Synthesis and spectral characterization of new azo dye derived from benzimidazole and its complexation with selected transition metal ions.

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ABSTRACT: The preparation and spectral characterisation of 2-[6-(benzimidazolylazo)] as an organic heterocyclic azo dye compound containing benzimidazole. The reaction of benzimidazole diazoniumbromid with 2,4-dibromo phenol in alkaline alcoholic solution yielded -2,4-dibromo phenol (BIADBrP). Spectral analyses have been used to study the structure of the azo dye ligand such as H1NMR, mass spectrum, IR, UV-Vis and element analysis. New six complexes with Co(III), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) ions were prepared and identification by several physiochemical techniques; such as C.H.N element, magnetic susceptibility, atom absorption, molar conductivity, IR and electronic spectra. The used techniques showed the formation of all complexes 1:2 [M:L] complexes and suggested octahedral geometry with d2sp3 hybridization of Co(III) and sp3d2 with residulechelat complexes. The coordination number of the metal ion is found to be six with binding through the phenolate O, azo N3 and with the imidazole N3 atom. The stability, geometrical, and electrical features of metal complexes have also been studied theoretically. The energy levels of the ligand and metal complexes' high occupied molecular orbital HOMO and low unoccupied molecular orbital LUMO were used to compute electrochemical potential, electrophilicity index, and chemical hardness.

Key words: Computational study, Azo dye ligand, benzimidazole, hybridization, physicochemical properties.

INTRODUCTION

The ligands of Benzimidazolyl azo are characterized by the –N=N- (azo) group have been observed in many biological compounds (1). Benzimidazole as an imidazole derivative has been shown to enter into the field of medical science applications due to its chemotherapeutic properties (2,3). It has had success in its use as dyes on propylene fibres, cotton and synthetic textiles (4-6). Benzimidazolylazo dyes are known for being efficient analytical reagents in the spectrophotometric determination of metal ions (7-9). Therefore 2-aminobenzimidazole and other benzimidazole derivatives are used as complexing agents in purification of water containing heavy metals (10). There are surveys focused on benzimidazole derivatives as an effective drug in selectively inhibiting endothelial cell growth and angiogenesis in vitro and in vivo (11). The present work describes the synthesis and characterization of new ligand 2-[6-(benzimidazolylazo)]-2,4-dibromo
phenol(BIADBrP) and its metal chelate complexes with CO(III), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) ions.

EXPERIMENTAL

Materials and Measurements

The analysis of the ligand and its complexes was performed by an EA 3000A C.H.N. Microanalytical Module. Elements Analyzer (Ahl al-Bayt University, Jordan). The H1NMR spectrum of the ligand was obtained in CDCl3 solution as solvent using a Bruker Ultra Shield 400 MHZ spectrophotometer (TrabitModaris University, Iran). Mass spectrometry of the ligand using Agilent Technologies 5975C at 70e and MSD using direct input probe (Acq method 10 W power) at 90-1100 °C (Tribet University, Madras, Iran). and its complexes in KBr medium on an 8400S FTIR shimadzu spectrophotometer in the wavenumber in the range (4000-400) cm⁻¹. The electronic spectrum of the ligand and its complexes in absolute ethanol (10-4) M was recorded as a solvent on a shimadzu dual-beam spectrophotometer. 1700 UV-Vis Spectrophotometer. The mineral contents of the complexes were measured using atomic absorption technology by shimadzu AA-160. Magnetic susceptibility was measured for the complexes on a MSB-MKI magnetic balance at room temperature using Faraday's method, as well as the magnetic correction was carried out using Pascal constants. The molar conductivity was measured in ethanol and DMF (10-3) solution at room temperature using the conductivity bridge model 31A, and the electrothermal melting point model 9300 was used to measure the melting point of the ligand and its complexes. pH was measured with a Philips PW 9421 -0.001 pH meter. The chloride ion in Co(III) was determined by mohr method. (12)

Synthesis of The Azo Dye Ligand(BIADBrP)

The heterocyclic azo dye ligand (BIADBrP) was synthesized by diazotization coupling reaction by flow methods proposed by Shibata et al. (13) and Mohamed et al. (14) With some modification (Scheme 1) to make a BIADBrP linker. 2-aminobenzimidazole (1.33 g, 0.01 mol), dissolved in a mixture of 40 mL distilled water and 4 mL of concentrated HCl.

Cool and stir constantly until temperature is reached(0-5) 0 °C, the solution was shifted with (0.75 g, 0.01 mol) sodium nitrate in 20 mL distilled water, then a drop was added to the 2-aminobenzimidazole solution and stirred for 30 min at (0-5) 0 °C. In an ice bath the color will change to yellow. The distilled solution of diazonium bromide was added to the mixture containing 4,6-dibromophenol (2.5 g, 0.01 ml) and 6% sodium hydroxide in 50 ml ethanol with constant stirring at (0-5) 0 °C, orange-colored solution. Darkness is observed, and when the addition process is finished, the solution is left in a continuous state for an hour, then the solution is left until the next day. The crystals are filtered and left to air dry. The precipitate was collected and dried in an electric oven under 70 °C for 6 h. The product was recrystallized with ethanol and dried in an oven at 500°C for several hours. Purity was confirmed by elemental analysis and TLC techniques. The ligand structure (BIADBrP) is transformed by H1NMR, mass spectrometry, infrared, visible and ultraviolet radiation.
Scheme (1):-Synthesis of azo dye ligand (BIADBrP).

Synthesis of metal complexes
Metal chelate complexes were prepared by adding 0.792 g (0.002 mol) of the ligand (BIADBrP) dissolved in ethanol with a stoichiometric stirring of 1:2 [M:L] molar ratio (0.001 mol) of carbon dioxide (III), Ni chloride salts (II), Cu (II), Zn (II), Cd (II), and Hg (II) which dissolve in the optimization of buffer solution (ammonium acetate) at the optimum pH for each metal ion. The reaction mixture was heated to 50-60 °C for 30 min, until the solid was precipitated and left overnight. The solid product was filtered and washed with distilled water several times. To remove any trace of unreacted material it is washed with 10 mL of absolute ethanol and dried in driers over anhydrous CaCl2. Yield %, MP, PH, color and analytical data are collected in Table 1.

Table (1):- Analytical and physical data of ligand (BIADBrP) and its complexes

| No. | Compound       | pH    | Color        | m.P °C | Yield % | (Mol.Wt) | Found (Calc.)% |
|-----|----------------|-------|--------------|--------|---------|----------|----------------|
| 1   | LH=BIADBrP     | 6.0   | Dark RED     | 119    | 79      | 396.03   | 39.26 1.95 13.97 |
| 2   | [Co(L)₂]Cl₂H₂O | 7.5   | Purpleblue   | 173    | 74      | 902.47   | 34.38 1.68 12.29 | 6.32 |
| 3   | [Ni(L)₂]H₂O    | 6.0   | Dark purple  | 130    | 81      | 866.77   | 35.92 1.73 13.06 | 6.56 |
| 4   | [Cu(L)₂]H₂O    | 6.5   | Reddish Purple | 165   | 82      | 871.63   | 35.62 1.76 12.72 | 7.04 |
| 5   | [Zn(L)₂]H₂O    | 7.5   | Reddish Purple | 167   | 77      | 873.46   | 35.49 1.74 12.96 | 7.14 |
| 6   | [Cd(L)₂]H₂O    | 7.5   | Purple       | 183    | 69      | 920.491  | 33.75 1.63 ___   |      |
| 7   | [Hg(L)₂]H₂O    | 7.5   | Purple       | 200    | 72      | 1008.67  | 30.77 1.49 11.99 |      |

Result and discussion
characterization of ligand (BIADBrP) and its complexes
The heterocyclic azo dye ligand (BIADBrP) was dark red crystals, the chelating complexes of this bonding gave different crystals or powder depending on the metal ion and optimum PH. The ligand and its complexes are soluble in most organic solvents including ethanol, methanol, acetone, DMSO, DMF and ether, stable to air at room temperature and in water soluble, purity of azo dye complexes tested by C.H.N. Elemental analysis and other techniques.

**Metal :ligand ratio**

The molar ratio method was adopted to determine the metal:ligand [M:L] ratio of the chelated complexes at a constant concentration and optimum PH at maximum wavelength absorption (\(\lambda_{\text{max}}\)). The solution of the prepared complexes increases the intensity of the colors as a point of approach to the intersection. when passing this point , ratio and the color remain stable, indicating that mean the compound has formed \(^{1(10)}\). This ligand was found to form a 1:2 [M:L] mole ratio with all metal ions indicating compound formation.

**Micro analysis**

Element analysis data of the ligand (BIADBrP) and its complexes are as shown in Table-2. It was found that the existing data are in agreement with the theoretical value indicative of the healthy structures of the complexes

**Table(2):- The results of the precise elemental analysis (C.H.N) of each of the ligand (BIADBrP) and its prepared metal complexes,**

| Compounds        | C% | H% | N% | C% | H% | N% |
|------------------|----|----|----|----|----|----|
|                  | cal | found | cal | found | cal | found | cal | found |
| HL=BIADBrP       | 39.43 | 39.26 | 14.14 | 13.97 | 2.04 | 1.95 |     |     |
| [Co(L)\(_2\)]Cl.H\(_2\)O | 34.60 | 34.38 | 12.42 | 12.29 | 1.79 | 1.68 | 6.53 | 6.32 |
| [Ni(L)\(_2\)].H\(_2\)O | 36.03 | 35.92 | 12.93 | 13.06 | 1.86 | 1.73 | 6.77 | 6.56 |
| [Cu(L)\(_2\)].H\(_2\)O | 35.83 | 35.62 | 12.86 | 12.72 | 1.85 | 1.76 | 7.29 | 7.04 |
| [Zn(L)\(_2\)].H\(_2\)O | 35.75 | 35.49 | 12.83 | 12.96 | 1.85 | 1.74 | 7.27 | 7.14 |
| [Cd(L)\(_2\)].H\(_2\)O | 33.93 | 33.75 | 12.17 | 11.99 | 1.75 | 1.63 |     |     |
| [Hg(L)\(_2\)].H\(_2\)O | 30.98 | 30.77 | 11.12 | 11.24 | 1.60 | 1.49 |     |     |

**Calculation of metal complexes stability constant**

The stability constant of metal complexes are determined spectrophotometrically by measuring the absorbance of mixture of solution of azo ligand (BIADBrP) and metal ions at fixed wavelength(\(\lambda_{\text{max}}\)), concentration and optimum PH values depend on the metal ions. The degree of formation of the complexes are calculated based on the relationship: \(\beta= (1-\alpha) / (4\alpha^2 C^2)\) for 1:2 [M:L] metal complexes and \(\alpha= Am-As/Am\) were Am and As are the absorbance of the fully and partiallyformed chelate.
complexes respectively (19,20) . The calculated \( \beta \) and log \( \beta \) value for the prepared complexes are listed in Table -3.

**Conductivity measurement**

The molar conductance measurement of the prepared metal complexes were measure in ethanol and DMF solvents \((10^{-3})\)M at room temperature. The high value of molar conductance of the Co(III)-complex indicating that the complex is 1:1 electrolyte with ion nature but showed the low value of molar conductance of the Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) indicating that non-electrolyte and no conductive species exist (21-23), the value as shown in Table -3.

**Table (3):** Stability constant value \((\beta \text{ and } \log \beta)\), molar conductivity, optimal concentration, maximum wavelength \((\lambda_{\text{max}})\) and molar absorptivity \((\varepsilon)\) of metal complexes

| Ligand   | Metal ion | Optimal molar conc. \(\times 10^{-4}\)M | Optimal wavelength \((\lambda_{\text{max}})\) nm | Molar absorptivity \(\varepsilon \times 10^{3}\) L.mol\(^{-1}\).cm\(^{-1}\) | Stability Constant \(\beta\) \(\times 10^{11}\) | Log\(\beta\) | Molar conductivity (EtOH) | Molar conductivity (DMF) |
|----------|-----------|----------------------------------------|---------------------------------------------|-------------------------------------------------|---------------------------------------------|----------------|---------------------------|---------------------------|
| BIADBrP  | Co(III)   | 1.25                                   | 601                                         | 1.232                                          | 0.131\(\times 10^{11}\)                         | 10.11          | 43.87                     | 81.09                     |
|          | Ni(II)    | 1.5                                    | 511                                         | 1.809                                          | 0.616\(\times 10^{12}\)                         | 11.78          | 10.56                     | 24.13                     |
|          | Cu(II)    | 1.00                                   | 518                                         | 1.518                                          | 0.879\(\times 10^{12}\)                         | 11.94          | 9.37                      | 21.68                     |
|          | Zn(II)    | 1.25                                   | 538                                         | 1.286                                          | 0.814\(\times 10^{10}\)                         | 9.91           | 14.01                     | 26.43                     |
|          | Cd(II)    | 1.00                                   | 527                                         | 1.808                                          | 0.677\(\times 10^{4}\)                          | 10.83          | 12.85                     | 22.97                     |
|          | Hg(II)    | 0.75                                   | 538                                         | 2.404                                          | 0.554\(\times 10^{11}\)                         | 10.74          | 13.74                     | 27.11                     |

**Effect of pH**

Effect of PH values on absorbance was demonstrated by studying metal compounds in 50% (v/v) ethanol as shown in Figure 1 and 2. Transmitting ligand azo dye (BIADBrP) complexes very stable metal ions Co(III) and Ni(II) And Cu(II), Zn(II), Cd(II), and Hg(II) have a wide PH range (6-8.0), and the absorption spectra did not change over the course of the developing resonance. The pH value was adopted at pH> 8.5 decrease in absorbance may be due to the hydrolysis of metal complex and also which pH< 6.0 a decrease in absorbance occur due to form azoliumcation result from the reaction hydrogen ions and the ion pair of electron which found in the nitrogen atoms for benzimidazole ring (22,24).
Effect of time

The effect of time on the absorption of mineral compounds in an ethanolic solution was studied. The reaction was absorbed and completed within 10 minutes at room temperature and remains stable for at least 24 hours. This indicates that an azo dye ligand (BIADBrP) appears Strong coordination with all metal ions (25,26). The results are shown in Figure 3.

Effect of the solvent

Several solvents such as ethanol, methanol, acetone, ether and DMF were used to study the effect of the solvent. The absorption spectra of the ligand (BIADBrP) were known in these solvents. A strong dependence on the solvent was demonstrated by the visible absorption spectra of the bonds, and a pathochromic shift caused by the lack of uniform contrast with the polarity of the solvent. Figure 4 shows the spectra of the ligand in several solvents (27).
Figure (3): The effect of time on the absorbance of the metal complexes with Ligand (BIADBrP).

Figure (4): Absorption spectra of the ligand (BIADBrP) in different solvent
Mass spectra of azo dye ligand
The mass spectra fragmentation of azo dye ligand (BIADBrP) shown in schem-2 and figure 6. The base peak of azo dye ligand at m\(\text{/e}^+\)=396.03 is attributed to the original molecular weight of the ligand. The peak at 368.1 due to the loss of two nitrogen atoms (azo group). The loss of two chlorine atoms (2Cl) give a peak at m\(\text{/e}^+\)=210.2. The peak at m\(\text{/e}^+\)=155 due to loss of C\(_2\)H\(_2\). The loss of one oxygen atom give a peak at m\(\text{/e}^+\)=145. The peak at m\(\text{/e}^+\)=77.2 is belong to C\(_6\)H\(_+\)ion. The same spectra shown peak at m\(\text{/e}^+\)=56 corresponding to loss C\(_2\)H\(_2\) group.

**Figure (5):** Mass spectra of azo dye ligand (BIADBrP)
Scheme (2):- The mass spectra fragmentation of azo dye ligand (BIADBrP)

**H¹NMR spectrum of azo dye ligand**

The H¹NMR spectrum of the ligand (BIADBrP), figure (6), measured by using CDCl₃ solvent. The results of azo dye ligand spectral show single peak at 6.896 ppm due to OH-Ar, and double peak at 6.783-6.741 ppm due to proton of NH-benzimidazole. The same spectrum show double peaks between 7.131-7.058 ppm due to the presence of protons H₃ and H₅ of phenol ring. There is a complex overlap peaks 7.113-7.094 ppm attributed to the presence of proton H₄ and H₇ of Ar-benzimidazole. The single peak which appeared at 7.437 ppm in the spectrum of azo dye ligand is due to the presence of protons H₅ and H₆ of Ar-benzimidazole. The singles peak at 2.462 ppm due to the existence of CDCl₃ solvent (29,30).
Infrared spectra

Azo dye ligand (BIADBrP) and some metal complexes been studied with infrared spectra shown in figure 7, 8, 9 and 10. The important IR assignment of ligand and its complexes (KBr disk) are listed in table 4. A comparison of IR spectra between the ligand and metal complexes has been noticed appear the binding mode of ligand to metal ions which is formation of the coordination complexes, noticed by shift in the positions of absorption bands. The IR spectrum of free ligand (BIADBrP) shows a broad medium band around 3626 cm\(^{-1}\) is Refers to OH of the phenolic group. This band is change in position and intensity in all the metal complexes indicating coordination through the deprotonated phenolic OH group \(^{(31,32)}\). The strong band at 3433 cm\(^{-1}\) in the spectrum of free ligand may be attributed to NH stretching vibration of benzimidazole moiety. This band in all metal complexes is unchanged indicating that the NH group does not participate in coordination \(^{(30)}\). The presence of water molecule in the complexes can be seen by spectra of all metal complexes that shows a broad bands around at (3240-3402)cm\(^{-1}\)\(^{(33,34)}\). The weak band at 3116 cm\(^{-1}\) in the spectra of the ligand is due to \(\tau(C-H)\) aromatic. This band has stabilization in intensity and position for both ligand and chelate complexes. The IR spectrum of free ligand showed a strong band at 1558 cm\(^{-1}\) due to (C=H) aromatic. This band is has stabilization in intensity and position for both ligand and chelate complexes. The IR spectrum of free ligand showed a strong band at 1558 cm\(^{-1}\) due to (C=N) benzimidazole nitrogen. This band decrease in intensity in all metal complexes indicating that it has been affected upon coordination to the metal ions \(^{(35)}\). The azo group (-N=N-) stretching vibration at 1458 cm\(^{-1}\) in the spectrum of free ligand which shifted to lower frequency when compared the spectra of ligand with the spectra metal complexes. This shows the involvement of the azo group (N3) in coordination with metal ions \(^{(36)}\). For all metal complexes, the far infrared spectrum shows new bands observed in the spectrum (416-594) cm\(^{-1}\), which we can see in the free bonding spectrum. This bands due to \(-\cdot(M\cdotN)\) and \(-\cdot(M\cdotO)\) also indicated the bonding of nitrogen and oxygen to the metal ions \(^{(37)}\). Therefore, The ligand (BIADCIP) as shown by infrared spectra behaves as a three-dimensional chelating agent through the position of the hydroxyl oxygen, and the nitrogen atom of the azo group (N3) closest to the phenolic ring and nitrogen (N3) of the benzimidazole ring to give two of the five members, dog rings.
| Compound                  | $\nu$ (O-H) | $\nu$ (N-H) | $\nu$ (C=O) | $\nu$ (N=N) | $\nu$ (C=N) | $\nu$ (CN=N) | $\nu$ phenyl ring | $\nu$ (M-O) | $\nu$ (M-N) |
|--------------------------|------------|------------|------------|------------|------------|------------|-------------------|------------|------------|
| HL=ligand(BIA DBrP)      | 3626 m. br.| 3433 S.    | 1558 m.    | 1458 m.    | 1288 w.    | 1272 m.    | 841 m.           | ---        | ---        |
|                          |            |            | 16 82 S.   |            |            |            |                   | 748 s      |            |
| [Co(L)$_2$]Cl.H$_2$O      | 3425 s.    | 3425(a) s. | 17 36 s.   | 1596 m.    | 1411 m.    | 1474 m.    | 1273 m.          | 594 416 w  |
|                          | s.br.      | s.br.      |            |            |            |            |                   | 687 w.     |            |
| [Ni(L)$_2$]H$_2$O         | 3302(a) s. | 3302(s)    | 16 31 s.   | 1473 m.    | 1412 m.    | 1474 m.    | 1273 m.          | 501 424 w  |
|                          | s.br.      | s.br.      |            |            |            |            |                   | 856 w.     |            |
| [Cu(L)$_2$]H$_2$O         | 3196 m.br. | 3240(a) m.br.| 16 80 s. | 1542 m.    | 1412 m.    | 1272 s.    | 1219 m.          | 509 424 w  |
|                          | m.br.      | m.br.      |            |            |            |            |                   | 740 s.     |            |
| [Zn(L)$_2$]H$_2$O         | 3341 w.br. | 3198 m.br. | 16 82 s.   | 1543 m.    | 1412 m.    | 1273 m.    | 1218 m.          | 518 428 w  |
|                          | m.br.      | m.br.      |            |            |            |            |                   | 740 Vs.    |            |
| [Cd(L)$_2$]H$_2$O         | 3402 w.br. | 3341 w.br. | 16 34 s.   | 1643 m.    | 1404 m.    | 1273 m.    | 1195 m.          | 540 470 w  |
|                          | w.br.      | w.br.      |            |            |            |            |                   | 687 m.     |            |
| [Hg(L)$_2$]H$_2$O         | 3240 m.br. | 3194 m.br. | 16 82 s.   | 1543 m.    | 1412 s.    | 1273 s.    | 1219 s.          | 522 436 w  |
|                          | m.br.      | m.br.      |            |            |            |            |                   | 740 v s.   |            |
Figure (7): IR spectrum of ligand (BIADBrP)

Figure (8): IR spectrum of [Co(L)2]Cl.H2O complex
Electronic spectra and magnetic susceptibility measurements

The electronic spectra of azo dye ligand (PIADBrP) and its complexes were recorded in absolute ethanol (10^{-3})M. Metal complexes magnetic susceptibility have been recorded at room temperature. This data are given in table-5. The free ligand (BIADBrP) spectrum gives three bands were detected first band located at 413 nm (24213cm^{-1}) for (n→π) transition of the azo group (N=N), this band showed a red shift because of coordination between ligand and metal ion. The second band observed...
at 219nm (34364 cm⁻¹) due to (π→π*) transition to the (C=C) groups of benzimidazole and aromatic rings\(^{(20,37)}\). While the third band at 283nm (42017 cm⁻¹) for (n→π*) of the hydroxyl group (OH).

**Cobalt (III) complex**

Two bands observed at 651nm (16639 cm⁻¹) and 523nm (19120 cm⁻¹) for the electric spectrum of the Co(III)-complex in absolute ethanol (10⁻³ M) corresponding to the transition \(^1\text{A}_2\text{g}→^1\text{T}_1\text{g}(\text{F})\) and \(^1\text{A}_1\text{g}→^1\text{T}_2\text{g}(\text{F})\) transition respectively. The magnetic susceptibility for cobalt complex has been found to be \(\mu_{\text{eff}} = 0.0\) B.M, diamagnetic, which suggest a low spin (\(t^6\text{g} e^0\)) within range of regular octahedral geometry and d²sp³ hybridization because of the Co(II) ion is oxidized to Co(III) ion during complexation. The change of oxidized to Co(III) in the presence of strong ligand such as benzimidazolyl azo compound\(^{(26,31,38)}\).

**Nickel (II)-complex**

Three absorption bands at 958nm (10438 cm⁻¹), 511nm (19569 cm⁻¹) and 473nm (21142 cm⁻¹) for the electronic spectrum of Nickel (II)-complex in 10⁻³ M absolute ethanol, which suggesting the existence of \(^3\text{A}_2\text{g}→^3\text{T}_2\text{g}(\text{F})\), \(^3\text{A}_2\text{g}→^3\text{T}_1\text{g}(\text{F})\) and \(^3\text{A}_2\text{g}→^3\text{T}_1\text{g}(\text{P})\) transition respectively. The magnetic moment of Nickel (II)-complex has been found to be 2.91 B.M because of presence of two unpaired electrons which may suggested high spin, a regular octahedral geometry (\(t^6\text{g} e^2\)) and sp³d² hybridization\(^{(15,20,26,39)}\).

**Copper(II)-complex**

The electronic spectrum of this complex showed a broad band around at 518 nm (19305 cm⁻¹) which may be assigned to \(^2\text{E}_g→^2\text{T}_2\text{g}\) transition in an approximately octahedral configuration\(^{(15,20,31)}\). The magnetic moment of the Cu(II)-complex is 1.72 B.M due to presence one electron unpaired which may suggest an distorted octahedral geometry (Z-in or Z-out), \((t^6\text{g} e^1\text{g})\) and sp³d² hybridization\(^{(17,23,40)}\).

**Zinc (II), cadmium(II) and mercury (II) complexes**

The electronic spectra of Zn(II), Cd(II) and Hg(II) complexes were studied in absolute ethanol (10⁻³ M), do not show any d-d transition because they are saturated with electrons (d⁰). The absorption bands at 534nm (12727 cm⁻¹), 527nm (18975 cm⁻¹) and 538nm (18587 cm⁻¹) these are assigned to a charge transfer (M→L, CT) transition to Zn(II), Cd(II) and Hg(II) complexes respectively. The magnetic moment of these metal complexes have diamagnetic (\(\mu_{\text{eff}} = 0.0\) B.M) with an octahedral spatial configuration (\(t^6\text{g} e^4\text{g}\)) and sp³d² hybridization\(^{(13,20,26)}\).

The obtained magnetic moment values show the presence of Para magnetic characterization for Co(II), Ni(II) and Cu(II) complexes and diamagnetic characterization for Zn(II), Cd(II) and Hg(II) complexes. Figures 11, 12, 13 and 14 shows the spectra of ligand (BIADClP), [Ni(L)₂].H₂O, [Cu(L)₂].H₂O and [Hg (L)₂].H₂O.
Figure (11):- UV-visible spectrum of Ligand (BIADBBrP)  

Figure (12):- UV-visible spectrum of [Ni(L)2].H2O complex  

Figure (13):- UV-visible spectrum of [Zn (L)2].H2O complex  

Figure (14):- UV-visible spectrum of [Cu(L)2].H2O complex  

Table (5):- Electronic spectra magnetic moments, geometry and hybridization

| Complexes      | $\lambda_{\text{max}}$ (nm) | Absorption bands (cm$^{-1}$) | Transition | $\mu_{\text{eff}}$ (B.M) | Geometry | Hybridization |
|----------------|-----------------------------|------------------------------|------------|--------------------------|----------|---------------|
| HL$_2$=ligand (BIADBBrP) | 413                         | 24213                        | $\pi \rightarrow \pi^*$ |             |          |               |
According to the results and discussed through different techniques, the structural formula of chelate complexes prepared may be proposed as shown in Figure 15.

![Figure 15](image)

According to the results and discussed through different techniques, the structural formula of chelate complexes prepared may be proposed as shown in Figure 15.
Where :- M=Co(III), Ni(II) , Cu(II), Zn(II) , Cd(II) and Hg(II) Ions.

Computational Study

A quantum chemical approach of Density function theory DFT with Becke three parameter hybrid method (41) using the Lee-Yang-Par correlation functional(P3LYP) (42) and 3-21G(d,p) basis set have been employed to determined the Global reactive descriptors for (BIADBrP) ligand and Its Metal Complexes

| Compound    | HOMO/eV | LUMO/eV | ΔE HOMO-LUMO /eV | IE /eV | EA /eV | η /eV | ω /eV |
|-------------|---------|---------|-----------------|--------|--------|-------|-------|
| LH=ligand   | -5.246  | -2.942  | -2.304          | 5.246  | 2.942  | 1.152 | 4.094 |
| (BIADBrP)   |         |         |                 |        |        |       |       |
| [Co(L)_2]Cl | -6.011  | -3.625  | -2.386          | 6.011  | 3.625  | 1.193 | 4.818 |
| H_2O        |         |         |                 |        |        |       |       |
| [Ni(L)_2] H_2O | -5.81  | -3.632  | -2.178          | 5.81   | 3.632  | 1.089 | 4.721 |
| [Cu(L)_2] H_2O | -4.571 | 2.321   | -6.892          | 4.571  | 2.321  | 3.446 | 1.125 |
| [Zn(L)_2] H_2O | -4.662 | -1.623  | -3.039          | 4.662  | 1.623  | 1.5195| 3.1425|
| [Cd(L)_2] H_2O | -4.875 | -1.452  | -3.423          | 4.875  | 1.452  | 1.7115| 3.1635|
| [Hg(L)_2] H_2O | -5.897 | 0.548   | -6.445          | 5.897  | 0.548  | 3.2225| 2.6745|

Where : IE= Ionization potential , EA=Electron affinity , η=Hardness , ω= Electronegativity and ω= electrophilicity index

Conclusion

In this work we reported the synthesis and spectral characterization of new azo dye derived from benzimidazole (BIADBrP) and its metal complexes with Co(III), Ni(II) , Cu(II), Zn(II) , Cd(II) and Hg(II) Ions.

The ligand BIADBrP has several coordination which are suitably spatially arranged to bind with metal ions which require hexa coordination .As a general conclusion , the azo dye ligand BIADBrP behave as a mono basic . The metal complex was found to possess metal ions to ligand ratio [M:L] with tridentate ONN donors derived from the phenolic oxygen , nitrogen of azo group (N3) and nitrogen of benzimidazole (N3) forming two five – membered chelate rings . The metal complexes for Ni(II)
Cu(II), Zn(II), Cd(II) and Hg(II) ions are non ionic but ionic character with Co(III)-complex to give 1:1 electrolyte. The geometry is proposed for all complexes octahedral structure and not effect by air, light and a moisture, suggesting high stability plus high degrees of melting points that gives another evidence of the stability of prepared metal complexes.

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