
Qusay A. Nema, Hassan A. Alshamsi

Department of Chemistry, Education College, University of Al-Qadisiyah

Abstract: This work involves synthesis and spectral identification of azo ligand 7-[2-(Benzimidazolyl)azo]-8-Hydroxy quinoline (BIAHQ) and preparation of its complex with Au (III). The ligand and its complex were examined using UV-Vis spectroscopy, FT-IR spectroscopy, and photoluminescence spectroscopy (PL). In order to reach the optimal conditions for the degradation of the complex, impact of several factors on photodegradation were studied which include: Study the effect of the complex concentration, temperature range 20-35°C, and acidic function within range 4-10.

Keywords: Azo imidazole, Metal Complexes, Identification, Metal: Ligand Ratio, Infrared Spectra, Electronic Spectra, PL spectra, Photo degradation of complex

1. Introduction

The gold compounds contain some unique properties like unique electronic properties (1) gold metal have ability to form strong gold – gold bonds (sometimes called aurophilic interactions) (2). The most important oxidation of gold are Au(I) and Au(III) (3). In the presence of strong ligand such as Azo Dye Ligand, the ligand prevent gold redox to metal, in general the gold (III) compounds are very toxic, so less researcher study it (3) gold(III)have configuration and square planar tetra – coordination (4) the gold(III) complexes have many structural chemistry such as [gold(III) porphyrin, dinuclear gold(III) complexes, classical mononuclear gold(III) complexes and organogold(III) compounds] (5) gold(III) complexes can be used in several ways such as anticancer drugs (8). The imidazole ligands and its derivatives azo dyestuffs of heterocyclic compounds can be used in broad range duto plays important role in the organic and in organic chemistry (9). The azo dyes heterocyclic compounds have large size in this racetrack (10) because it contain one or more active group that have tendency to form colored chelate complexes compound that can be specialization with metal ions like Au(III) by using UV-Vis, IR radiation spectrum techniques (11). We can see in the [Au(BIAHQ)]Cl2H2O complex the ligand Behaves like a weekend tri-Age coordinate from imidazole ring nitrogen atom(N) and far azo group belong ring nitrogen atom and Oxygen hydroxyl groupquinolone Which leads to the formation of complexes hexagonalchelate symmetry (12) [Au(BIAHQ)]Cl2H2O complex Characterized that have Distinctive color and fixed dye, so it can be used in Industrial area and medical area like pesticide, Antifungal and antibiotic, or can be used like Additives to lubricating oil Through high efficiency in the inhibition of corrosion processes in machines and equipment (13). The important think in azo imidazole ligand is contain acidic and / or basic groups which increase chromatic intensity of ligand and there complexes such as (Br, -Cl, OCH3,-CH3) (14), but some thisimth groups increase sensitivity mostly when used in analytical chemistry (15). The imidazole azo is very reactive with transition Elements ions such as Au(III) or other metals.

2. Experimental

2.1 Materials

All chemical materials and solvents were used in this work of high purity from commercial source such as Merck, Fluka and Aldrich and other. All chemicals are used without any further additional purification. We used Imidazole (C7H7N2), Sigma-Aldrich. Ammonium acetate (CH3CO2NH4) from FLUKA. Sodium hydroxid (NaOH) from B.D.H. Sodium nitrite (NaNO2) from B.D.H. Hydrochloric acid (HCl) from B.D.H. Ethanol absolute (CH3OH) from J.T.BAKER. 2-Amino benzimidazol (C7H7N2) from Sigma-Aldrich. 8-hydroxy quinolone (C8H8NO) from Sigma-Aldrich. Hydrogentetrachlororourate (II)[AuCl4]-4H2O from Sigma-Aldrich, CaCl2 from FLUKA. distilled water.

2.2 Measurements

We used Hot plate LMS – 1003, Labtech, Korea. pH-meter 211-Instrument Hanna, Romania.Electronic Balance BL 2105 sartorius Ag Gottingen, Germany. Oven memort LDO-080N labtech, Korea. Ultrasound path 405 power sonic Hwashin Korea. Water Bath WB 710M Optima, Japan. Melting point apparatus Electrothermal 9300 M.P Japan. source light 400 W Osram German. FT-IR spectra were recorded usedKBr discs in the range (400-4000)cm-1 on a FT-IR spectrophotometer by (shimadzu model 840 S FT-IR test scan series ) Japan. Electronic spectra were obtained on a UV-vis by ( Shimadzu model 1650 pc ) Japan . Fluorescence spectromer by Agilent Technologies.

2.3 Synthesis of the Azo Dye Ligand:

The heterocyclicazo dye ligand (BIAHQ) has been Synthesized by the diazotization coupling reaction by using shibat methodwith some modification (Scheme1).2-Amino benzimidazol (1.33 gm,0.01 mole) wasdissolved in mixture
30 ml distilled water and 5 ml of concentrated hydrochloric acid and 20 ml ethanol. The filtered solution was diazotized at 0-5 °C with (0.75 gm, 0.01 mol) sodium nitrite in 25 ml distilled water drop wise, and stirred for 20 min at 0-5°C. The resulting diazonium chloride solution was added drop wise with cooling and stirring continuously at 0-5 °C to alkaline solution of 8-hydroxy quinoline (1.45 gm, 0.01 mol), dissolved in mixture of 150 ml absolute ethanol and 30 ml of 8% sodium hydrosulphide solution in the mixture was stirred continuously for 1 hour at 0-5 °C in ice-bath and allowed to stand over night. The mixture was acidified with dilute hydrochloric acid until pH=6. The precipitate was filtered and washed several times with cold distilled water as well as with 10 ml absolute ethanol to remove the excess of unreacted substance. The isolated dark red crystals was recrystallized from hot ethanol and dried in oven at 60°C for several hours and stored in a desiccator over anhydrous calcium chloride. The yield was 83% and melting point found to be 238.2°C.

Scheme 1: Synthesis of azo dye ligand 7-[2-(Benzimidazolyl)azo]-8-Hydroxy Quinoline (BIAHQ)

Preparation Metal Complex

The metal complex which prepared using metal salt (hydrogentetrachloroaurate(III) H[AuCl4].4H2O) and the azo dye ligand (BIAHQ). The amount of 0.45gm (0.002 mol) from azo dye ligand was added dissolved in 50 ml hot ethanol which was added in drops with stirring continuously to (0.001mol), 1:1 [M: L] for H[AuCl4].4H2O dissolved in 40 ml hot buffer solution (ammonium acetate) at pH=7. The mixture was heated to 70°C for 30 min., then left over night. The separated solid complexes were filtered off, washed with distilled water and then little warm ethanol to remove any traces of unreacted materials. The complex obtained was finally dried under vacuum desiccators over fused CaCl2.

3. Result and Discussion

3.1 Metal: Ligand Ratio

To finding the expected structure formula of prepared complex were studied by molar ratio method at λ max. The solution of prepared complex increase the intensity of the color as approach of point intersection ratio. (M:L) and colors continuosconcentatant passing this point which indicate that the complex formed in constant. Solution19.

The physical properties of (BIAHQ) ligand and [Au(BIAHQ)Cl]Cl.H2O can be shown in table (1)

<table>
<thead>
<tr>
<th>M : L</th>
<th>Absorbance of complexes Au(III)</th>
<th>Molar Absorptivity (ϵ) of (BIAHQ) ligand and its Au(III) complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:00.3</td>
<td>0.521</td>
<td>103 ϵ×10⁻³ M⁻¹cm⁻¹</td>
</tr>
<tr>
<td>1:00.5</td>
<td>0.57</td>
<td></td>
</tr>
<tr>
<td>1:00.7</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>1:01.0</td>
<td>0.63</td>
<td></td>
</tr>
<tr>
<td>1:01.3</td>
<td>0.63</td>
<td></td>
</tr>
<tr>
<td>1:01.5</td>
<td>0.64</td>
<td></td>
</tr>
<tr>
<td>1:01.8</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>1:02.0</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>1:02.2</td>
<td>0.651</td>
<td></td>
</tr>
<tr>
<td>1:02.5</td>
<td>0.66</td>
<td></td>
</tr>
<tr>
<td>1:02.8</td>
<td>0.67</td>
<td></td>
</tr>
<tr>
<td>1:03.0</td>
<td>0.67</td>
<td></td>
</tr>
</tbody>
</table>

Scheme 2: ration mole curveof Au(III)- (BIAHQ) complex with ligand
3.2 Infrared Spectra

The infrared spectroscopic data of the azo dye ligand and its Au(III)-complex have been studied in lab. The comparison between spectra of the ligand with the coordination Au(III)-complex have apparent, characteristic differences of some of these main shifts along with conclusion are give below.

1) The spectrum of free ligand (BIAHQ) show abroad a weak absorption band around at 3380 cm\(^{-1}\) due to \(\nu\) (OH)\(^{(20)}\). This abroad due to strong inter molecular hydrogen bonding\(^{(21)}\). The spectrum of Au(III)-complex show abroad a weak band around at 3218 cm\(^{-1}\) which evidence to the coordination of water molecule\(^{(22)}\).

2) In the spectrum of free ligand Two weak bands had been observed at 3047 cm\(^{-1}\) and 2661 cm\(^{-1}\) because of \(\nu\) \((C\equiv H)\) aromatic and aliphatic respectively\(^{(23)}\). These bands are the same location in Au(III)-complex.

3) In the free ligand shows a medium band at 1572 cm\(^{-1}\) became because \(\nu\) \((C\equiv O)\) of 8-hydroxy quinoline\(^{(24)}\). This band ambulant at 1562 cm\(^{-1}\) in Au(III)-complex\(^{(25)}\).

4) In ligand \(\nu\) \((C\equiv N)\) of benzimidazole 8-hydroxy quinolin shows respectively two absorption bands at 1580 cm\(^{-1}\) and at1505 cm\(^{-1}\). In the spectra of Au (III)–complex these bands shift to lower frequencies at1516 cm\(^{-1}\) and 1606 because of linkage with nitroge of hetero cyclic benzimidazole ring\(^{(26,27)}\).

5) The spectrum of free ligand shows two absorption bands at 1473 cm\(^{-1}\) and 1411 cm\(^{-1}\) due to azo group \(\nu\) \((N=N)\). The position of these bands in Au (III)–complex are shifted to a lower frequencies at 1465 cm\(^{-1}\) and 1419 cm\(^{-1}\) this indicates that it have been effected on coordination with Au (III)\(^{(28)}\).

Table 2: Some physical properties for ligand (BIAHQ) and its Au(III) complex

<table>
<thead>
<tr>
<th>Compound</th>
<th>m.p(C)</th>
<th>Colour</th>
<th>m.f(m.wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L=BIAHQ</td>
<td>238</td>
<td>Dark red</td>
<td></td>
</tr>
<tr>
<td>[Au(L)Cl]Cl.H2O</td>
<td>275</td>
<td>Earthy</td>
<td></td>
</tr>
<tr>
<td>C27H18N2O4</td>
<td></td>
<td></td>
<td>(289.266)</td>
</tr>
<tr>
<td>C27H18N2O4ClAu</td>
<td></td>
<td></td>
<td>(710.917)</td>
</tr>
</tbody>
</table>

3.3 Electronic Spectra

The electronic Spectra of azo dye ligand and its Au (III) – complex were studied in absolute ethanol as a solvent(10\(^{-3}\)M). The free ligand (BIAHQ) spectrum gives three absorption bands, the first band show at 517 nm (19342 cm\(^{-1}\)) for \(n\rightarrow p^*\) transition of the azo group\(^{(29)}\). The second band is observed at 310 nm (32258 cm\(^{-1}\)) due to \(p\rightarrow p^*\) transition to the \((C=C)\) group in heterocyclic benzimidazole and hydroxyl quinoline rings\(^{(30)}\). The third band show at 241 nm (41949 cm\(^{-1}\)) for \(n\rightarrow p^*\) transition to the \((C=N)\) group in the ligand structure\(^{(30)}\). The electronic Spectra of Au(III)–complex show band at 385nm(25974 cm\(^{-1}\)) assigned to \(\sigma\rightarrow \pi^*\) transition. So the Square Planer geometry and hybridization \(sp^3\) are suggested. Fig 2 show the spectra of ligand and its complex with Au(III) ion\(^{(32)}\).
3.4 PL spectra

The room-temperature PL spectra are showed in Fig. 4a and 4b. Each spectrum of the ligand and its complex consists of some sharp bands in the visible region of spectra. The peak centered at approximately 3.2 eV known as the green defect luminescence. The (BIAHQ) ligand and its complex generally attributed to oxygen vacancies, another assignment was also proposed in the literature. The peak centered at 3.49 eV for the ligand spectrum appeared in 355 nm, show in Fig 4a. While in the Au(III)-complex, the peak centered at 3.22 appeared in 385 nm.

3.5 Photodegradation of complex

3.5.1 The effect of irradiation time in Dark Reaction (Adsorption Reaction)

This experiment was carried out in the absence of U.V by using 0.4 gram of Au-(BIAHQ) complex. We show the result in the plot (AbsorptionEffect ) in figure 5. The result indicate that there is no reaction in the absence of UV, because the wavelength was small change with increase the time. This indicate that the Au-(III) complex is high stability.

3.5.2 Effect of irradiation time and concentration of complex

We studied the irradiation time on the complex dissociation rate with $1 \times 10^{-4}$ M concentration, 298 K temperature and 400Watt light intensity.

We observed in figure 5 that the absorption spectrum curve of complex decrease in increase of irradiation time.

3.5.3 Effect of concentration of Au-(BIAHQ) complex

In this experiment we used different dosages of Au-(BIAHQ) complex. As we show in figure 6. The other factors kept constant like (initial pH solution 7, light intensity 400Watt and temperature 298 K. According to the result, we found that 0.3
gram of Au-(BIAHQ) complex gives optimum photocatalytic activity.

Figure 6: The change of Adsorption time in different concentration with [Au(BIAHQ)]Cl\(_2\)H\(_2\)O

Figure 7: The change of adsorption time in different pH of solution with [Au(BIAHQ)]\(_2\)Cl\(_2\)H\(_2\)O

3.5.4 Effect of Initial pH Solution for Au-complex

The pH play an important role in the production of hydroxyl radical. In this experiments we fix the experimental conditions such as light intensity 400Watt), Au-(BIAHQ) complex concentration (0.4g/200mL of Ethanol) and temperature 298K. figure 6 show the degradation increase with increase of initial pH solution up to pH 7 then decrease in pH (9,3,5 and 4).so the best pH of Au-(BIAHQ) complex is pH 7.

3.5.5 Effect of Temperature on Au-(BIAHQ) complex decomposition

In this experiments we show that the higher temperature can fast the Au-(BIAHQ) complex decomposition when fix other condition such as light intensity 400Watt), Au-(BIAHQ) complex concentration (0.4g/200mL Ethanol), initial pH Solution equal 7 as we show in figure 15. we used different temperature with Au-(BIAHQ) complex in the range (278–293K). Its found that the complex decomposition increase when the tempreture increase.

Figure 8: The change of Adsorption time in different temperature of solution with [Au(BIAHQ)]\(_2\)Cl\(_2\)H\(_2\)O

References
