Theoretical Study of the Azo Dye Derived From 2-[6-(benzimidazolyl)azo]-2,4-di chloro phenol and Its Metal Complexes

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Abstract

Metal complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) of the azo dye ligand derived from 2-[6-(benzimidazolyl)azo]-2,4-di chloro phenol have been theoretically study in order to determine their stability, geometrical and electronic properties. Electrochemical potential, electrophilicity index and chemical hardness were calculated based on the energy level of high occupied molecular orbital HOMO and the energy level of low unoccupied molecular orbital LUMO of the ligand and metal complexes. The experimental electronic spectral and IR data were compared with the theoretically calculated data. Global reactive descriptors for (BIADClP) ligand and Its metal complexes in order to predict some important properties of the metal complexes.

Keywords: benzimidazolyl azo, reactive descriptors, physicochemical properties

Introduction

Benzimidazolyl azo ligands (figure 1) have a group –N=N- (azo) as a Distinctive feature. It is part of some of the essential biological molecules (1). Imidazole derivatives such as benzimidazole are widely used in a variety of medical applications due to their high chemotherapeutic properties (2,3). It is used as a stable dyes, applicable to synthetic textiles, cotton, and propylene fibers (4-6). These dyes are also known as good analytical reagents for the spectral identification of metal ions (7-9). In the same context, 2-amino benzimidazole and other benzimidazole derivatives are used as complex agents in the purification of water from heavy metals (10). It was previously mentioned that benzimidazole derivatives could be used as an important drugs that can selectively blocks the growth of endothelial cells and inhibits vascular formation in the laboratory and in vivo (11).

This theoretical study is based on a previous work (12) which included the synthesis and characterization of 2-[6-(benzimidazolyl)azo]-2,4-dichloro phenol (BIADCIP) and its metal cheated complexes with Co(III), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II).
Figure -1 : Structure of 2-[6-(benzimidazolyl)azo]-2,4-dichloro phenol (BIADCIP)

**Computational Strategy**

A quantum chemical approach of density functional theory DFT with Becke three parameter hybrid method (13) using the Lee-Yang-Par correlation functional (P3LYP) (14) and 3-21G(d, p) basis set have been employed in this study.

**Results and Discussion**

**IR spectra for ligand and complexes**

The IR spectrum of the azo dye ligand (BIADCIP) which obtained experimentally and theoretically shown in (Table 1 and Figures 2-4) are compared to ascertain the mode of bonding between the ligand and the metal ions. The IR spectra of the ligand and metal complexes explain the binding mode of ligand to metal ions which are forming the coordination complexes.

IR spectrum of free ligand (BIADCIP) show a broad medium band around 3638 cm⁻¹ refers to OH of the phenolic group. Change in position and intensity of this band are observed in all the metal complexes coordination through deprotonated phenolic OH group (15,16). The strong band at 3441 cm⁻¹ in the spectrum of free ligand assignable to NH stretching of benzimidazole moiety. The unchanged of this band in all metal complexes indicating that the NH group does not participate in coordination (17). IR spectra of all complexes shows a broad bands around at (3363-3456)cm⁻¹ indicate the presence of water molecule in this complexes (18,19). The weak band at 3116 cm⁻¹ in the spectrum of the ligand may be attributed to ṽ (C-H) aromatic. This band is stable in position and intensity for both ligand and chelate complexes. IR spectrum of (BIADCIP) ligand exhibit a strong band at 1689cm⁻¹ due to (C=N) of N3 benzimidazole nitrogen. This band
decrease in intensity in all metal complexes indicating that it has been affected upon coordination to the metal ions \(^{(20)}\).

Azo group (-N=N-) stretching vibration at 1506 cm\(^{-1}\) in the spectrum of ligand was shifted to lower frequency compared with those of the metal complexes indicating the participation of the azo group (N\(_3\)) in coordination to the metal ions \(^{(21)}\).

There are new bands observed in the spectrum of complexes in the range of \((424-570)\) cm\(^{-1}\) which did not present in the spectrum of ligand. This bands are due to \(\nu\) (M-N) and \(\nu\) (M-O) also indicated the bonding of nitrogen and oxygen to the metal ions\(^{(15)}\).

So, the IR spectra indicate that the ligand (BIADCIP) behaves as a tridentate chelating agent coordination through the position of hydroxyl oxygen, nitrogen atom of azo group (N\(_3\)) nearest to phenolic ring and nitrogen (N\(_3\)) of benzimidazole ring to give two five–membered chelate rings.

Despite the close value of bands wave length between theoretical and experimental results, a clear difference in the intensity of the bands has been noticed, It is believed to be due to negligible of molecules population in the ground level \(\nu=0\) compare with \(\nu=1,2,3\ldots\) according to Boltzmann distribution law in the theoretical calculations.

**Table (1):- Selected data (4000–400) cm\(^{-1}\) for ligand (BIADCIP) and its complexes experimentally\(^{(12)}\) and theoretically**

| Compound | Experimentally/theoretically |
|----------|-------------------------------|
| LH=ligand(BIADCIP) | 3638/3645 | 3441/3450 | 1689/1682 | 1506/1499 | 1380/1391 | 1273/1277 | 810/808 | --- | --- |
| [Co(L\(_2\)]Cl.H\(_2\)O | 3425/3448 | 3379/3371 | 1682/1675 | 1473/1468 | 1412/1405 | 1248/1411 | 809/801 | 517/513 | 424/419 |
| [Ni(L\(_2\)]H\(_2\)O | a | 3364/3361 | 1681/1677 | 1474/1467 | 1404/1401 | 1262/1258 | 810/805 | 522/520 | 435/431 |
| [Cu(L\(_2\)]H\(_2\)O | a | 3317/3314 | 1681/1675 | 1475/1467 | 1396/1393 | 1295/1291 | 812/810 | 518/515 | 425/423 |
| [Zn(L\(_2\)]H\(_2\)O | 3510/3508 | 3363/3358 | 1683/1679 | 1474/1471 | 1404/1438 | 1211/1209 | 756/751 | 517/512 | 427/425 |
| [Cd(L\(_2\)]H\(_2\)O | 3525/3523 | 3456/3454 | 1635/1633 | 1473/1471 | 1404/1400 | 1280/1918 | 825/822 | 519/516 | 423/420 |
| [Hg(L\(_2\)]H\(_2\)O | 3549/3546 | 3379/3377 | 1638/1635 | 1474/1471 | 1358/1356 | 1281/1278 | 918/914 | 521/518 | 431/428 |

\(a = \text{The bands have disappeared because of interface between OH and NH groups}\)
Azo dye ligand spectral results show single peak at 5.23 ppm attributed to OH-Ar, and NH-benzimidazole. Triplet peaks between 6.71-6.83 ppm due to protons H3 and H5 of phenol ring.
The complex Overlap peaks 7.02 - 7.41 ppm assigned to proton H₄ and H₇ of Ar-benzimidazole. The single peak noticed at 8.01 ppm is attributed to the presence of protons H₅ and H₆ of Ar–benzimidazole \(^{(17,22)}\). Figure 5 and 6 show NMR spectrum of ligand that measured experimentally and theoretically

![Figure 5: \(^1\text{H}-\text{NMR spectrum of azo dye ligand (BIADClP)/Experimentally}^{(12)}\)](image)

![Figure 6: \(^1\text{H}-\text{NMR spectrum of azo dye ligand (BIADClP)/theoretically}\)](image)

**Electronic spectra**

Electronic spectra of BIADCIP ligand and its metal complexes (Table 2 and Figures 7-8) were recorded. Experimental spectral data theoretical data show very good agreement. The spectrum of (BIADCLP) \(^{(12)}\) gives three bands located at 417 nm, 317 nm and 283 nm. First band due to (n→π*) transition of the azo group (N=N), this band showed a red shift in complexes because of coordination between ligand and metal ion. The second band observed is due to (π→π*) transition of (C=C) groups in benzimidazole and aromatic rings. While the third band due to (n→σ*) of the hydroxyl group (OH) \(^{(23,24)}\).

| Complexes | Experimental wavelength/nm \(^{(12)}\) | Calculated wavelength/nm | Transition \(^{(12)}\) |
|-----------|---------------------------------|------------------------|--------------------|

*Table 2: Experimental and computed wavelength of the (BIADCIP) ligand and its metal complexes*
| LH=ligand (BIADCIP) | 417 | 420 | n→π* |
|---------------------|-----|-----|-------|
|                     | 317 | 319 | π→π*  |
|                     | 283 | 279 | n→σ*  |
| [Co(L)_2]Cl \_H_2O | 571 | 568 | ^1A_g→^1T_1g(F)(\nu_1) |
|                     | 513 | 515 | ^1A_g→^1T_2g(F)(\nu_2) |
| [Ni(L)_2] \_H_2O   | 918 | 915 | ^2A_g→^3T_2g(F)(\nu_3) |
|                     | 591 | 588 | ^1A_g→^3T_1g(F)          |
| [Cu(L)_2] \_H_2O   | 608 | 602 | ^2E_g→^2T_2g             |
| [Zn(L)_2] \_H_2O   | 482 | 478 | M→L, CT                  |
| [Cd(L)_2] \_H_2O   | 498 | 494 | M→L, CT                  |
| [Hg(L)_2] \_H_2O   | 538 | 533 | M→L, CT                  |

Figure 7: Electronic spectrum of the ligand calculated theoretically

Figure 8: Electronic spectrum of ligand measured experimentally

Global reactive descriptors for (BIADCIP) ligand and Its Metal Complexes:
Hardness, Electrochemical Potential, Electrophilicity and electronegativity can be calculated from the frontier molecular orbitals HOMO and LUMO. The energy of the HOMO (Figure 9-16) is directly proportional to the ionization potential

$$\text{IE (Ionization potential)} = -E_{\text{HOMO}}$$

While LUMO is directly proportional to the electron affinity:

$$\text{EA (Electron affinity)} = -E_{\text{LUMO}}$$

Activation hardness has been also defined on the basis of the HOMO–LUMO gap. The qualitative definition of hardness is closely related to the polarizability, since a decrease of the energy gap usually leads to easier polarization of the molecule\(^{(25)}\). Chemical hardness (\(\eta\)) measures the resistance of an atom to a charge transfer.

$$\eta (\text{Hardness}) = (\text{IE} - \text{EA})/2$$

Chemical hardness fundamentally signifies the resistance towards the deformation or polarization of the electron cloud of the atoms, ions or molecules under small perturbation of chemical reaction. A hard molecule has a large energy gap and a soft molecule has a small energy gap\(^{(26,27)}\).

The electronegativity is the measure of the power of an atom or group in withdraw electrons. It can be estimated by using the following equation:

$$\chi (\text{electronegativity}) = (\text{IE} + \text{EA})/2$$

Electronegativity, hardness and softness have proved to be very useful quantities in the chemical reactivity theory. For a reaction of two systems with different electronegativities the electronic flow will occur from the molecule with the lower electronegativity towards that of higher value, until the chemical potentials are equal for both molecules\(^{(28,29,30)}\).

The electrophilicity index (\(\omega\)), shows the ability of the molecules to accept electrons. It is a measure of the stabilization in energy after a system accepts additional amount of electron charge from the environment. They defined Global electrophilicity index:

$$<\omega> = -\chi^2 / 2\eta$$

According to this definition, this index measures the propensity of chemical (Tab.3) species to accept electrons. A good, more reactive, nucleophile is characterized by lower value of \(\omega\); and conversely a good electrophile is characterized by a high value of \(\omega\)\(^{(31)}\).

**Table 3**: Measures the propensity of chemical species to accept electrons

| Compound | HOMO/eV | LUMO/eV | ΔE | IE /eV | EA /eV | \(\eta\)/eV | \(\Delta\)/eV | \(\omega\) |
|----------|---------|---------|----|--------|--------|------------|------------|--------|
|          |         |         |    |        |        |            |            |        |
The HOMO–LUMO gap, is an important stability index, where large HOMO–LUMO gap pointing to high stability for the molecule. It is seen from the table that metal complexes are more reactive than the ligand, the stability results are closely agreement between experimental and theoretical study based on HOMO–LUMO energy gap for the complexes.

| LH=ligand (BIADCIP) | -6.436 | -1.933 | -4.503 | 6.436 | 1.933 | 2.2515 | 4.1845 | -19.71 |
|---------------------|--------|--------|--------|-------|-------|--------|--------|--------|
| [Co(L)$_2$]Cl.H$_2$O | -5.911 | -3.463 | -2.448 | 5.911 | 3.463 | 1.224 | 4.687 | -13.44 |
| [Ni(L)$_2$.H$_2$O]  | -5.53  | -3.144 | -2.386 | 5.530 | 3.144 | 1.193 | 4.337 | -11.22 |
| [Cu(L)$_2$.H$_2$O]  | -2.242 | 0.097  | -2.339 | 2.242 | -0.097 | 1.169 | 1.072 | -0.672 |
| [Zn(L)$_2$.H$_2$O]  | -3.988 | -1.316 | -2.672 | 3.988 | 1.316 | 1.336 | 2.652 | -4.698 |
| [Cd(L)$_2$.H$_2$O]  | -3.725 | -1.039 | -2.686 | 3.725 | 1.039 | 1.343 | 2.382 | -3.810 |
| [Hg(L)$_2$.H$_2$O]  | -3.354 | 0.192  | -3.546 | 3.354 | -0.192 | 1.773 | 1.581 | -2.215 |

Figure 9 : HOMO of LH=ligand (BIADCIP)

Figure 10 : HOMO of Co complex
Figure 11: HOMO of Ni complex

Figure 12: HOMO of Cu complex

Figure 13: HOMO of Zn complex
The analytical data indicates that theoretical values are in good agreement with the experimental values. The experimental data of the ligand and its metal complexes are compared with the computationally generated IR data of the same investigating compounds. The data in the table indicate that the experimental data are in good agreement with the calculated data which is supported by the correlation coefficient. The NMR and electronic spectra also confirms bonding between the metal ion and donor atoms of the ligand. Finally, stability study gives the last evidence of the high agreement between experimental and theoretical study, which will be useful to predicate some properties of metal complexes before preparing them laboratory.

Figure 14: HOMO of Cd complex

Figure 15: HOMO of Hg complex
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