

Preparation, Spectral and Biological Studies of Azo Ligand Derived from Proline with Cu(II), Ag(I) and Au(III) Metal Ion

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Abstract: In the present communication a synthesized ligand 4-[2-(1-methyl benzimidazolyl) azo] proline (MBP) was used to prepare three new complexes of Cu(II), Ag(I) and Au(III). The ligand and its complexes were characterized by elemental analysis (CHN), A.A, UV-Vis, FTIR and HNMR spectroscopy, magnetic susceptibility measurement, thermal analysis and molar conductivity measurement. Chloride ion content was also evaluated by Mohr method. The result was showed that the ligand was acted as N,N-bidentate. The preparation of the complexes was conducted after fixing the optimum concentration and pH. UV-Vis spectra of these complex solutions were investigated studied for a range of pH (5-9) and concentration (1×10^{-5} - 3×10^{-5}) which obey Lambert-Beers Law. The stoichiometry of the complexes was deduced according to mole ratio and Job methods which were obtained from spectroscopic studies of the complex solutions. The ratio of metal: ligand have been obtained was (1:2) for Cu(II) and Ag(I) complexes while Au(III) complex has (1:1) mole ratio. The antibacterial activities and dyeing achievement for the ligand and its complexes were test.

Keywords: Spectral studies, Proline, Benzimidazolyl azo, Antibacterial Activity, thermal analysis.

I. Introduction:

Azo compounds are one of the main varieties ligand that featuring by the presence of one or more azo moiety with lone pair of electron on the nitrogen atom activates a coordinating site for complexation with metal ion [1, 2]. And so this type of ligands were formed stable chelated complexes of five or six membered ring when there another coordination site at ortho position to azo moiety, which may be provided by the presence of donor atom like oxygen, nitrogen and sulfur on the aromatic rings or heterocyclic ring. The success of azo compounds is owing to the simplicity of their synthesis by diazotization and azo coupling as well as their excellent thermal and optical properties in many applications like toner [3], optical recording medium [4] and ink-jet printing [5]. Newly, azo metal chelates have similarly found excessive attention due to their significant electronic and geometrical buildings in joining with their use for molecular memory room [6]. In this effort, a ligand of azo moiety derivative from 2-amino-1-methylbenzimidazole as diazo component and proline as coupling agent, were prepared. The complexes of this ligand with metal ions [Cu(II), Ag(I), Au(III)] have been also prepared and described physicochemically. The antibacterial activities for the ligand and its complexes were tested as well as the dyeing achievement was also studied.

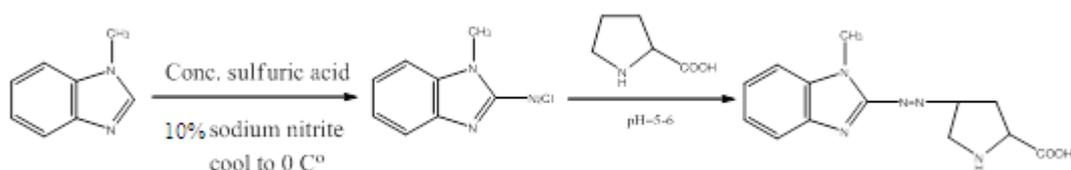
II. Experimental:

2.1 Materials and Instruments:

All substances and solvent are of top purity and used as found from the productions. Microelemental analysis (C.H.N) was gained on a (Eure EA 3000 Elemental analyzer) in Ibn AL- Haitham- College of Education For Pure Science . UV-Vis Spectra were performed in ethanol on a (Shimadzu UV-160A) ultra violet-visible spectrophotometer. FTIR-spectra were recorded on a (Shimadzu FTIR-8400s Fourier Transform Infrared) spectrophotometer ($200-4000$) cm^{-1} using CsI discs. The ¹HNMR spectra were gained on a (¹HNMR Spectrometer 400 MHz, Avance III 400 Bruker, Germany) in Isfahan University (Iran) using DMSO as a solvent. Conductivities were determined for (10^{-3} M) of complexes in DMSO at 25°C using (HANNA instruments / Conductivity Tester). pH measurement were performed using (HANNA instruments pH Tester / Pocket pH Tester). Melting points have been gained by using (Stuart Melting Point Apparatus). The percentage of metal in complexes was done in the University of Baghdad / College of Science using a "GBC 933 Plus" Flam Atomic Absorption Spectrophotometer.

2.2 Synthesis of 4-[2-(1-methylbenzimidazolyl)azo]proline (MBP):

Was synthesized according to the method reported in the literature [7] with some modifications as shown in scheme (1):



Scheme (1): preparation of MBP ligand

2.3 Preparation of the buffer solution:

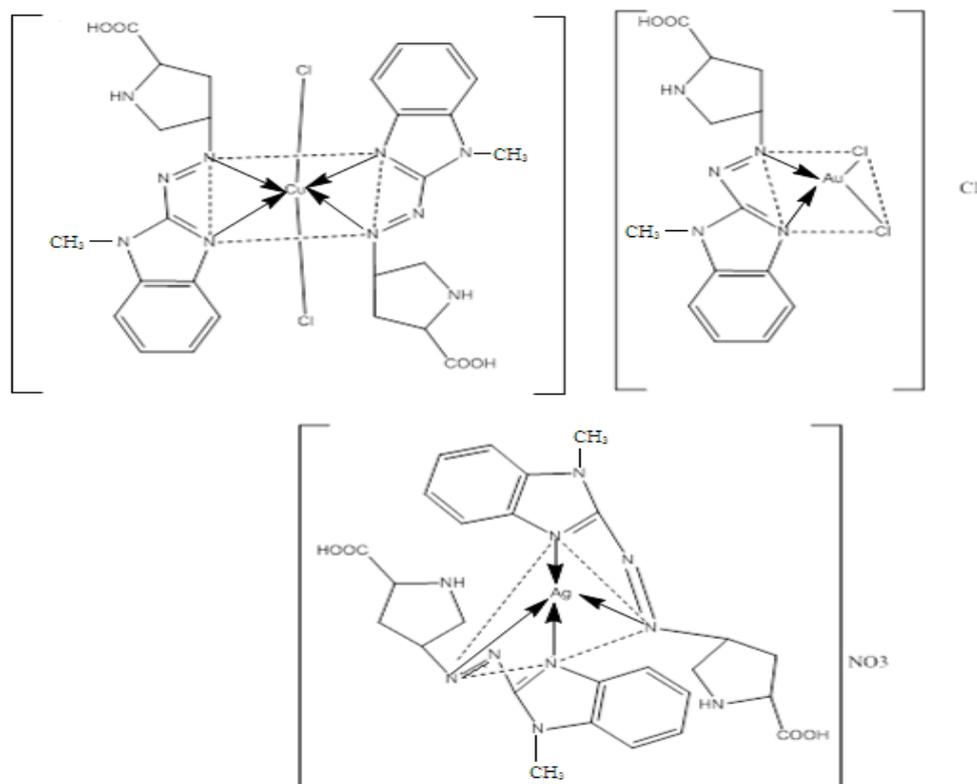
Buffer solutions, covering the pH values from 5 to 9, of acetic acid-ammonium acetate-ammonia (0.01M, 0.77gm) were prepared in one liter of deionized doubly distilled water.

2.4 Preparation of the standard solution:

The metal salt solutions (1×10^{-5} - 3×10^{-5}) were prepared via dissolving the appropriate weights of each of the following salts [CuCl₂, AgNO₃ and HAuCl₄.xH₂O] in the prepared buffer solutions. At the same time the range of concentration was used to prepare the ligand solutions which were obtained via dissolving the appropriate weight of (MBP) in ethanol.

2.5 Synthesis of complexes:

The complexes were prepared via adding gradually with stirring hot ethanolic solution of (2mmole) ligand to stoichiometry quantity of M: L ratio of (1:2) for [(Cu(II) and (Ag(II)) and (1:1) for [Au(III)] which were dissolved in the prepared buffer solution at optimum pH. The mixture was heated to (60°C) with stirring for (3 hour), then left to cool at room temperature. The colored precipitate was filtered, washed and desiccated in vacuum desiccator. The suggested stoichiometry structure of complexes is shown in scheme (2).



Scheme (2): the suggested structure for the prepared complexes.

III. Results And Discussions

The reaction of the prepared ligand (MBP) with selected metal ions [Cu(II), Ag(I) and Au(III)] at optimum concentration and pH, which leads to formation complexes with formula [Cu(MBP)₂Cl₂], [Ag(MBP)₂]NO₃ and [Au(MBP)Cl₂]Cl. The ligand acts as N,N'-chelator, where N(azo) and N'(imidazole). The

composition of the complexes is supported by the analytical and spectral studies results. All the prepared complexes were not hygroscopic, stable in air and soluble in most organic solvents like DMSO, DMF, acetone ...etc. The molar conductivity measurements of (10^{-3} M) in DMSO display non electrolyte for Cu(II) while Ag(I) and Au(III) have been shown (1:1) electrolyte, supporting the ionic behavior for Ag(I) and Au(III) complexes, Table (1).

Table (1): physical-chemical properties, elemental analysis, mole ratio, molar conductance for the ligand (MBP) and selected metal ions

Compounds (M.Wt) gm/mol	pH	M:L	M.P (% Yield)	Color	%Found %(Calculated)					Λ_m ($S.mol^{-1}.cm^2$)
					C	H	N	M	Cl	
MBP ($C_{13}H_{15}N_3O_2$) (274.13)	—	—	173 (85)	Orange	56.87 (56.907)	5.38 (5.471)	25.47 (25.535)	—	—	—
[Cu($C_{26}H_{30}N_{10}O_4$)Cl ₂] (682.7)	6	1:2	170 (66.88)	Violet	44.51 (45.7)	4.47 (4.39)	19.85 (20.5)	9.15 (9.30)	10.20 (10.39)	—
[Ag($C_{26}H_{30}N_{10}O_4$)]NO ₃ (718.13)	7	1:2	160 (70.77)	Purple	42.24 (43.44)	4.31 (4.17)	21.99 (21.4)	15.11 (15.02)	—	35
[Au($C_{13}H_{15}N_3O_2$)Cl ₂]Cl (577.6)	6.5	1:1	140 (76.98)	Orange	26.09 (27.015)	2.57 (2.597)	11.99 (12.57)	34.21 (34.10)	18.48 (18.43)	36

The UV-Vis spectra of the prepared ligand under investigation Fig. (1) shows mainly two peaks observed in DMSO (10^{-4} M) within the range (250-1100) nm. The first peak at (300) nm was assigned to the $\pi \rightarrow \pi^*$ transition of the aromatic rings. The second peak (λ_{max}) at (471) nm was related to the $\pi \rightarrow \pi^*$ transition of (GT) intermolecular charge-transfer taken place through the azo group (-N=N-), also showed shoulder band inherent to (λ_{max}) may be attributed to ($n \rightarrow \pi^*$) transition for (C=O) and (C=N) group[8].

It have been observed red shift in the visible region when a competitive study between the spectra of mixing aqueous solutions for [Cu(II), Ag(I) and Au(III)] with ethanolic solutions of ligand (MBP) as was shown in Figure (2). The change in the color of free ligand solutions and high shift in the (λ_{max}) gives a good indication for coordination and complex formation [9].

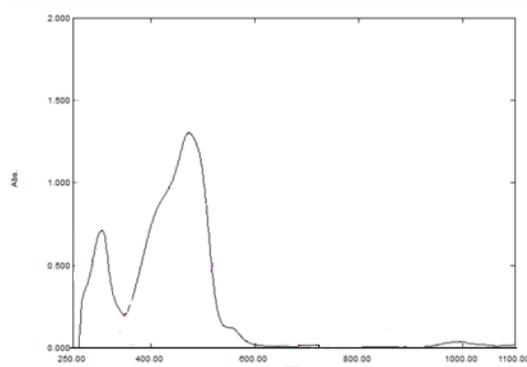


Fig. (1): UV-Vis spectrum of Ligand(MBP)

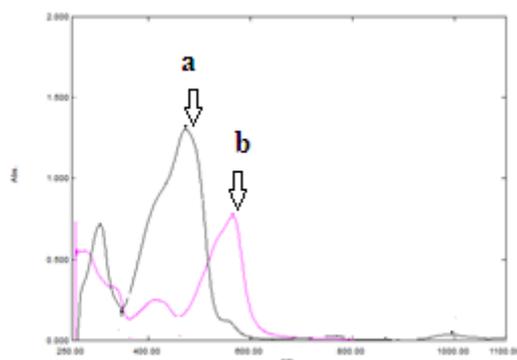


Fig. (2): UV-Vis spectra of solutions: a)ligand (MBP); b)[Cu(MBP)₂]Cl₂

The UV-Vis spectra were studied for mixed solutions of [Cu(II), Ag(I) and Au(III)] and ligand within the concentration range of (10^{-3} - 10^{-6}) molar, while the pH sequence was (5-9). Not all concentration suitable for spectral measurements. Whereas the solution in 10^{-5} M concentration followed Lambert-Beer's law and appeared

an obvious color. Fig. (3) was showed best fit straight lines, with correlation factor($r > 0.998$) when the absorbance plotted versus molar concentration in the rang (1×10^{-5} - 3×10^{-5}) molar.

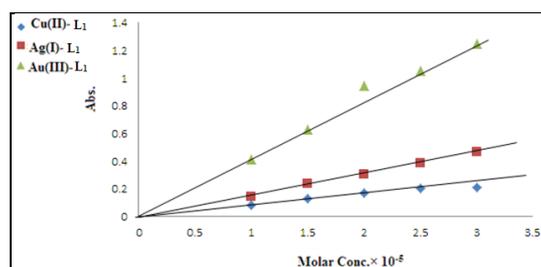


Fig.(3) : Linear relationship between molar concentration and absorbance for metal ions complexes at optimum pH and λ_{max} .

The optimum concentration for the complexes was taken when gave ascent to study (λ_{max}) at divers pH. The pH effect was also investigated at the range (5-9) Fig. (4) was showed the absorbance-pH curves which are completed at (λ_{max}) and several concentrations for each metal ion solution under study. A high band of the curves at the pH which was, it is considered as a mark of the complex formation and acceptance as optimum pH for preparation complexes. But the descent part of the curves may be due to the dissociation of complex. In doing so, we conclude that all prepared chelate complexes with selected metal ions are formed in neutral or basic medium [10, 11].

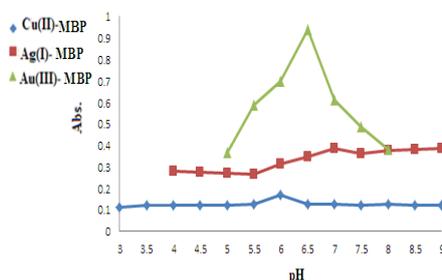


Fig.(4): Effect of pH on absorbance at λ_{max} for metal ions-MBP complexes solution.

The composition of complexes formed in solutions has been established by mole ratio and job methods[12]. In both cases the results reveal a mole ratio [M:L] [1:2] for [Cu(II) and Ag(II)] and [(1:1) for Au(II)] metal to ligand ratio. The two methods support same result about mole ratio of the complexes. Fig. (5 and 6) explain that:

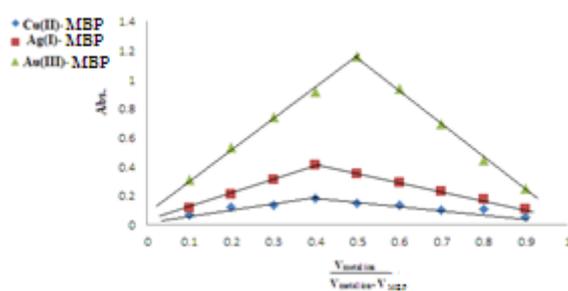


Fig.(5):Mole ratio plot of metal ion- MBP ligand complexes solution at optimum pH and λ_{max} .

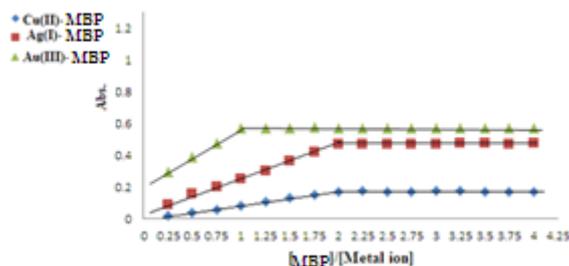


Fig. (6): Job Method plot of metal ion-MBP ligand complexes solution at optimum pH and λ_{max} .

3.1 Determination of Stability Constant and Gibbs Free Energy

The stability constant (K) for Cu(II) and Ag(I) complexes in a mole ratio (M:L)(1:2) was computed based on the equation

$$K = \frac{1-\alpha}{4\alpha^3 C^2}$$

As for the stability constant for Au(III) complex in a mole ratio (M:L) (1:1) was computed based on the equation :

$$K = \frac{1-\alpha}{\alpha^2 C}$$

Where:

$$\alpha = \frac{A_m - A_s}{A_m}$$

α = degree of dissociation.

A_s = the absorption of solution containing a stoichiometric volume of ligand and metal ion.

A_m = the absorption of solution containing the same volume of metal and excess of ligand.

c = the concentration of the complex solution in mole/ L.

from Table (2) we calculated that Cu(II) and Ag(I) complexes more stable than Au(III) complex. The thermodynamic parameters of Gibbs free energy (ΔG) were also studied. The ΔG data have been calculated from the equation below:

$$\Delta G = -R T \ln k$$

Where R = gas constant = 8.3 J.mol⁻¹.K, T = absolute temperature (Kelvin).

From Table (2) indicated that the prepared of all complexes are spontaneous.

Table (2): stability constant (K) and Gibbs free energy (ΔG) for the prepared complexes

Complexes	A_m	A_s	α	K	Log K	ΔG
[Cu(MBP) ₂ Cl ₂]	0.171	0.079	0.5380	1.8543×10 ⁹	9.26818	-53138.53125
[Ag(MBP) ₂]NO ₃	0.471	0.250	0.4692	2.0555×10 ⁹	9.31292	-53395.06319
[Au(MBP)Cl ₂]Cl	0.567	0.294	0.4814	7.4870×10 ⁴	4.87430	-27946.54857

3.2 Electronic Spectra and Magnetic measurement for solid complexes:

The UV-Vis spectrum Fig. (7) for Cu-Complex was shown three absorption bands. The first band at the (565nm, (17699)cm⁻¹). This transition is assigned to (²B_{1g}→²A_{1g}). The second band at (412nm, (24271) cm⁻¹) which is attributed to the transition (²B_{1g}→²B_{2g}). The third band at (276nm, (36231)cm⁻¹) is assigned to (²B_{1g}→²E_g). These three transitions are due to strong distortion octahedral (d⁹) to D_{4h} geometry with sp³d² hybridization Copper complex was showed paramagnetic property [13]. As for the Ag-complex (d¹⁰) diamagnetic, the UV-Vis spectrum Fig. (8)was shown a sharp splitting absorption band at (513 and 546)nm (19493 and 18315)cm⁻¹, which is assigned to transition ($\pi \rightarrow \pi^*$)(MLCT) with sp³ hybridization [14]. Recently in Au(III) complex the UV-Vis spectrum Fig. (9) for (d⁸) diamagnetic, lowspin square planer structure, sp³d hybridization were appeared (d-d) transition. [Au(MBP)Cl₂]Cl complex we observed three bands at (769, 557 and 485)nm, (13003, 17953 and 20618)cm⁻¹ which belong to the transition ¹A_{1g}→¹A_{2g}, ¹A_{1g}→¹E_g and ¹A_{1g}→¹B_{1g} respectively [15].

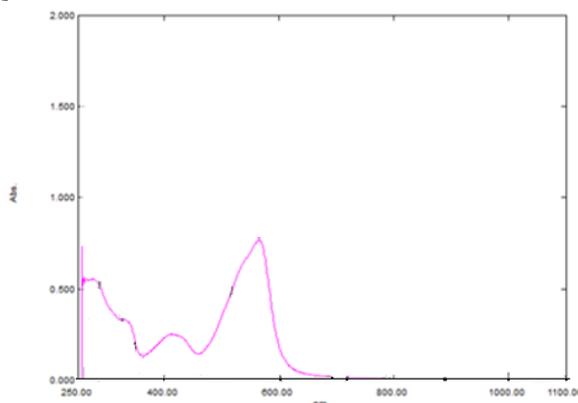


Fig.(7): UV-Vis spectrum of the Cu-MBP complex

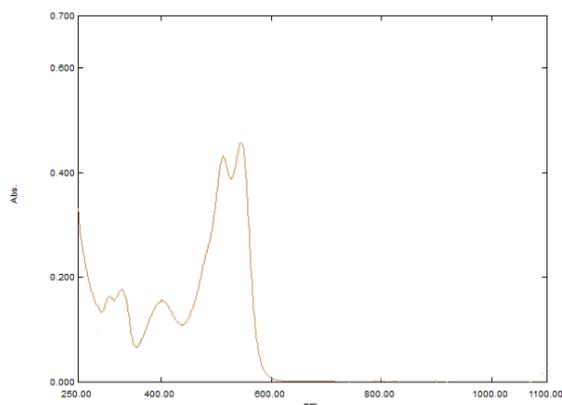


Fig.(8): UV-Vis spectrum of the Ag-MBP complex

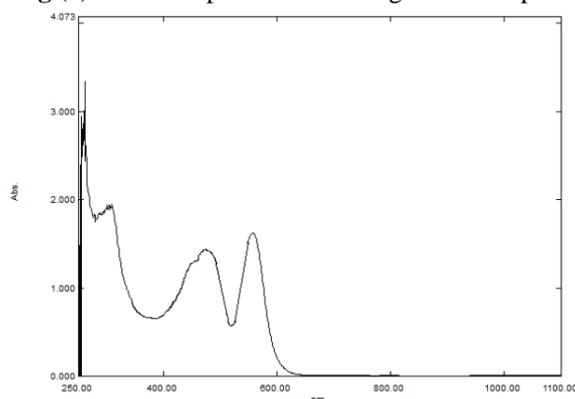


Fig.(9): UV-Vis spectrum of the Au-MBP complex

Table (3): the UV-Vis result and magnetic measurement

Compound	λ (nm)	Wave Number (cm^{-1})	$\epsilon_o \times 10^4$ $\text{L.mol}^{-1}.\text{cm}^{-1}$	Assignment
[Cu(MBP) ₂ Cl ₂]	565	17699	1.695	${}^2B_{1g} \rightarrow {}^2A_{1g}$
	412	24271	0.547	${}^2B_{1g} \rightarrow {}^2B_{2g}$
	276	36231	1.235	${}^2B_{1g} \rightarrow {}^2E_g$
[Ag(MBP) ₂]NO ₃	513	19493	0.460	$\pi \rightarrow \pi^*$ (MLCT)
	546	18315	0.430	$\pi \rightarrow \pi^*$ (MLCT)
[Au(MBP)Cl ₂]Cl	769	13003	0.013	${}^1A_{1g} \rightarrow {}^1A_{2g}$
	557	17953	1.622	${}^1A_{1g} \rightarrow {}^1E_g$
	485	20618	2.480	${}^1A_{1g} \rightarrow {}^1B_{1g}$

3.3 IR Spectra of prepared Ligands and Complexes:-

The FT-IR spectra for the complexes and ligand (MBP) in CsI Fig. (10-13) were compared them with some other for reaching to a binding sites. A broad medium band exhibited (3562 and 3425) cm^{-1} due to $\nu(\text{OH})$ and $\nu(\text{NH})$ in proline moiety. These band not affected on coordination but stay at nearly the same location [16]. The spectrum for the ligand appears a doublet bands at (1622 , 1602 and 1436 , 1404) cm^{-1} back to ($\text{C}=\text{N}$) and ($\text{N}=\text{N}$) respectively these two band were suffered some changes in location and shape in the spectra of the prepared ligand owing to coordinating meanwhile the N3 for benzimidazole moiety and nitrogen for azo moiety [17]. In addition there are new set of bands do not exist in the spectra of free prepared ligand but display in the spectra of the complexes such as $\nu(\text{M}-\text{N})_{\text{azo}}$, $\nu(\text{M}-\text{N})_{\text{im}}$, $\nu(\text{M}-\text{Cl})$ and ($\text{M}-\text{NO}_3$) [18]. These mention to the coordination places of the prepared ligands (MBP and BMP) with metals ion Table (4).

Table (4): FTIR for MBP and its Complexes

Compound	MBP	[Cu(MBP) ₂ Cl ₂]	[Ag(MBP) ₂]NO ₃	[Au(MBP)Cl ₂]Cl
$\nu(\text{N}-\text{H}_{\text{pro}})$	3562 m, br.	3558 br.	3562	3552 br.
$\nu(\text{O}-\text{H})$ in COOH	3425 m, br.	3421 br.	3425	3423 br.
$\nu(\text{N}-\text{H}_{\text{imd.}})$	—	—	—	—
$\nu(\text{C}-\text{H}_{\text{Ar.}})$	3058 br.	3053	3060	3059
$\nu(\text{C}-\text{H})$ of (CH ₃) in imidazole ring (L1)	3010 w.	3012	3011	3010

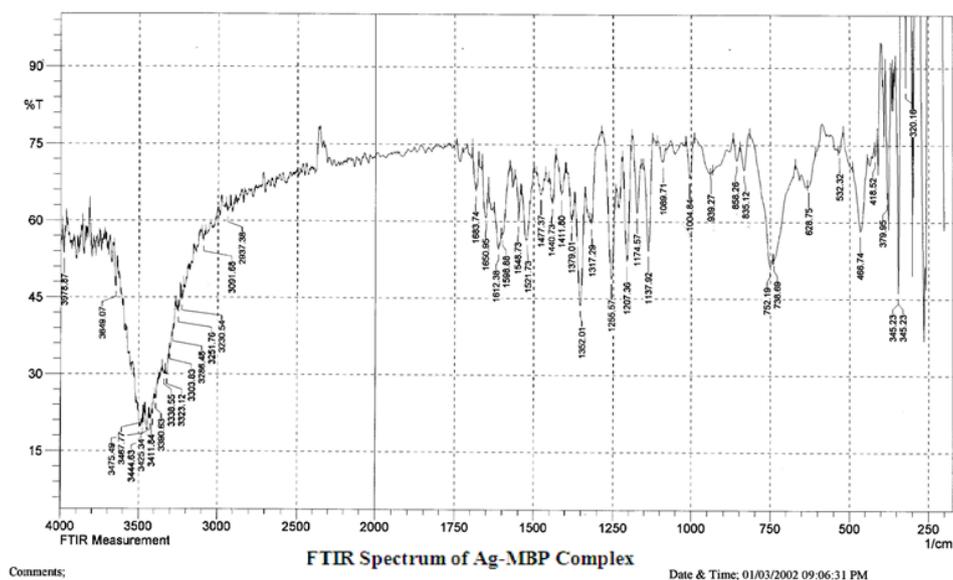


Fig. (12): FTIR spectrum of Ag-MBP complex

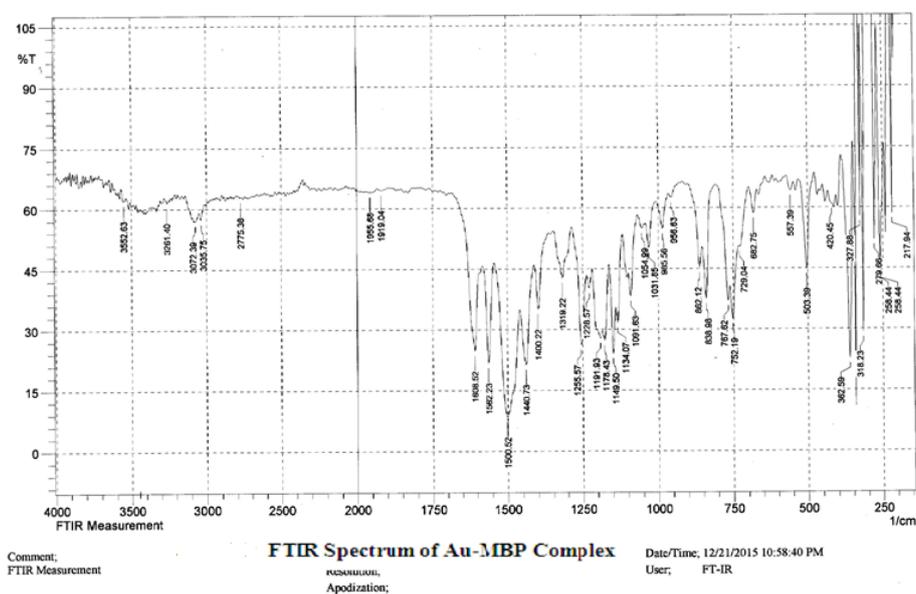


Fig. (13): FTIR spectrum of Au-MBP complex

3.4 ¹H NMR Spectrum:

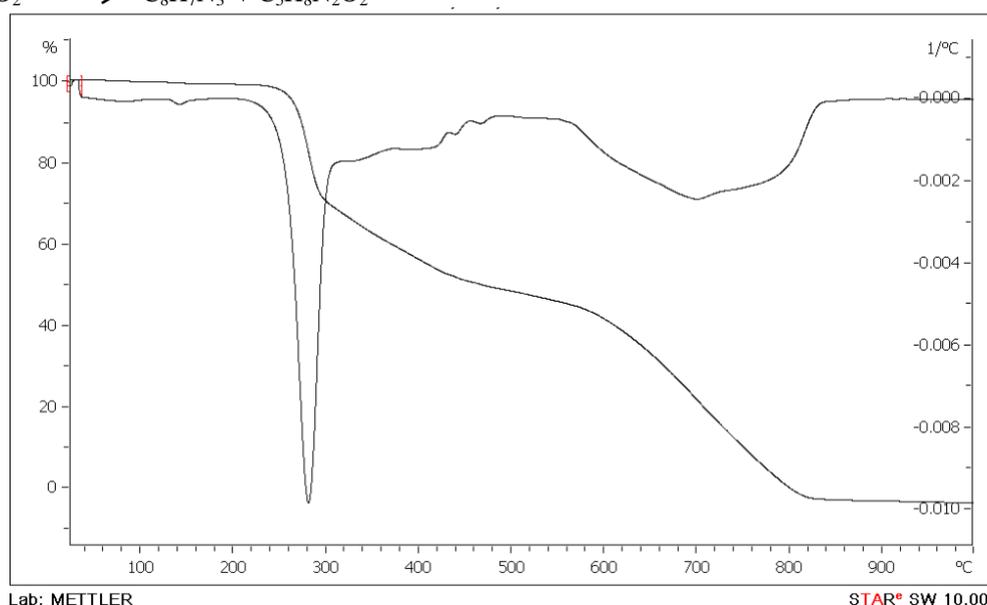
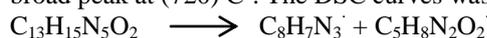
¹H NMR spectra for ligand (MBP) and its complexes with (Cu(II), Ag(I) and Au(III)) in DMSO are shown in Fig. (14- 17) and peak assignments are illustrated in Table (3-18). A singlet peak was appeared at $\delta(15.75)$ ppm in the spectra for ligand (MBP) which was due to one proton of free carboxyl moiety in proline [19]. This signal peak don't affect in coordination but stay almost without any chemical shift. The multiple signals noted in the region $\delta(8.45- 7.2)$ ppm for MBP, these were referred to aromatic proton (4H) in benzene ring in imidazole moiety. So light shift occur when complex formation. Moreover a singlet signal observed in the region $\delta(2.5)$ ppm for MBP which was attributed to (-NH) proton of proline [19], there is no shift was seemed in the position in the spectra of the complexes. Furthermore another signal peaks were appeared in the spectra of the prepared ligand (MBP) and its complexes which were described in Table(5):

Table (5): ¹HNMR spectra of MBP and its Complexes

Compound	-COOH	Ar-H	-CH ₃ (imd.)	-NH ₁ (Pro.)	Aliph-H ₁ (Pro.)
C ₁₃ H ₁₅ N ₅ O ₂ (L ₁)	15.75	(8.45-7.2)	3.47	2.5	(1.1-1.0)
[Cu(C ₂₆ H ₃₀ N ₁₀ O ₄)Cl ₂]	15.76	(8.4-7.0)	3.45	2.5	(1.1-1.0)
[Ag(C ₂₆ H ₃₀ N ₁₀ O ₄)]NO ₃	15.77	(8.40-6.9)	3.44	2.5	(1.1-1.0)
[Au(C ₁₃ H ₁₅ N ₅ O ₂)Cl ₂]Cl	15.73	(8.5-6.7)	3.45	2.5	(1.1-1.0)

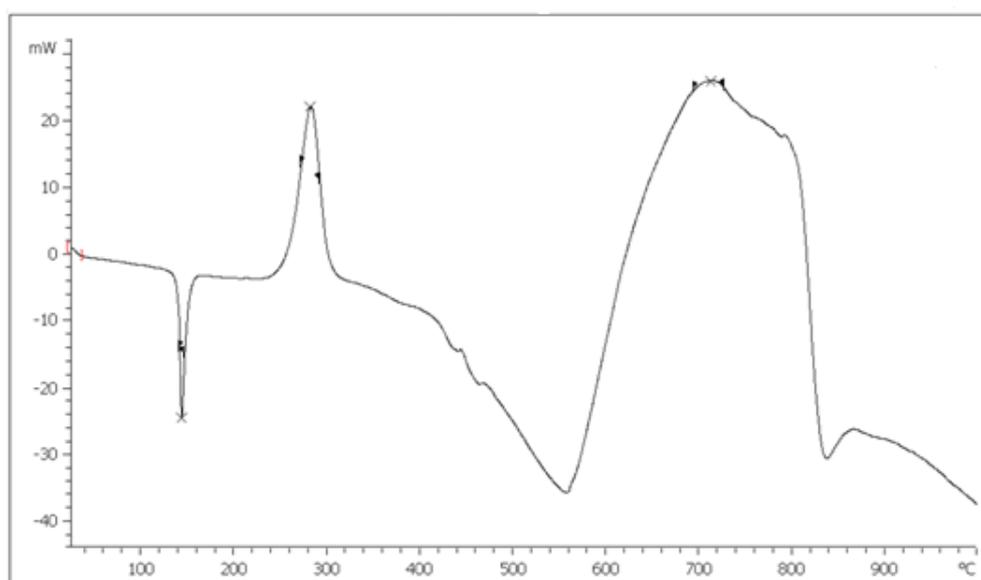
3.5 Thermal Analysis:

Figure (18) have been represented the thermogravimetric analysis (TG and DTG) curves temperature up to (900) C⁰ under helium as inert gas and differential scanning calorimetric (DSC) curves. The thermal decomposition for (MBP) ligand with formula (C₁₃H₁₅N₅O₂) explaining two decomposition step. The first step which was referred to mass loss of 6-methylbenzimidazole moiety and one nitrogen atom for the azo moiety by breakage the azo bond (-N=N-) around (40-520)C⁰ with an estimated loss (52.231%) (Calculated 52.702%) and DTG peak at (280) C⁰. This decomposition stage shows an endothermic peak at (142) C⁰ in the DSC curve. In the second thermal decomposition the second step referred to the mass loss of proline moiety and other nitrogen atom for azo moiety with an estimated mass (47.4287%) (Calculated 46.52%) around (520-860) C⁰ with DTG broad peak at (720) C⁰. The DSC curves was shown the exothermic peaks at (283) C⁰.



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Fig. (18): TG and DTG for MBP Ligand**Fig. (19):** DSC for MBP Ligand

3.6 Antibacterial Activity:-

Two kinds of bacteria were tested, Gram Negative Bacteria, *Escherichia Coli* (*E-Coli*), and Gram Positive Bacteria, *Staphylococcus Aureas* (*Staph.*). These bacteria were diagnosed and cultured on Nutrient Ager media for use in this experiment, and in measuring the deactivating capacity of the prepared compounds.

The deactivating capacity agent of the isolated bacteria of these compounds was tested by using the holes method. In this method the holes were saturated with 100 μ m of (10^{-4} M) of given compound and left for about 15 min in order to spread on the medium then incubated at 25 °C for 24 hours. The deactivated diameters were measured by a special rule designated for this purpose. Fig. (20) was shown that the ligand (MBP) and its complexes have good antibacterial activity towards the two type of tested bacteria when compared with ciprofloxacin. Table (6) included all data.

Table (6): Diameters (mm) of deactivation of bacteria of the ligands MBP and its complexes

No.	Compound	G+(Staph)	G-(E-Coli)
1	MBP	16	12
3	[Cu(MBP) ₂ Cl ₂]	12	18
5	[Ag(MBP) ₂]NO ₃	17	18
7	[Au(MBP)Cl ₂]Cl	15	15
9	Ciprofloxacin	18.15	18.5
10	Control (C)	0	0

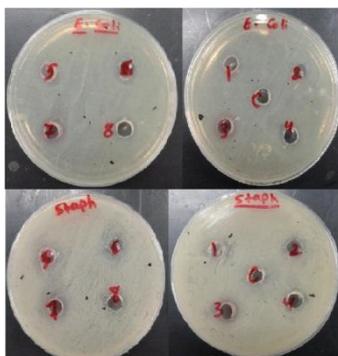


Fig. (20): biological activity of ligand MBP and its studied complexes

3.7 Dying performance:

The dying process of the ligand and its studied complexes were applied on wool fabric. These prepared dyes have been given colors in the rang orange, brown, red and purple. Fig. (21) with good luster and clear color on the fabric.



Fig. (21): Dying of Ligands (MBP) and its complexes.

IV. Conclusion

Cu(II), Ag(I) and Au(III) complexes with azo ligand (MBP) derived from 1-methyl-2-aminobenzimidazole as diazotized component and proline as a coupling component were synthesized and characterized by various physio-chemical methods. The analysis confirmed the structures and composition of the gained complex together. The ligand (MBP) was acted as natural bidentate and its coordinated with selected metal ions through nitrogen and the imidazole moiety nitrogen. All prepared compounds were appeared a strong

deactivating ability against the thoughtful bacteria. Shing colors were watched by testing the dying performance of the ligand (MBP) and its complexes on wool.

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