

Synthesis and spectral characterization of some metal complexes containing azo derived from 2-aminobenzimidazole

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Moslem Hassan Mohamed

Haitham Khadim Dakhil

Dept. of chemistry - College of Education

AL-Qadisiya University

Abstract

New complexes of 2[(2- Benzimidazole) azo] -4- Bromo aniline (BIABA) with Co(II), Ni(II), Cu(II), Zn(II) and Ag(I) were synthesized and characterized by infrared and electronic spectra and in addition of elemental analysis, molar conductance and magnetic susceptibility measurements. The data show that the ligand a bidentate and tridentate and coordinates of the metal ion via the group amine, nitrogen atom of azo and with imidazole (N₃) atom. Octahedral environment is suggested for Co(II), Ni(II) Cu(II), Zn(II) metal complexes and tetrahedral for Ag(I) complex. The analytical data show that the metal to ligand ratio (M:L) in all complexes is (1:2) but Ag(I) is (1:1) .

Introduction

A large number of (N,N) - donar ligand in azo imine family have been prepared in the last few year (1-3). This azo imine family contains aryl azo imidazoles (4). This type of molecules has several advantages. They are used as analytical reagents (5,6), and as a staining agents. (7). This class of azo compound possess active (π - acidic) azo imine (-N=N-C=N-), for this reason a number of these compound were synthesized and their abilities as chelating ligands (8-9). This work describe the preparation and characterization of some transition metal complexes, using the azo derived from 2- aminobenzimidazole (BIABA).

Experimental

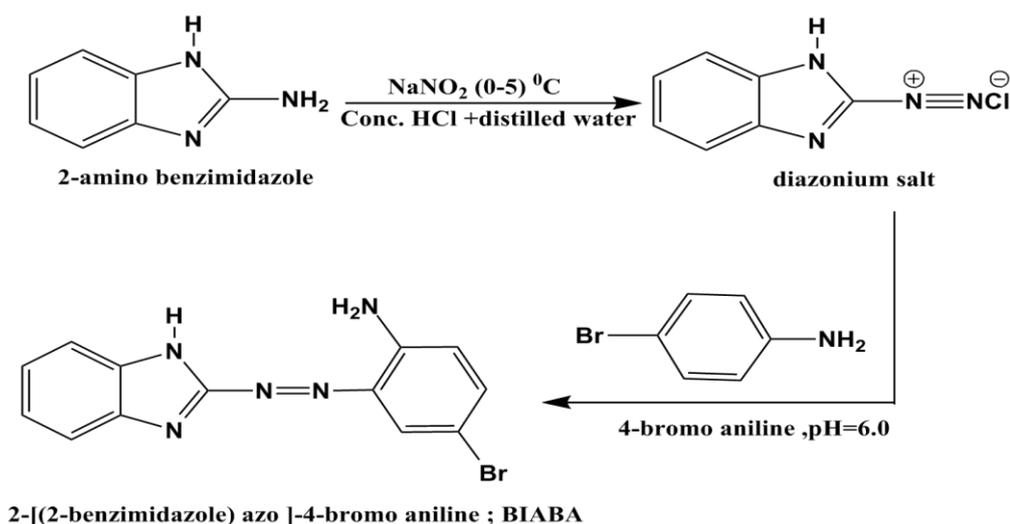
Materials and measurements

All chemical are supplied of (B.D.H. Fluka and Aldrich). Elemental analyses were carried out by means of micro analytical unit of 1108 C.H.N Elemental analyzer. The FTIR spectra in the range (4000-400)cm⁻¹ were recorded as potassium bromide disc FTIR-8300 shimadzu spectrophotometer. The UV spectra were measured in using Hitachi uv-2000 spectrophotometer in the range (200-900) nm. Magnetic susceptibility measurements for the complexes were obtained at room temperature using the susceptibility balance model MSB-MKI-Melting point of ligand and their complexes have measured using Gallen kamp M.F.B 600 and the molar conductivity

was measured by using electrolytic conductivity measuring set model (CRB3) using platinum electrode with cell constant (1 cm) concentration (10^{-3} m) in DMF as solvent.

Synthesis of the ligand (BIABA)

The azo ligand was synthesized according to following general procedure (10) (Scheme 1). 2-Aminobenzimidazole (1.33g, 0.01 mol) was dissolved in 15 ml of water, 5ml of concentrated hydrochloric acid and 10 ml of ethanol. The resulting mixture was stirred and cooled to 0 °C, then a solution of (1.4 g, 0.02 mol) of sodium nitrate in 30ml of distilled water was added dropwise with cooling and stirring continues at 0-5C⁰ to alkaline solution of (1.72g , 0.01 mol) 4-bromo aniline, in 150 ml of ethanol. The precipitate was filtered off, and recrystallized twice from hot ethanol and dried in a vacuum desiccator.



Scheme(1); Preparation of azo ligand 2-[(2-Benzimidazol) azo]-4-bromo aniline.

Synthesis of the metal complexes

The complexes were prepared by dissolving (0.316 g, 1 mol) of ligand in 50 ml of ethanol which then added drop wise with stirring to 0.5 mol of $\text{MCl}_2 \cdot \text{XH}_2\text{O}$ salt [$\text{M} = \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}, \text{Zn(II)}$ and AgNO_3 dissolved in 10 ml hot ethanol. The resulting solutions were stirred and heated on Water bath at 70 °C for 30 min. The crystal product, were collected by filtration, washed with EtOH and water, and finally dried under vacuum.

Result and discussion

The azo ligand was reddish brown, but the isolated metal complexes were found to be different color crystals depending on the nature metal ion and stable at room temperature. The ligand and its complexes were insoluble in water, but soluble in most organic solvents. The analytical and physical data of ligand and its complexes are given in (Table 1).

Table (1): Analytical and physical data of the (BIABA) ligand and its complexes

Compound	color	m. p °C	Yild %	Formula (Mol. Wt)	Found (calc.) %			
					C	H	N	M
L=(BIABA)	Reddish brown	148	79	C ₁₃ H ₁₀ N ₅ Br (316.17)	48.92 (49.38)	3.31 (3.18)	22.39 (22.15)	–
[Co (L) ₂ Cl ₂]	Dark purple	170	78	C ₂₆ H ₂₀ N ₁₀ Br ₂ Cl ₂ Co (762.24)	41.01 (40.97)	2.71 (2.64)	18.53 (18.37)	7.41 (7.73)
[Ni (L) ₂ Cl ₂]	brown	167	67	C ₂₆ H ₂₀ N ₁₀ Br ₂ Cl ₂ Ni (761.95)	40.31 (40.98)	2.61 (2.64)	18.21 (18.38)	7.91 (7.70)
[Cu(L) ₂ Cl ₂]	Dark green	162	63	C ₂₆ H ₂₀ N ₁₀ Br ₂ Cl ₂ Cu (766-78)	40.28 (40.72)	2.72 (2.62)	18.73 (18.26)	7.98 (8.28)
[Zn (L) ₂ Cl ₂] H ₂ O	purple	178	66	C ₂₆ H ₂₂ N ₁₀ Br ₂ OCl ₂ Zn (786.63)	40.02 (39.70)	2.89 (2.81)	18.01 (17.80)	8.11 (8.31)
[Ag (L) (H ₂ O)] NO ₃	Reddish purple	174	53	C ₁₃ H ₁₂ N ₆ O ₄ BrAg (504.06)	30.49 (30.97)	2.71 (2.39)	17.43 (16.67)	21.87 (21.40)

Infrared spectra

The functional groups of the azo ligands and the metal complexes assigned by infrared spectra are given in Table 2. The band at 3441 cm⁻¹ due to ν (NH₂). This band is shifted in the complexes Cu(II) and Ag(I) toward lower frequencies because of the coordination of the nitrogen to the metal ion, but the complexes Co(II), Ni(II), and Zn(II) did not show any frequency shift of the ν (NH₂) band (11-13). In the spectra of Zn^{II} and Ag^I the broad band near 3370 cm⁻¹ indicates the presence of water molecule in these complexes (1,14,15). But the spectra of rest complexes band observed at 3163 cm⁻¹ assigned to ν (NH) group in imidazole ring does not participate (1). Spectra of

ligand shows two weak bands at 3070 cm^{-1} and 2977 cm^{-1} due to ν (C-H) aromatic and aliphatic respectively. These bands are stable in position and intensity in both ligand and its metal complexes (14,16). The I.R spectra showed a band at 1627 cm^{-1} due to ν (C=N) of (N₃) imidazole nitrogen. It is observed with a little change in the shape and shifted to lower frequencies $1593 - 1602\text{ cm}^{-1}$ in the prepared complexes spectra. These differences suggest the linkage of metal ion with nitrogen imidazole ring (14). The ν (N=N) stretching vibration appears at 1589 cm^{-1} in the free ligand spectra. This band appearing at $1535 - 1573\text{ cm}^{-1}$, both bands shifted and reduced intensity due to complex formation (17). New weak bands in the region $(422 - 537)\text{ cm}^{-1}$ which are never been observed in the free ligand spectrum, this may be attributed to ν (M-O), ν (M-N) and ν (M-N) azo, amine bands (14,18,19). Chelating agent, coordinating with metal ions by azo nitrogen, amino group and nitrogen in imidazole ring, to give five-membered chelating ring. Fig.(1-3), shows the spectra of ligand (BIABA), [Cu (L)₂] Cl₂ and [Zn (L)₂] Cl₂ H₂O.

Table (2): Selected IR Data (4000 – 400 cm⁻¹) of 2- [(2-Benzimidazole) azo] -4- Bromo aniline and its complexes.

Compound	ν (NH ₂)	ν (C=N)	ν (N=N)	ν (M-O)	ν (M-N)	ν (M-N) azo, amine
L= BIABA	3441	1627	1589	-	-	-
[Cu (L) ₂] Cl ₂	3440	1602	1542	-	516	447
[Ni (L) ₂] Cl ₂	3443	1596	1535	-	510	470
[Cu (L) ₂] Cl ₂	3394	1599	1573	-	537	477, 466
[Zn (L) ₂] Cl ₂ H ₂ O	3449	1599	1532	-	532	422
[Ag (L) (H ₂ O)] NO ₃	3409	1593	1550	515	470	455, 424

Magnetic susceptibility and electronic spectra measurements.

The electronic spectra of the azo ligand (BIABA) and its complexes were recorded in DMF and their assignments are given in Table 3. The free azo ligand spectral data display two bands of 239 nm (41841 cm^{-1}) and 299 nm (33444 cm^{-1}) attributed to $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ (amino ring), and whilst the peak at 364 nm (27472 cm^{-1}) was assigned to charge transfer (20). The magnetic moment of the cobalt (II) has

been found to be (5.0 B.M.), which is with the range of octahedral cobalt (II) complexes (13). The electronic spectra of this complex shows band at 207 nm (4830 cm^{-1}) and 275 nm (36363 cm^{-1}) which are assigned to ligand field. The bands at (549 nm) (18214 cm^{-1}), 581 nm (17211 cm^{-1}) and 931 nm (10741 cm^{-1}) pertaining to ${}^4T_{1g(F)} \rightarrow {}^4T_{1g(P)}(\nu_3)$, ${}^4T_{1g(F)} \rightarrow {}^4A_{2g(F)}(\nu_2)$ and ${}^4T_{1g(F)} \rightarrow {}^4T_{2g(F)}(\nu_1)$ transitions respectively. These electronic spectral data were consistent with high – spin octahedral configuration around Co(II) ion. (13, 21) For the nickel(II) complex, its magnetic moment (3.6 B.M) and d-d spectrum of this complex show band achieved at 940 nm (10638 cm^{-1}) attributed to ${}^3A_{2g} \rightarrow {}^3T_{2g(F)}(\nu_1)$ transition. The bands at 632 nm (15822 cm^{-1}) and 471 nm (121231 cm^{-1}) which are suggesting the existence of ${}^3A_{2g} \rightarrow {}^3T_{2g(F)}(\nu_2)$ and ${}^3A_{2g} \rightarrow {}^3T_{2g(P)}(\nu_3)$ transitions with an octahedral spatial configuration. (13) The magnetic moment value of the Cu(II)- complex is (1.8 B.M.) due to presence one electron unpaired which may suggest an octahedral structure. Its electronic spectrum shows a band centered at (644 nm) (15527 cm^{-1}) which may assigned to ${}^2E_{2g} \rightarrow {}^2T_{2g}$ transitions in octahedral environment. (13, 14) .For the Zn (II) – complex and Ag (I)– complex are diamagnetic and the electronic spectra of there complexes exhibit high intense charge transfer transitions in the visible region (509 – 530) nm which are assigned to a charge transfer ($M \rightarrow L$, CT).(22) Fig. (4-8) and Fig 9 shows the absorption spectra of Co (II), Ni(II), Cu(II) Zn(II), and Ag(II) complexes.

Conductivity measurements

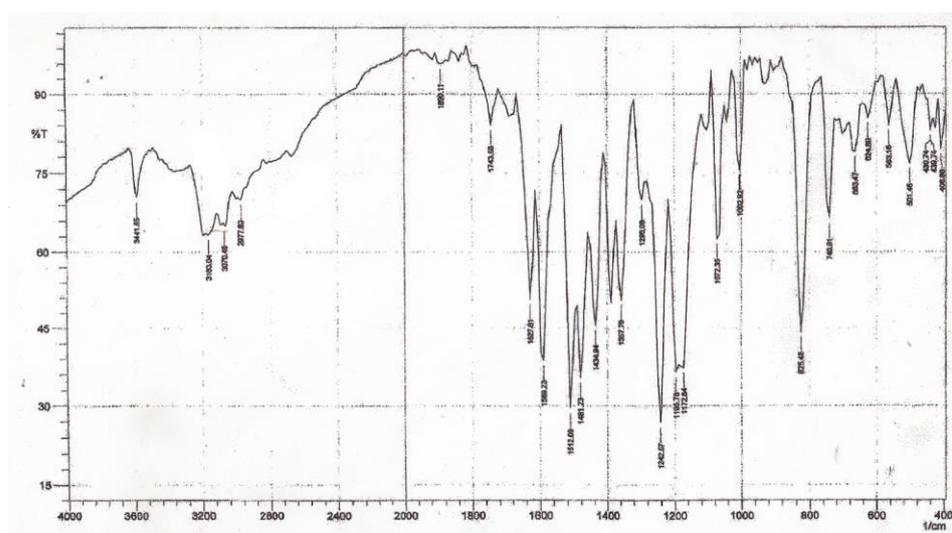
The conductivity value for the the Cu(II) – complex and Ag(I) – complex were found 142.16 and 78.10 $\text{S.mol}^{-1} \cdot \text{cm}^2$ respectively (Table 3) in DMF at room temperature, indicating that the Cu(II) – complex is (1:2) and the Ag(I) – complex is 1:1 ionic structure (14). But all complexes showed conductivity values ranged between 7.93 – 10.52 $\text{S.mol}^{-1} \cdot \text{cm}^2$, in the same solvent indicating non conductivity species (22). Prepared complexes in this work may be proposed in Fig 10,11 and Fig.12.

Table (3): Electronic spectra, conductivity and magnetic moment of chelate complexes

Complexes	Absorption Bands (cm ⁻¹)	Transition	Conductivity S.mol ⁻¹ .cm ²	μ _{eff} * (B.M)
[Co (L) ₂ Cl ₂]	10741	⁴ T _{1g} (F) → ⁴ T _{2g} (F) (u ₁)	9.67	5.0
	17211	⁴ T _{1g} (F) → ⁴ A _{2g} (F) (u ₂)		
	18214	⁴ T _{1g} (F) → ⁴ T _{1g} (p) (u ₃)		
[Ni (L) ₂ Cl ₂]	10638	³ A _{2g} → ³ T _{2g} (F) (u ₁)	10.52	3.6
	15822	³ A _{2g} → ³ T _{2g} (F) (u ₂)		
	21231	³ A _{2g} → ³ T _{2g} (p) (u ₃)		
[Cu (L) ₂] Cl ₂	15527	² E _{2g} → ² T _{2g}	142.16	1.8
[Zn (L) ₂ Cl ₂] H ₂ O	—	—	7.93	dia.**
[Ag (L) (H ₂ O)] NO ₃	—	—	78.10	dia.**

*μ_{eff} : Magnetic Moment in Bohr Magnetron

**dia. diamagnetic



Figure(1): IR spectrum of the ligand (BIABA).

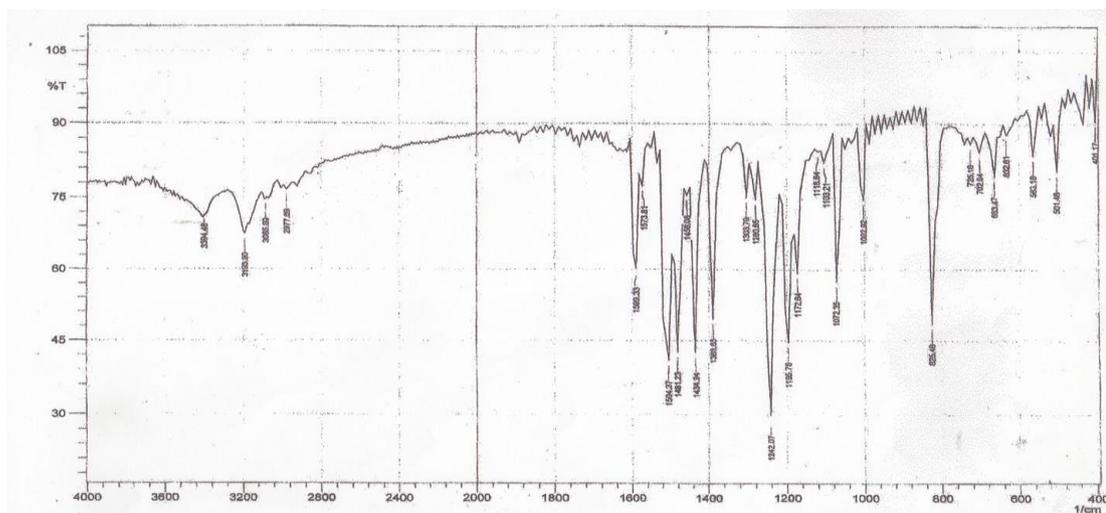
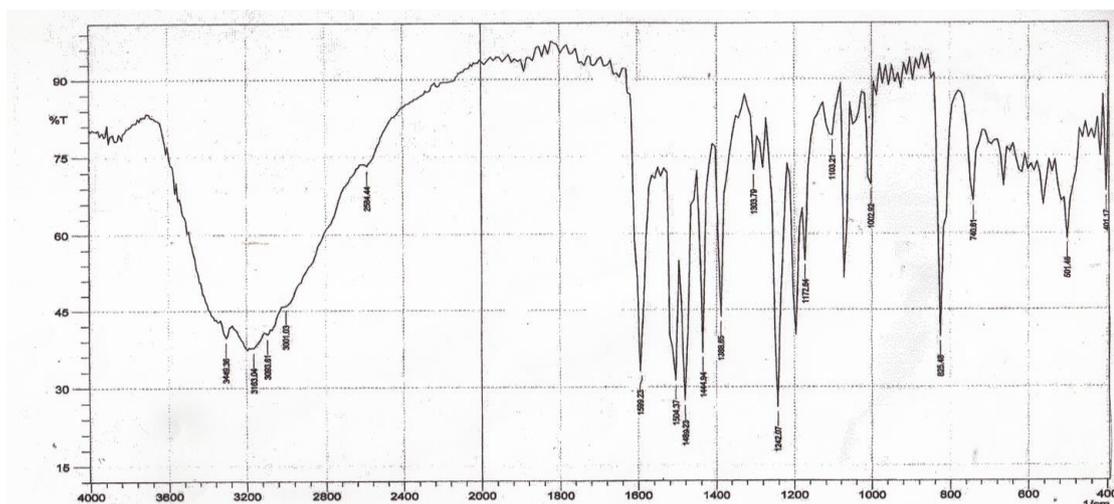
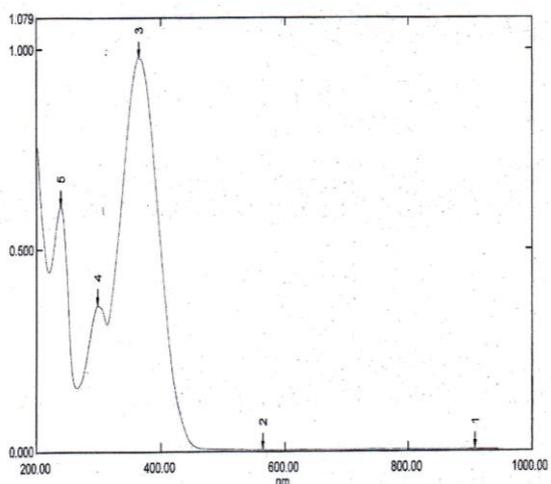


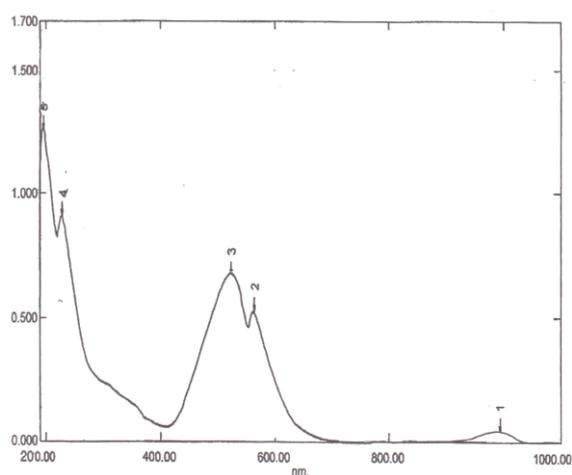
Figure (2): IR spectrum of the complex $[Cu (L)_2] Cl_2$



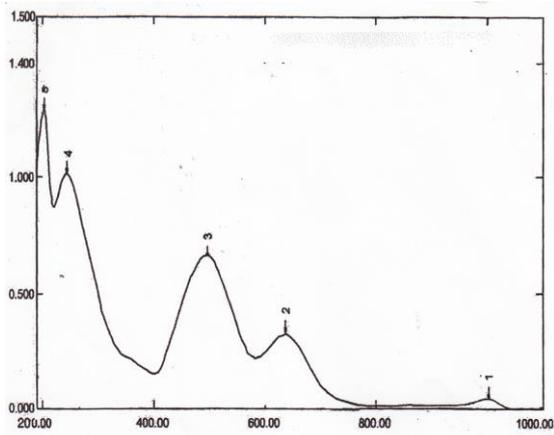
Figure(3): IR spectrum of the complex $[Zn (L)_2] H_2O$



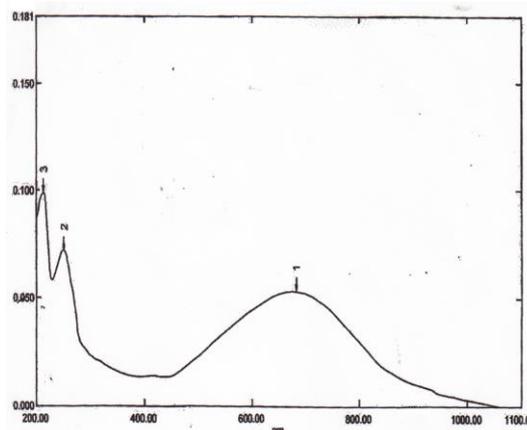
Figure(4): The absorption spectra of ligand (BIABA).



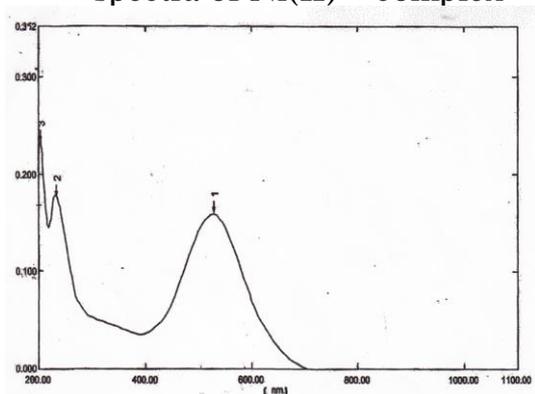
Figure(5): The absorption spectra of $Co(II)$ - complex



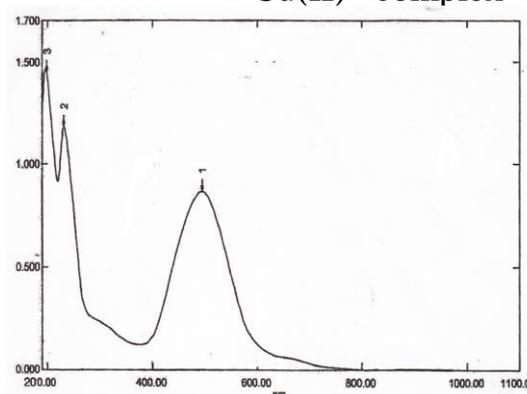
Figure(6): The absorption spectra of spectra of Ni(II) – complex



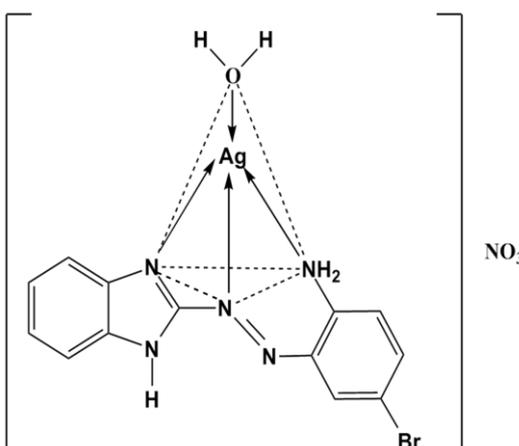
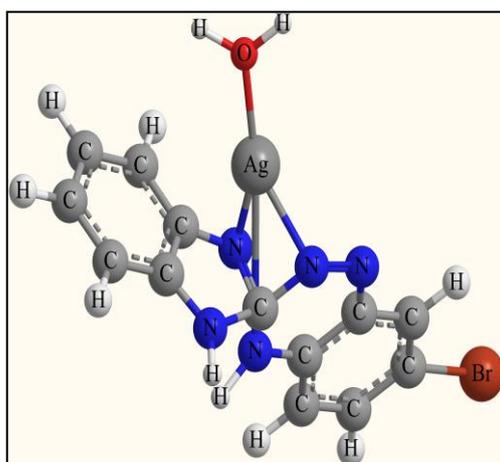
Figure(7): The absorption spectra of Cu(II)– complex



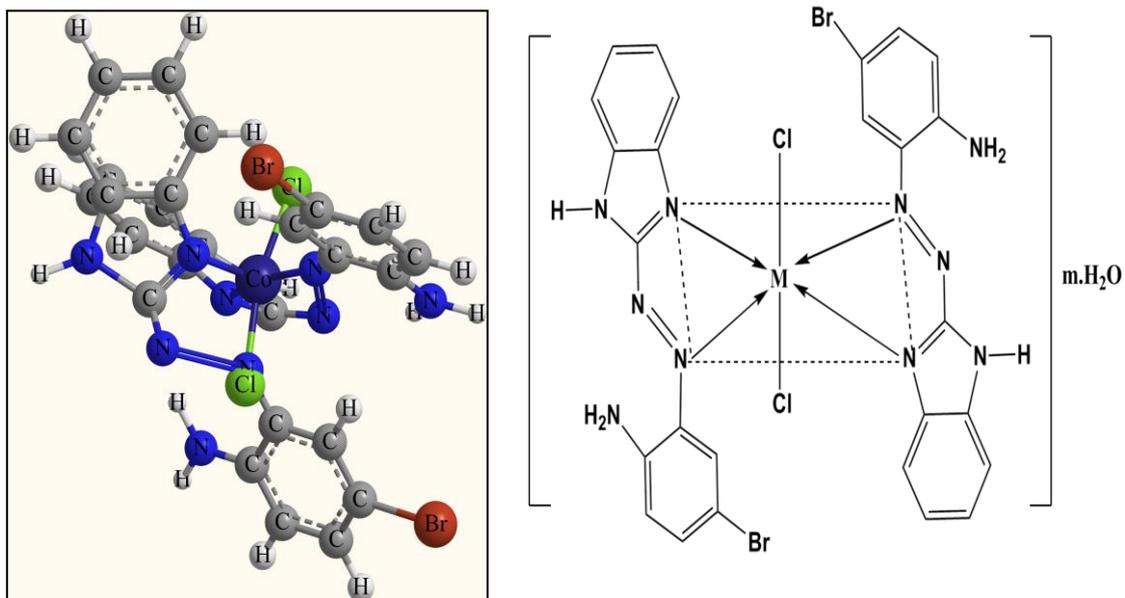
Figure(8): The absorption spectra of spectra of Zn(II) – complex



Figure(9): The absorption spectra of Ag(I) – complex

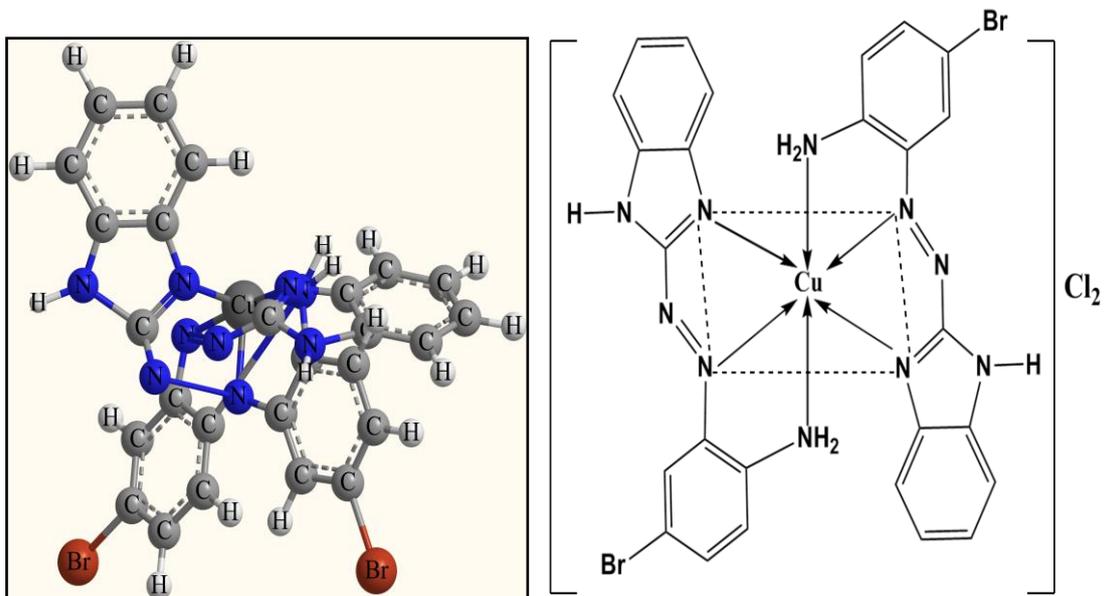


Figure(10): The proposed structural formula of Ag(I)– complex



M= Co(II), Ni(II), m=0
M= Zn (II), m=1

Figuer(11): The proposed structural formula of Co(II), Ni (II), and Zn(II) complexes.



Figuer(12): The proposed structural formula of Cu (II) complex.

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التحضير والتشخيص الطيفي للمعقدات بعض العناصر الانتقالية الحاوية على مجموعة ازو مشتقة من 2-امينو بنز اميدازول

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مسلم حسن محمد و هيثم كاظم دخيل

قسم الكيمياء / كلية التربية / جامعة القادسية .

الخلاصة

حضرت وشخصت معقدات جديدة من ليكاند 2- [2- (بنزاميدازول) أزو] -4- بروموانلين (BIABA) مع أيونات الكوبلت (II)، والنيكل (II)، النحاس (II)، الخارصين (II)، والفضة (I) باستخدام الأشعة تحت الحمراء والأطياف الإلكترونية، بالإضافة إلى التحليل الدقيق للعناصر والتوصيلية المولارية والحساسية المغناطيسية. واستناداً إلى تلك المعطيات التحليلية، فقد تبين أن الليكاند ثنائي وثلاثي السن، ويرتبط مع الأيون الفلزي من خلال مجموعة الأمين وذرتي نتروجين مجموعة الأزو و نتروجين (N₃) للإميدازول. تم اقتراح الشكل ثماني السطوح للمعقدات الفلزية لأيونات الكوبلت (II)، النيكل (II)، النحاس (II)، الخارصين (II) ومعقد الفضة (I) رباعي السطوح. بينت النتائج ان نسبة (الليكاند: الفلز) هي (2: 1) لجميع المعقدات عدا الفضة (1:1).