations of the samples were prepared (800, 400, 200, 100, 50, 25, 12.5) $\mu\text{g/mL}$, mixing 0.3 mL of the solutions prepared with a solution containing DPPH radicals in 2.7 mL of methanol so that the total volume became 3 mL. Thoroughly agitate the mixture and allow it to remain undisturbed for a duration of 60 minutes at ambient temperature. The assessment of DPPH radical scavenging activity involves the utilization of UV-Vis spectroscopy to measure the absorbance at a specific wavelength of 517 nm. All values were repeated three independent times to extract an average of the values. The same previous steps were repeated for ascorbic acid to ensure the accuracy and validity of the results. The percentage of antioxidant activity %RSA was calculated to determine the IC_{50} inhibitory concentration value. The lower the IC_{50} value, the higher the antioxidant efficiency. %RSA values were obtained using Graph Pad Prism 8.3.1 software [24].

3.Results and Discussion

By reacting diacetylmonoxaime with rthophenyldiamine as a first step, then reacting the product with 4-amino antipyrine as a second step, the new compound was prepared, which reacted with both metal chlorides and silver nitrate dissolved in ethanol. The Cu(II), Ag(I), Cd(II), and Pd(II) complexes were synthesized at a M:L ratio of 1:1. The physical characteristics and elemental analysis of all ligands and complexes are presented in Table 1.

Table (1): Physical properties and elemental analysis C.H.N for ligand and its complexes

Compound (Chemical Formula)	Color	M. P (°C)	Yield %	M.wt g/mol	Calc. (Found)%			
					C	H	N	M
Ligand C ₂₁ H ₂₄ N ₆ O	brown	140-141	90	376.50	67.00 (68.15)	6.43 (7.76)	22.32 (23.44)	(----) (----)
[Cu(L)Cl ₂].H ₂ O C ₂₁ H ₂₆ Cl ₂ CuN ₆ O ₂	black	155-157	75	529.02	48.00 (49.37)	5.01 (6.23)	16.02 (17.55)	12.01 (12.77)
[Ag(L)].NO ₃ C ₂₁ H ₂₄ AgN ₇ O ₄	Dark brown	164-166	68	546.32	46.17 (47.34)	4.42 (5.26)	18.01 (19.84)	19.74 (20.24)
[Cd(L)Cl ₂].H ₂ O C ₂₁ H ₂₆ Cl ₂ CdN ₆ O ₂	Dark brown	178-180	83	577.78	43.65 (44.73)	4.53 (5.62)	15.01 (16.23)	19.45 (20.85)
[Pd(L)Cl ₂].H ₂ O C ₂₁ H ₂₆ Cl ₂ PdN ₆ O ₂	brown	176-177	73	571.79	44.11 (45.27)	4.60 (5.81)	14.71 (15.64)	18.61 (19.56)

Infrared Spectra of Complexes

A comparison is made between the spectra of the new ligand complexes and the spectrum of the ligand. Table 2 illustrates the phenomenon of band displacement, band disappearance, and band emergence. This observation signifies the presence of coordination relations between ions, metals, and bonds. The most important signal of the oxime azomethine group in the spectrum of the free ligand is at 1660 cm⁻¹, where it was shifted towards a lower frequency compared to the spectra of the complexes[25], as it gave a shift of 15-27 cm⁻¹ after coordination with the metal ions [26]. The appearance of broad aggregates at 3461, 3606, 3492 cm⁻¹ resulting from the overlap of the absorption band of the oxime hydroxyl group $\nu(\text{C}=\text{N}-\text{OH})$ with the hydroxyl group of in the spectra of all complexes of Cu(II), Pd(II), and Cd(II), respectively, while the absorption band of the oxidized hydroxyl group $\nu(\text{C}=\text{N}-\text{OH})$ appeared at 3447 cm⁻¹ in the Ag(I) complex [27].

Table (2): Infrared spectrum of the ligand and its metal complexes

Compound	$\nu(\text{O}-\text{H})$ (H ₂ O)	$\nu(\text{O}-\text{H})$ Oxime	$\nu(\text{N}-\text{H})$ 2°amine	$\nu(\text{C}-\text{H})$ aromatic	$\nu(\text{C}-\text{H})$ aliphatic	$\nu(\text{C}=\text{N})$ Imine, Oxime	$\nu(\text{C}=\text{C})$ aromatic	$\nu(\text{M}-\text{N})$
Ligand	-----	3394.48	3365.05	3047.32	2893.02 2808.16	1660.52	1589.23 1458.08	-----
Cu-L complex	3461.93 Overlap		3321.28	3053.16	2978 2850	1645.28	1589.34 1435.04	491.85 447.49
Ag-L complex	-----	3447.13	3334.14	3043.34	2834.14	1633.71	1585.49 1435.04	513.07 412.71
Cd-L complex	3606.89	3390.86	3321.42	3032.71	2930.02 2893.02	1633.71	1591.27 1429.25	489.92 422.41
Pd-L complex	3492.71 Overlap		3341.63	3072.40	2807.54	1633.71	1590.42 1440.83	495.71 412.77

The ^1H -NMR Spectra of the Ligand

The ^1H -NMR spectrum of the ligand, using DMSO-d_6 as a solvent and TMS, shows the appearance in the ligand spectrum of a signal (s, 3H, $\delta = 1.93\text{ppm}$) protons of the methyl group CH_3 - of the pyrazole ring. The signal is (s, 6H, $\delta = 2.10\text{--}2.11\text{ppm}$) then it returns to the other methyl group attached to azomethine [28]. Signal (s, 3H, $\delta = 3.02\text{ ppm}$) proton of the methyl group attached to the nitrogen atom of the pyrazole ring. Signals (M, 4H, $\delta = 7.74\text{--}7.23\text{ ppm}$) appeared for the protons of the phenyl ring belonging to O-phenyldiamine. Signals appeared (M, 5H, $\delta = 7.46\text{--}7.35\text{ ppm}$) for the protons of the phenyl ring of the pyrazole, a signal (s, 1H, $\delta = 9.12\text{ ppm}$) for the two protons of the secondary amine group $-\text{NH}_2$ [29]. the appearance of a signal (s, 1H, $\delta = 11.45\text{ ppm}$) for the protons of the oxime hydroxyl group.

The ^{13}C -NMR Spectra of the Ligand

The ^{13}C -NMR spectrum of the ligand gives a signal at (9.83 ppm) belonging to the carbon atom (C27) of the methyl group attached to the oxime group, and a signal at (10.37 ppm) dating back to the carbon atom (C24) of the methyl group (CH_3 -) attached to the pyrazole ring. The signal at (23.23 ppm) belongs to the carbon atom (C4) of the methyl group (CH_3 -) attached to the azomethine group [30]. The signal (38.72 ppm) belongs to the carbon atom (C25) of the methyl group (CH_3 -) linked to the nitrogen atom of the pyrazole ring, while the signals at 125.61-122.33 ppm belong to the carbon atoms (C11-C8) of the phenyl ring linked to the two azomethine groups, and signals appear At (123.87-125.61 ppm) the carbon atoms (C23-C19) belong to the phenyl group attached to the nitrogen atom of the pyrazole ring. A signal at (135.40 ppm) belongs to the carbon atom (C17) of the pyrazole ring attached to the methyl group. A signal at (136.03 ppm) belongs to an atom. The carbon (C18) of the phenyl ring linked to the nitrogen atom of the pyrazole ring, a signal at (140.39 ppm) which belongs to the (C7) carbon atom of the phenyl ring linked to the azomethine group and the carbon atom (C6) of the phenyl ring linked to the azomethine group linked to the pyrazole ring. [31]. The signal (152.80 ppm) belongs to the C15 carbon atom of the pyrazole ring. A signal at (153.56 ppm) belongs to the carbon atom (C2) of the oxime group, and finally the spectrum showed a signal at (161.88 ppm) belonging to the carbon atom (C3) of the azomethine group attached to the methyl group[32]. As in the figure1,2 below.

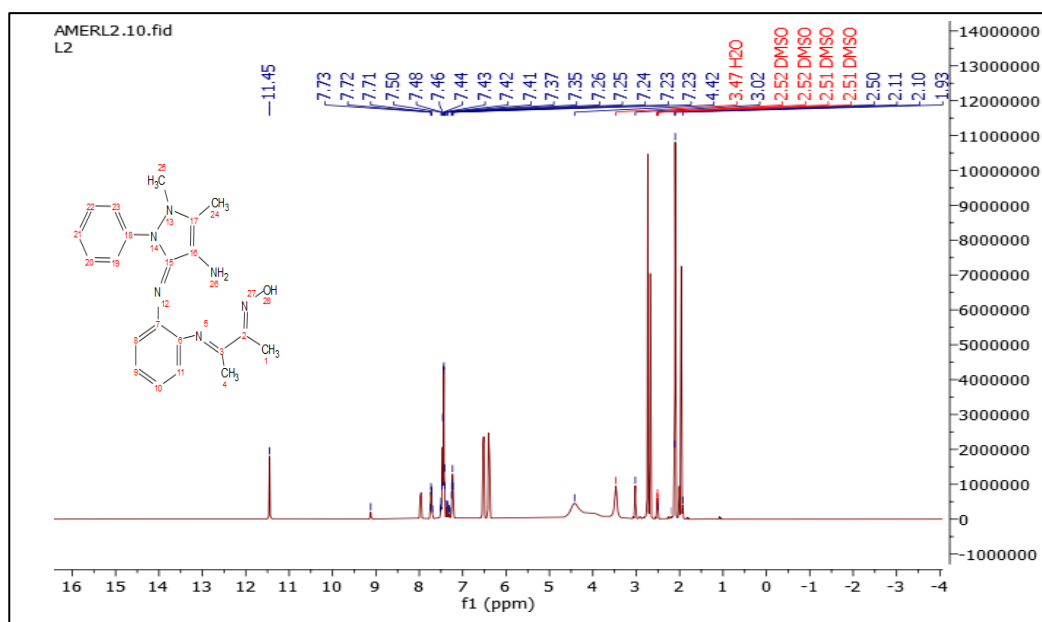


Figure (1): ^1H -NMR spectrum of ligand in DMSO-d_6 solvent

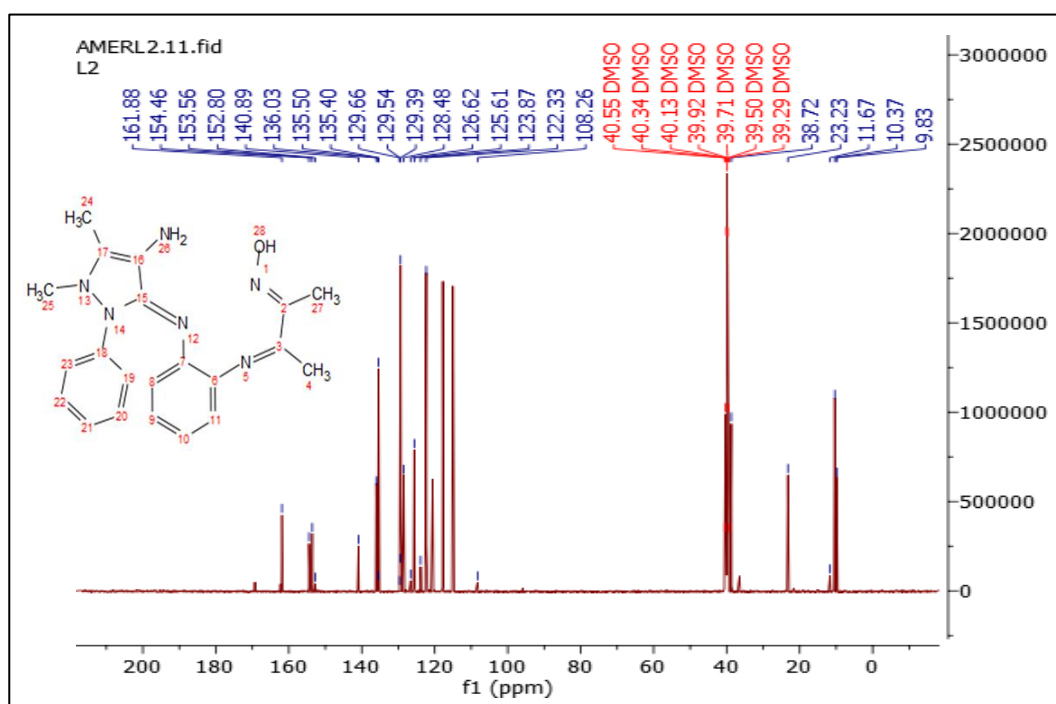


Figure (2): ^{13}C -NMR spectrum of ligand in DMSO-d_6 solvent

Electronic Spectra and conductivity of ligand and its complexes

The ligand spectrum shows three absorption peaks at 47393 cm^{-1} and 41322 cm^{-1} , which belong to the transitions $\pi\text{-}\pi^*$ and 29585 cm^{-1} , which belong to the transitions $\text{n-}\pi^*$ belonging to the azomethine group ($\text{C}=\text{N}$) [33]. The spectrum of the Cu(II) complex showed absorption peaks at 45871 cm^{-1} , 39840 cm^{-1} and 29239 cm^{-1} dating back to the ligand field spectrum. The appearance of a broad absorption peak

at 15290 cm^{-1} dating back to the ${}^2B_{1g} \rightarrow {}^2E_g$ transition. Show The peak results from the overlap of three peaks in the octahedral field due to the distortion occurring in this type of complex as a result of the Jan Teller effect [34]. The absence of (d-d) transitions in the electronic spectra of Ag(I) and Cd(II) complexes can be attributed to the saturation of electrons in the (d) orbitals. Consequently, the electronic spectra of these complexes are not suitable for determining their structure and stereoscopic shape [35]. These complexes showed peaks in the range ($46728\text{--}30287\text{ cm}^{-1}$) that belong to the ligand field. As for the peaks ($25575, 25316\text{ cm}^{-1}$) in the Ag(I) and Cd(II) complexes respectively, these indicate charge transfers of the (M-L) [36]. The appearance of absorption peaks for the pd(II) complex indicating the ligand domain at 47393 cm^{-1} , 36101 cm^{-1} and 26595 cm^{-1} . While the absorption peaks at 20366 cm^{-1} , 17006 cm^{-1} and 16103 cm^{-1} indicate the electronic transitions ${}^1A_{1g} \rightarrow {}^1E_g$, ${}^1A_{1g} \rightarrow {}^1B_{1g}$, and ${}^1A_{1g} \rightarrow {}^1A_{2g}$, respectively, so it turns out that the shape of the complex is a square planar (II). It has diamagnetic properties [37], As shown in Table 3.

Table (3): UV-Vis spectrum values, magnetic properties, geometric structure, and hybridization of ligand and its metal complexes

Compounds	λ (nm)	ν (cm^{-1})	Transitions	μ_{eff} (B.M)	Geometry
Ligand	211 242 338	47393 41322 29585	$\pi\text{--}\pi^*$ $\pi\text{--}\pi^*$ $n\text{--}\pi^*$	—	—
[Cu(L)Cl ₂].H ₂ O	218 251 342 654	45871 39840 29239 15290	Ligand Field Ligand Field Ligand Field ${}^2B_{1g} \rightarrow {}^2E_g$	(Para.) 1.79	Octahedral sp^3d^2 distorted
[Ag(L)].NO ₃	217 244 327 391	46082 40983 30581 25575	Ligand Field Ligand Field Ligand Field Charge transfer (MLCT)	(Dia.)	Tetrahedral sp^3
[Cd(L)]Cl ₂ .H ₂ O	214 237 328 395	46728 42194 30287 25316	Ligand Field Ligand Field Ligand Field Charge transfer (MLCT)	(Dia.)	Tetrahedral sp^3
[Pd(L)]Cl ₂ .H ₂ O	211 277 376 491 588 621	47393 36101 26595 20366 17006 16103	Ligand Field Ligand Field Ligand Field ${}^1A_{1g} \rightarrow {}^1E_g$ ${}^1A_{1g} \rightarrow {}^1B_{1g}$ ${}^1A_{1g} \rightarrow {}^1A_{2g}$	(Dia.)	Square planar dsp^2

Ray Diffraction Analysis

The spectrum of the ligand has a crystalline structure because all the peaks were sharp, as well as its complexes, including Cu(II) complexes, in which the crystalline structure is dominant because there are very many sharp peaks, while the spectra of

the Cd(II), Pd(II) and Ag(I) complexes showed Sharper peaks so it is crystalline. Upon conducting a comparison between the intensities and positions of the peaks observed in the acquired findings and those indicated by the international standard cards, it becomes evident that these observed locations can be attributed to the presence of basic chemicals. Likewise, no strange location or peak was observed dating back to a substance that is not present in the basic compounds, as in Figure 3 and Table 3 [39,38].

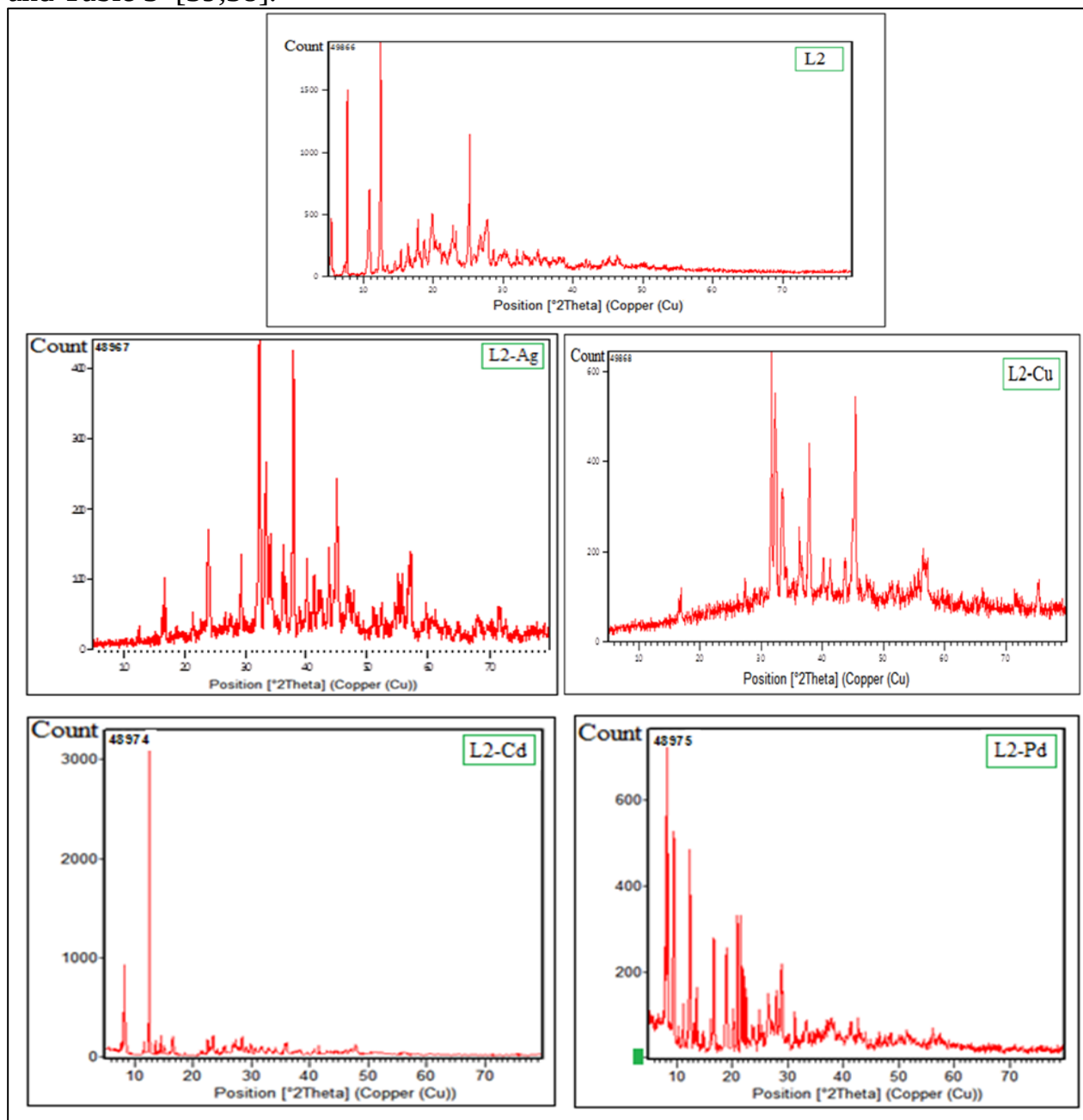


Figure (3): XRD diffraction spectra of ligand and its metal complexes

Table (3): Crystallographic data for the ligand and its complexes

Compound	No.	Peak Position $^{\circ}2\theta$	d-spacing (Å)	Rel. Int. [%]	Height [cts]	FWHM	Width	Crystallite Size. (nm)	Lattice Strain
Ligand $C_{21}H_{24}N_6O$	1	5.397	0.2134	24.93	422.78	0.213	0.1065	37.33853592	0.043804432
	2	7.599	0.0280	100.00	1695.73	0.028	0.014	84.3495948	0.008113654
	3	10.795	0.1452	61.28	1039.19	0.145	0.0725	55.03220905	0.059778191
	4	12.458	0.2328	86.30	1463.47	0.233	0.1165	34.29815134	0.110964676
	5	25.119	0.1300	87.12	1477.33	0.13	0.065	62.60808215	0.126370456
[Cu (L) Cl.H ₂ O]	1	31.66	0.0100	100.00	308567.50	0.01	0.005	825.7450374	0.012371639
	2	32.245	0.1447	0.21	645.08	0.145	0.0725	57.03122809	0.182883416
	3	33.42	0.5138	0.14	429.14	0.514	0.257	16.13725389	0.673283361
	4	37.828	0.3150	0.17	513.51	0.315	0.1575	26.65940834	0.470953555
	5	45.409	0.2236	0.22	690.55	0.224	0.112	38.44474465	0.408938942
[Ag (L)]NO ₃	1	23.954	0.2848	38.11	217.74	0.285	0.1425	28.49500657	0.263802393
	2	32.278	0.2910	100.00	571.34	0.291	0.1455	28.4199892	0.367424339
	3	33.467	0.2464	60.11	343.44	0.246	0.123	33.72183182	0.322712876
	4	37.834	0.2192	96.21	549.71	0.219	0.1095	38.34641236	0.327480761
	5	45.012	0.3025	55.03	314.41	0.302	0.151	28.47420369	0.545980655
[Cd(L)]Cl.H ₂ O	1	18.667	0.2695	26.19	386.95	0.27	0.135	29.81805203	0.193628178
	2	19.843	0.3341	43.89	648.43	0.334	0.167	24.14641229	0.254911838
	3	22.778	0.2090	35.38	522.61	0.209	0.1045	38.77445599	0.183696067
	4	25.119	0.1300	100.00	1477.33	0.13	0.065	62.60808215	0.126370456
	5	27.662	0.0186	41.11	607.38	0.019	0.0095	43.6058573	0.020410532
[Pd(L)]Cl.H ₂ O	1	5.384	0.0100	100.00	4578.25	0.104	0.052	76.47178536	0.021336485
	2	7.599	0.0285	42.36	1939.16	0.028	0.014	84.3495948	0.008113654
	3	17.7	0.1542	4.09	187.15	0.01	0.005	80.0009345	0.006793776
	4	22.74	0.3504	10.13	463.95	0.01	0.005	81.3320458	0.00877423
	5	46.407	0.2141	4.78	218.67	0.214	0.107	40.38993639	0.400273773

Field-Emission Scanning Electron Microscope

The ligand surface morphological features, shape, and size of the granules are also assessed using scanning microscopy technology [40]. It was discovered that the ligand contains some Spherical shape, average particle size 69.26 nm. As for the FESEM image of Ag(I) Complexes of heterogeneous granular and spherical shape appear Average particle size 47.71 nm, FESEM image of Cu(II) complexes have conical shapes and an average particle size of 82.09 nm. While FESEM images of Cd(II) and Pd(II) complexes showed heterogeneous crystals with an average size of 79.12 nm and 77.85 nm, respectively. Materials of interest that are crystalline, granular, and nano scale in nature because of the possibility of making use of them in the fields of industrial, thermal, electrical conduction, or medicine Pharmacy,

such as treating some cancerous tumors or some dangerous bacteria[41]. as shown in the figure 4.

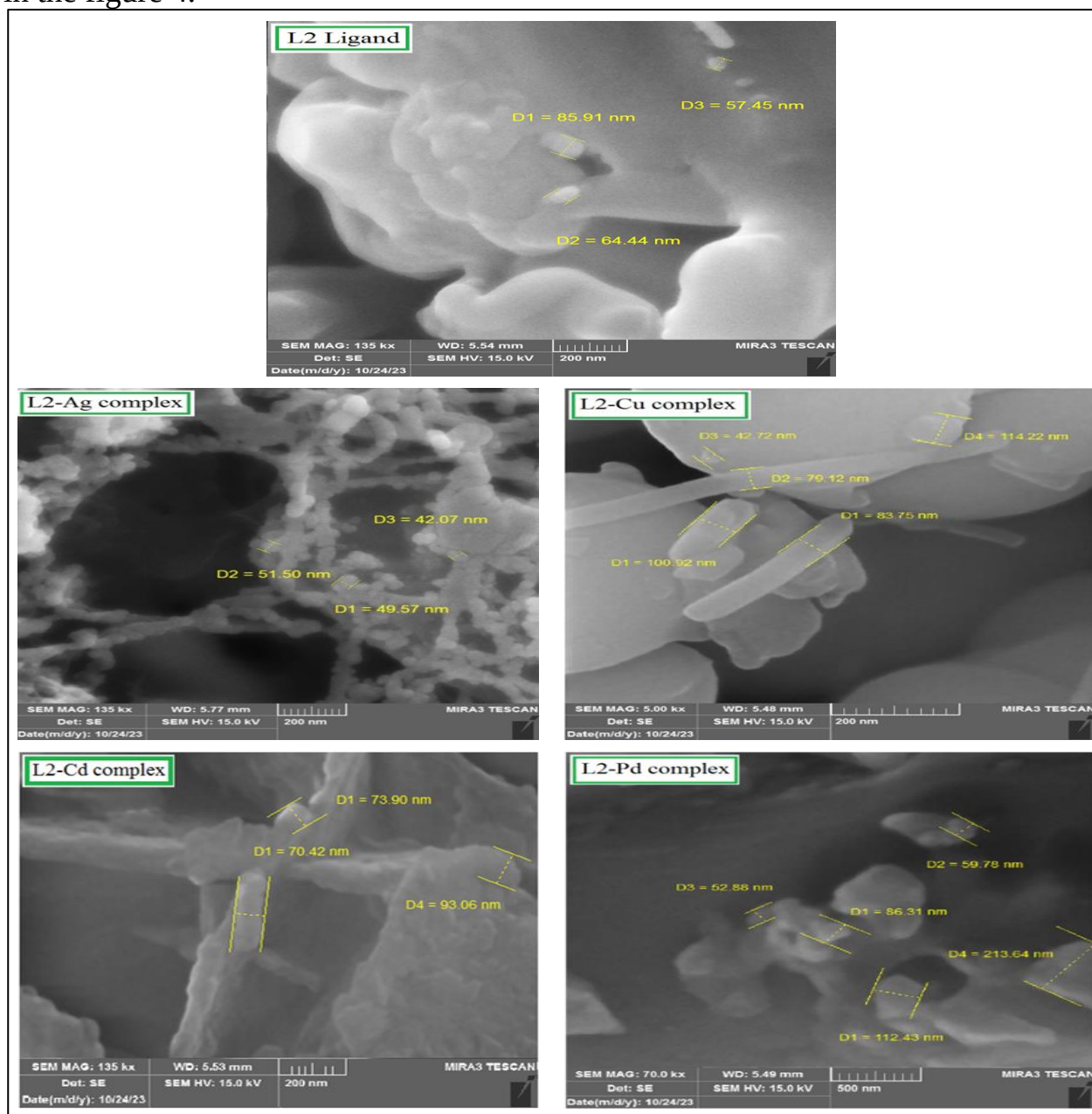


figure (4): FESEM images of ligand and metal complexes

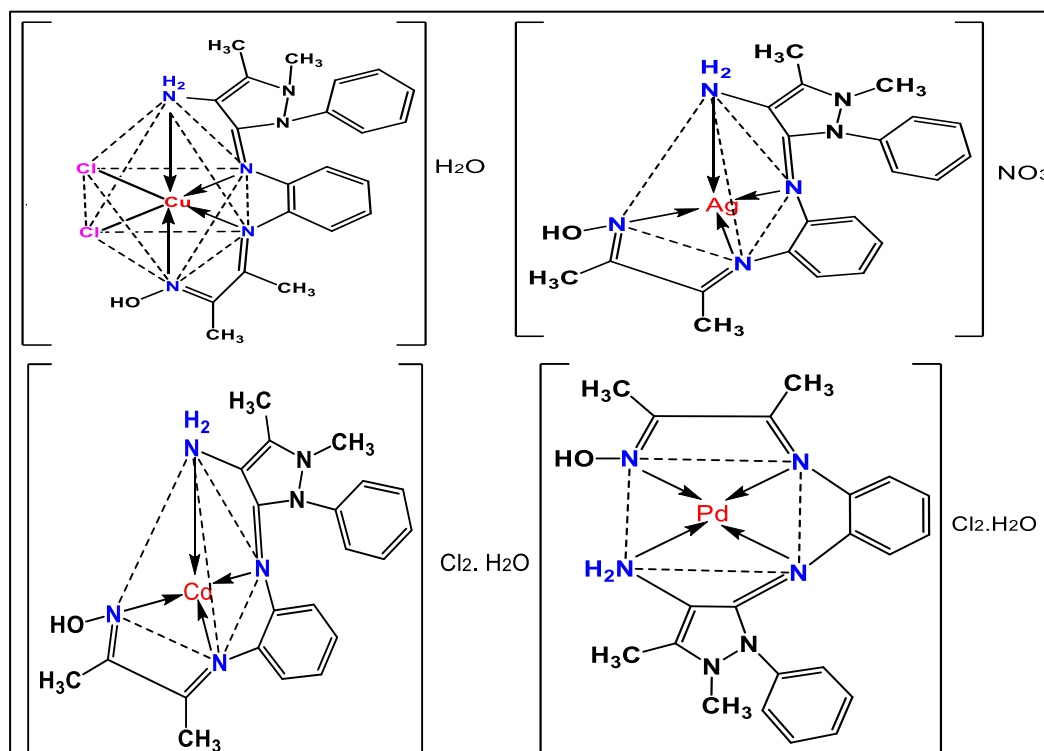


Figure (5): The proposed stereoscopic shape of the ligand complexes of Cu(II), Ag(I), Cd(II), and Pd(II)

4. Applications

Antioxidant Activity

The efficacy of this test is contingent upon the DPPH radical return ratio. The color response of the radical DPPH, which exhibits a dark violet hue, indicates the existence of an antioxidant chemical that can donate an electron or a hydrogen radical [42]. It then turns into a stable molecule DPPH-H, which is a yellow solid [43]. It is calculated from the percentage inhibition rates as a function of concentration. solution, and this result is expressed in terms of the Inhibition Concentration Fifty IC_{50} , which is defined as the amount of antioxidants needed to inhibit %50 of the free radical DPPH and is inversely proportional to the amount of antioxidants, meaning that a low IC_{50} value indicates high antioxidant activity[44]. The ligand test was conducted with the Ag(I) complex and showed high antioxidant activity towards DPPH. Higher inhibition The percentage of compounds prepared at a concentration of 800 $\mu\text{g/mL}$ ranged between %71.71-81.32. While the lowest rate of inhibition was At a concentration of 12.5 g/mL , it ranges between %2.86-3.10. The IC_{50} value for the ligand is 130.06, while the IC_{50} value for the Ag(I) complex is

309.91. The lower the IC_{50} value, the greater the antioxidant capacity. Therefore, the ligand is considered better than the silver complex as an antioxidant., as shown in Table 4 and Figure 6.

Table (4): Inhibition percentage of ligand and Ag(I) complex with concentration

No.	Concentration $\mu\text{g/ml}$	L2 Ligand	Ag(I) complex
		%RSA	%RSA
1	800	81.3201	71.7105
2	400	78.8534	59.7105
3	200	65.8037	45.9581
4	100	27.2513	34.4152
5	50	10.6791	23.9772
6	25	4.35554	11.9772
7	12.5	2.86932	3.10096
	IC_{50}	130.06	301.91

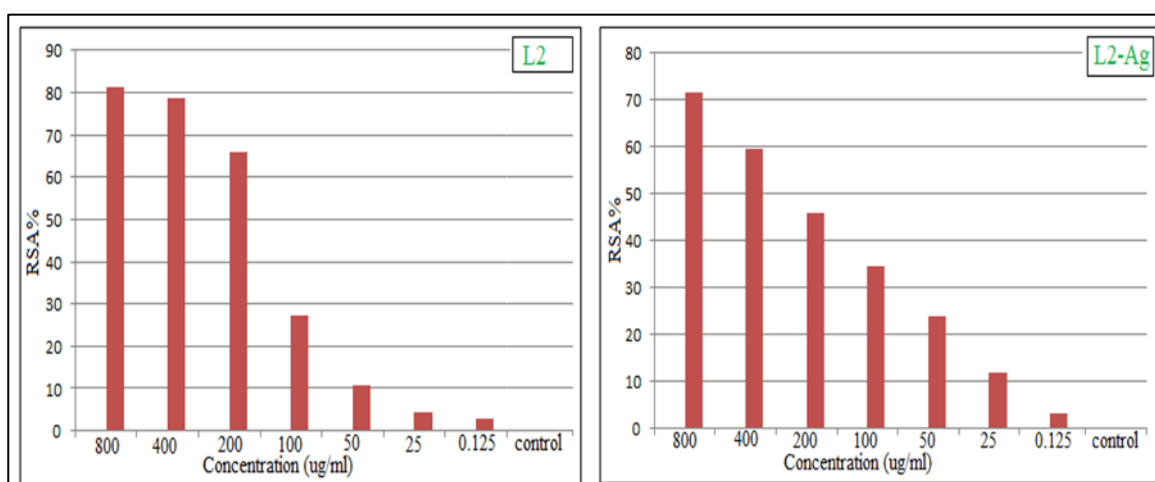


Figure (6): shows the comparison of the antioxidant activity of the ligand with the Ag (I) complex

Anticancer Activity

Conduct an MTT cytotoxicity test for each Free ligand and Ag(I) complex on MCF-7 breast cancer cell line because it is one of the most common types of cancer in women and leukemia line HL-60. By integrating MCF-7 cancer cells and HL-60 leukemia cells separately with cells prepared at 5% CO_2 in the atmosphere and 37°C for 24 hours at concentrations ranging From (500-5) $\mu\text{g/mL}$ and using an ELISA device, the absorbance was calculated at a wavelength of 570 nm, and the Inhibition Concentration Fifty IC_{50} was calculated. The percentage of inhibition of HL-60 cell line at the lowest concentration of 5 $\mu\text{g/mL}$ is 15.92727, 4.82 for the ligand and Ag(I) complex, respectively, of inhibition of MCF-7 cell line (9.38, 1.08%) for the ligand and the Ag(I) complex, respectively. while the percentage of inhibition of

HL-60 at the highest concentration of 500 $\mu\text{g/mL}$ for the ligand and Ag(I) complex is (87.1515, 92.0969%) respectively. The percentage of inhibition at MCF-7 the ligand and the Ag(I) complex is (56.07, 79.96%) respectively. The IC_{50} value for the HL-60 cell line for the ligand was 74.43 $\mu\text{g/mL}$, while for the Ag(I) complex it was 162.9 $\mu\text{g/mL}$. While the IC_{50} value for the MCF-7 cell line for the ligand is 443.8 $\mu\text{g/mL}$, while for the Ag(I) complex it is 316.8 $\mu\text{g/mL}$. The results showed that the toxic activity of the ligand against cancerous lines is better than the Ag(I) complex and this is evident from the IC_{50} value, as the lower its value, the better its toxic susceptibility.

Table (5): The effect of ligand and Ag(I) complex on (HL-60) and (MCF-7) cancer cells

Dose ($\mu\text{g/mL}$)	Cancer line cells HL-60				Cancer line cells MCF-7			
	Ligand		Ag(I) complex		Ligand		Ag(I) complex	
	Cell Viability Mean	% Cell Inhibition	Cell Viability Mean	% Cell Inhibition	Cell Viability Mean	% Cell Inhibition	Cell Viability Mean	% Cell Inhibition
0	100.00000	0.000000	100.00000	0.00000	100.000000	0.000000	100.000000	0.000000
5	84.0727272	15.92727	95.1757575	4.82425	90.6137184	9.38628	101.083032	-1.08303
10	85.8424242	14.15758	91.533333	8.46667	97.1720818	2.82792	117.689530	-17.68953
25	67.1757575	32.82425	89.1151515	10.88485	96.5102286	3.48977	108.002406	-8.00241
50	59.5878787	40.41213	92.7757575	7.22425	90.3128760	9.68712	104.632972	-4.63297
100	47.3454545	52.65455	64.5818181	35.41818	90.3128760	9.68712	95.4873646	4.51263
250	29.3818181	70.61811	39.0787878	60.92121	71.1793020	28.82069	67.3285198	32.67148
500	12.8484848	87.15152	7.90303030	92.09697	43.9229843	56.07702	20.0361010	79.96389
IC_{50}	74.43		162.9		443.8		316.8	

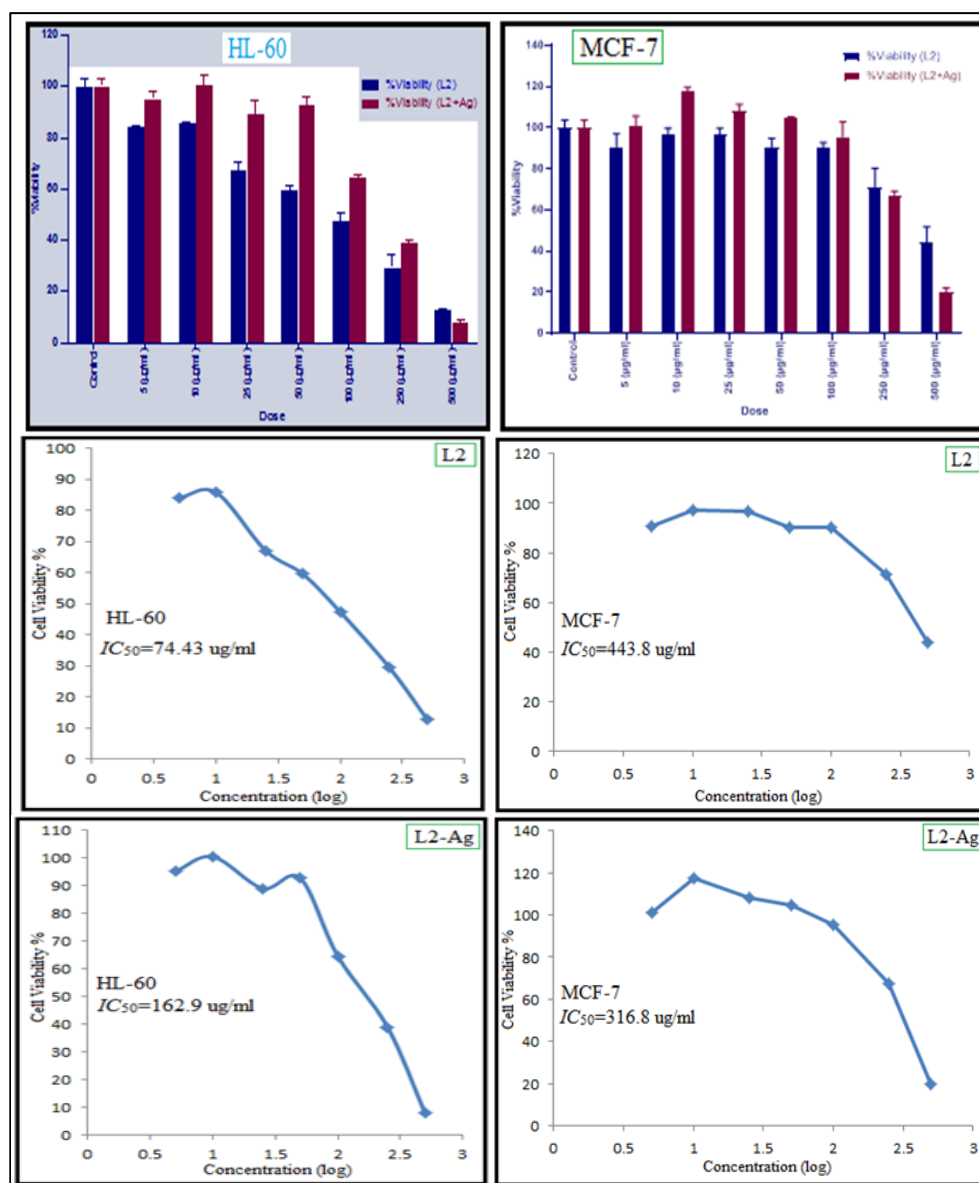


Figure (6): Comparison of HL-60, MCF-7 inhibition of ligand with Ag(I) complex with statement IC_{50} for both ligand and Ag(I) complex with HL-60 and MCF-7 cancer cells

5.Concluion

This paper has been prepared Complexes of tetra dentate ligand interaction with copper(II), silver(I), cadmium(II), and palladium(II) ions. Through spectroscopic methods, the method of bonding, geometric shape, and physical and chemical properties were determined. The molar ratio was examined and it was M:L 1:1. As for the biological effect, the ligand and the silver(I) complex were tested with leukemia (HL-60) and breast cancer (MCF-7) cell lines. The results showed that the inhibitory effect of the ligand was better than that of the silver complex

6.Ethical Clearance:

Permission for carrying out the study were obtained from the Department of chemistry, College of education/ University of Al- Qadisiyah, Iraq.

7.Financial Disclosure:

There is no financial disclosure.

8.Conflict of Interest:

None to declare.

9.References

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