Synthesis, characterization of new chelate complexes derived from Azo naphthoresorcenol ligand

Widad Ibrahem Yahya¹, Raheem Tahir Mahdi² and Hussein Kadhem Al-Hakeim
¹Department of Chemistry, College of Sciences/ University of Kufa, Iraq.
²Department of Chemistry, College of Education for Women/ University of Kufa, Iraq.

Abstract
Background: Azo compounds are the oldest and largest class of industrially synthesized organic dyes due to their versatile application in various fields and have attracted much attention in both academic and applied researches [1-3]. The latter included dyeing textile fiber, biomedical studies, advance application in organic synthesis and high technology areas such as laser, liquid crystalline displays, electro-optical devices and ink-jet printers. Therefore, current study was conducted to synthesize new azo-dyes and to study their chemical structures in details.

Methods: A new azo compounds is prepared by coupling the diazonium salts of (3-amino pyridine) with 1,3-dihydroxynaphthalene to form (E)-4-(pyridin-3-yldiazenyl) naphthalene-1,3-diol. The azo ligand was identified by: Mass, ¹H-NMR, ¹³C-NMR,UV-Vis. and IR spectra, in addition to elemental analysis measurement. The chelate complexes were characterized by elemental analysis, magnetic susceptibility, molar conductance, UV-Vis and IR spectra. Results: Analytical data revealed that all the complexes exhibited 1:2 metal-ligand ratios. On the basis of magnetic susceptibility measurements, suitable geometry was proposed for each complex. IR spectra of complexes showed that the ligand is coordinated to the metal ions in bidentate manner with Oxygen and Nitrogen donor sites of hydroxynaphthalene (OH) and azo Nitrogen. These findings suggested octahedral geometry for all complexes. Also, biological evaluation of all synthesized compound showed moderate to good activity against employed strains. All the complexes were stable, non-ionic and exhibited octahedral geometry around the metal center.

Keywords: Azo ligand, Metal complexes, Dihydroxynaphthalene, NMR, Chelate complexes.

1. INTRODUCTION

Azo compounds are the oldest and largest class of industrially synthesized organic dyes due to their versatile application in various fields and have attracted much attention in both academic and applied researches [1-3]. The latter included dyeing textile fiber, biomedical studies, advance application in organic synthesis and high technology areas such as laser, liquid crystalline displays, electro-optical devices and ink-jet printers. Therefore, current study was conducted to synthesize new azo-dyes and to study their chemical structures in details.

2. MATERIALS AND METHODS

2.1. Materials

All chemicals used in the preparation of azo ligand and metal complexes A. R. products from BDH and Merck.

2.2. Measurements

Melting points were determined by open capillary tube method and are uncorrected by using Stuart melting point model 9300.

Elemental analyses (C, H, N) were carried out using a C.H.N.S EA-3000 mth instrument. The metal contents of the complexes were measured using atomic absorption technique by Shimadzu AA-6300. IR spectra were recorded on a Shimadzu 1700 UV spectrophotometer in the (4000-400) cm⁻¹ range using KBr discs. Electronic spectra were obtained on a Shimadzu 1700 UV spectrophotometer using ethanol as solvent in the (1100-200) nm range. Magnetic susceptibilities are determined by faraday method at room temperature using Balance Model Sherwood Scientific, at Department of Chemistry, College of Sciences/ University of Al – Mustansiriyah. Apparatus and diamanagnetic corrections for the ligand were calculated using Pascal’s constant. Mass Spectra were recorded on AB Sciex 3200 QTRAP LC/MS/MS, (Mass range - m/z 5-2000-quad mode and 50-1700- linear ion trap mode). Molar conductance of the transition metal complexes were determined in (DMF) using Digital conductivity Series Ino. Lab- 720 at 25°C, the concentration of the solutions was (10⁻³ mol L⁻¹).

2.3. Synthesis of azo ligand

(PAN= H₂L) azo ligand is prepared according to the following general procedure [17] (Figure 1), 3-amino pyridine ( (4.32 g, 10 mmol) ) were dissolved in 30 ml of water and 6 ml of concentrated hydrochloric acid. The filtered solution was diazotized at (5 °C) 12 ml of aqueous (1.0 M) sodium nitrate. The resulting diazonium chloride solution was added drop-wise with stirring to the 1,3-dihydroxynaphthalene (2.24 g, 10 mmol) dissolved in 200 ml alkaline ethanol cooled below 0°C. After leaving in the refrigerator for 24 hours, the mixture was acidified with dilute hydrochloric acid until pH = 6. The precipitate was filtered off, recrystallized twice from hot ethanol and dried in oven at (70 °C) for several hours melting point (195-197°C ) , yield (85%).

2.4. Synthesis of metal complexes

The complexes were prepared by adding an appropriate amount of the metal salt (1 mmol), namely, Mn (II), Fe (II), Co (II), Ni (II) and Cu (II) hydrated metal chloride and anhydrous Zn (II), Cd (II) and Hg (II) chloride were dissolved in a least amount of distilled water to (0.786 g, 2 mmol) of ligand (PANR) dissolved in 50 cm³ of ethanol. The reaction mixture refluxed for 30 min with stirring. The precipitated solid complexes were filtered, washed with 3 ml of hot 50 vol. % ethanol to remove any traces of unreacted starting materials. Finally, the complexes were washed with 2 ml, diethyl ether and dried over anhydrous CaCl₂.

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3.3. Mass spectrum of azo ligand (PANR)

The mass spectra of synthesized azo ligand were recorded at room temperature. This spectrum confirms the proposed formula by showing a molecular ion peak (m/z) at 265 (M⁺) with a relative intensity 100% corresponding to the ligand molecule [C₁₅H₁₁N₃O₂] and the main mass fragment of organic ligand is given in Figure 3. The latter presents series of peaks at 78, 93, 105, 159, 160, 175, 187 and 236 u which were assigned to various fragments.

3.4. 1H-NMR spectrum of azo dye

The 1H-NMR spectrum of azo-compound (PANR) under study displayed a group of signals corresponding to the protons of each molecule. The spectrum of this compound was produced using d₆-DMSO as a solvent and (TMS) as a reference. The phenyl multiplets at 6.0-8.8 ppm were assigned to the aromatic protons. In general, the compounds exhibited the following characteristics chemical shifts as shown in Table 3. As previously reported, the compounds shown in Figure 4 were present in solution as a proton transfer equilibrium. In all cases, their 1H-NMR spectrum showed a signal with a chemical shift in the range of 17-11 ppm, corresponding to the O-H···N proton involved in the relevant intramolecular hydrogen bond. The signal at higher field, at 13.03 ppm for azo-compound, was due to the free OH group. In 1H-NMR spectra of ligand, it was seen that the signal of OH group (2-H) which made hydrogen bond is broader than the signal of free OH group [24-26].

3.5. 13CNMR spectrum of azo dye

The 13C NMR spectrum of azo ligand was measured at room temperature in D6-DMSO. A spectrum of the ligand is shown in Figure 5. The 13C NMR spectrum of the ligand displayed characteristic signals at 148.6 ppm and at 168.6 and 178 ppm due to >-(C-py pyridine ring) and >-(C-OH naphthol ring) azo ligand, respectively [27]. Moreover, the ligand spectrum showed another peaks in the regions of 99, 107.3, 129.6 and 140.8 ppm due to aromatic carbon atoms.
3.6. Electronic spectra

Electronic spectra provide the most detailed information about electronic structure. The UV-Vis spectrum of azo ligand (HL) exhibited three charge transfer (CT) bands at (245 nm; 39370 cm⁻¹), (304 nm; 32894 cm⁻¹) and (426 nm; 23474 cm⁻¹) attributed to π–π* and n–π* transition within the azo ligand. In the spectra of complexes, CT band at (326 nm) remains in agreement with the π–π* transition of azo ligand. The band observed at (426 nm) in the spectrum of the free ligand (HL), was red-shifted to (458–493 nm) in complexes due to ligand metal charge transfer (LMCT) transition [28,29] suggesting an octahedral geometry around metal (II) ion in complexes. The electronic spectra of the ligand and Co (II) complex are shown in Figures 6 and 7, whereas magnetic properties and conductivity values of the ligand and its complexes are listed in Table 3.

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption Bonds(nm)</th>
<th>Absorption Bonds(cm⁻¹)</th>
<th>Transition</th>
<th>μeff(B.M)</th>
<th>Conductivity S.mol⁻¹ . cm²</th>
<th>Geometry</th>
<th>Hybridization</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANR</td>
<td>304</td>
<td>32894</td>
<td>π→π*</td>
<td>--------</td>
<td>---------------------------</td>
<td>Octahedral</td>
<td></td>
</tr>
<tr>
<td>[Mn(PANR)₂(H₂O)₂]</td>
<td>481</td>
<td>20790</td>
<td>M→L,CT</td>
<td>5.2</td>
<td>7.23</td>
<td>Octahedral (regular)</td>
<td>sp'd'</td>
</tr>
<tr>
<td>[Fe(PANR)₂(H₂O)₂]</td>
<td>487</td>
<td>20533</td>
<td>M→L,CT</td>
<td>5.40</td>
<td>3.52</td>
<td>Octahedral (regular)</td>
<td>sp'd'</td>
</tr>
<tr>
<td>[Co(PANR)₂(H₂O)₂]</td>
<td>464</td>
<td>21551</td>
<td>M→L,CT</td>
<td>4.90</td>
<td>12.56</td>
<td>Octahedral distorted</td>
<td>sp'd'</td>
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<tr>
<td>[Ni(PANR)₂(H₂O)₂]</td>
<td>463</td>
<td>21598</td>
<td>M→L,CT</td>
<td>3.06</td>
<td>17.43</td>
<td>Octahedral (regular)</td>
<td></td>
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<tr>
<td>[Cu(PANR)₂(H₂O)₂]</td>
<td>473</td>
<td>21141</td>
<td>M→L,CT</td>
<td>1.79</td>
<td>11.97</td>
<td>Octahedral distorted</td>
<td>sp'd'</td>
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<tr>
<td>[Zn(PANR)₂(H₂O)₂]</td>
<td>459</td>
<td>21786</td>
<td>M→L,CT</td>
<td>Dia</td>
<td>10.22</td>
<td>Octahedral (regular)</td>
<td>sp'd'</td>
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<tr>
<td>[Cd(PANR)₂(H₂O)₂]</td>
<td>458</td>
<td>21834</td>
<td>M→L,CT</td>
<td>Dia</td>
<td>9.65</td>
<td>Octahedral (regular)</td>
<td>sp'd'</td>
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<tr>
<td>[Hg(PANR)₂(H₂O)₂]</td>
<td>493</td>
<td>20283</td>
<td>M→L,CT</td>
<td>Dia</td>
<td>11</td>
<td>Octahedral (regular)</td>
<td></td>
</tr>
</tbody>
</table>
17.43 S.mol⁻¹.cm⁻² that were non-electrolyte and no conductive this work showed conductivity values were ranged from 9.65 to 19.21 S.mol⁻¹.cm⁻².

Molar conductivity measurement

The high spin magnetic moment value of Mn (II) complex has been found 5.93B.M. The Fe (III) complex showed magnetic moment value of 2.9–3.3 B.M for a high-spin Ni (II) complex depended on the magnitude of the orbital contribution. The Cu (II) complex shows a magnetic moment value of 1.79 B.M monomeric and consistent with a distorted octahedral geometry.

3.8. Molar conductivity measurement

Molar conductance of the metal complexes was measured in DMSO as a solvent at room temperature. All chelate complexes prepared in this work showed conductivity values were ranged from 9.65 to 17.43 S.mol⁻¹.cm⁻² that were non-electrolyte and no conductive species. According to these results, the structural formulas of this ligand and chelate complexes can be proposed as in Figure 8.

CONCLUSIONS

In the current study we had explored the synthesis and coordination chemistry of some monomeric complexes obtained from the reaction of the dinitratoazo ligand PANR with some metal ions. The mode of bonding and overall structures of the complexes were determined through physico-chemical and spectroscopic methods. All the complexes were stable, non-ionic and exhibited octahedral geometry around the metal center.

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Conflict of Interest: None to declare.

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