Preparation, Spectroscopic of the new complexes with ligand 4,4'-Bis(3-hydroxy phenol azo)-O-tolidine

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Abstract-- new Fe(III), Co(III) metal complexes were synthesize with aryl azo 4,4'-Bis(3-hydroxy phenol azo)-O-tolidine [BHPAT] derived from O-tolidine and resorcinol. The ligand and it's complexes were characterized by H NMR, FTIR, UV-Vis. spectra and conductivity measurements. The ligand behaves as bidentate (N,O) of the ligand forming chelates with (2:1) (metal:ligand). The molar conductance values of the Fe(III) and Co(III) complexes of the bidentate ligand indicate their non-ionic character, Octahedral environment is suggested for metal complexes.

Index Term-- Azo, O-tolidine, resorcinol, complex Fe(III) and complex Co(III)

INTRODUCTION
Azo dyes are important class of organic colorants consists of at least a conjugated chromospheres azo (-N=N-) group and largest and most versatile class of dyes. There may be more than one azo group present in the dye molecules and thus classified into mono azo[1-3], diazo and poly azo according to the number azo group in the dye molecules[4,5]. Azo compounds containing hetroaryl ring systems can form varieties of metal complexes with transition metal ion as chelating agent. Synthesis azo compounds were widely used in different fields, such as dyeing industry[6], Inhibition of aluminum corrosion[7], polymerization[8,9], biological activity[10], and study effect it on the Ach enzyme. This paper describe the synthesis and characterization of a new bisazo ligand and some of its transition metal complexes.

EXPERIMENTAL
Apparatus and materials
All the reagents and solvents were of reagent-grade quality and purchased from commercial suppliers. The Melting points were determined on a Electrothermal melting point, GOWLLANDS, England. H NMR spectrum solvent (DMSO) (400 MHz), IR spectra were recorded using KBr discs 4000-400 cm-1 on FTIR Test scan Shimadzu model 8400S, while the UV-Vis. Spectra were recorded in ethanol on Shimadzu model 1800. Molar conductance measurements were determined in ethanol by using a Alpha Digital conductivity meter model 800. H NMR spectrum was taken using (BRUKER) using (DMSO) as the solvent and SF(400MHz).

Preparation of ligand (BHPAT)
Ligand was prepared according to the following general procedure[11]. The procedure was seen in Schem.(1). (0.212 gm, 0.001 mole) of O-tolidine was dissolved in 30 ml of water and using concentrated hydrochloric acid (pH = 5). The filtered solution was diazotized below 5ºC with 20 ml of aqueous (0.138 gm, 0.002 mol) sodium nitrate. The result diazonium chloride solution was mixed with 3-hydroxy phenol (0.22 gm, 0.002 mole) dissolved in 50 ml alkaline ethanol cooled below 0ºC. After leaving in the refrigerator for 30 minutes. A solution of one molar sodium hydroxide was used to precipitate the product the pH of the solution should be maintain at (9–10). A dark brown crystals were precipitated, and a recrystallization from ethanol was done twice before using, m.p. 123–121 C° The percentage yield 63%.
Preparation of the solid complexes

An aqueous of the metal salt contains (0.002 mole) of FeCl₃ and Co(NO₃)₂.6H₂O (Oxidation Co(II) to Co(III) by add 2-3 drops from H₂O₂) was add gradually with stirring to the ethanol solution of the ligand (0.001mol at pH ≈ 7). A solid complexes were obtained, collected by filtration, washed by ethanol and water several times and dried.

Characterization of ligand and its complexes

The complexes were insoluble in water but soluble in DMF, DMSO and EtOH solvents. The ligand was Dark brown crystals. Table (1) appears some physical properties of the prepared of the ligand and complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Color</th>
<th>Yield(%)</th>
<th>M.P(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BHPAT</td>
<td>C26H22N4O4</td>
<td>deep brown</td>
<td>63</td>
<td>123-121</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSION

¹H NMR spectrum

The ¹H NMR spectrum of the ligand (BHPAT) in (DMSO) and SF(400 MHz) Fig(1). displayed the presence of the broad singlet signal due to the hydrogen with azo (toumerism), (2.546, 3.335 ppm, to solvent (DMSO))[12], (7.048-7.370 ppm, d, H-Ar)[13,14], (6.582, 6.602 ppm, d, H-O), (4.825 ppm, d, H-N (tou.t)) ] [15,16], (2.069-2.479ppm, d, H-C)[17].

Scheme (1): Preparation of the ligand (BHPAT).

Scheme (2):
Molar Conductivity

The molar conductance of the complexes as shown in Table (3) were carried out in ethanol at room temperature, the values indicate that the complexes are non-electrolytes nature[18,19], where the values suggest that no anions present outside the coordination spheres.

Table II

<table>
<thead>
<tr>
<th>Complex</th>
<th>M:L (10^-5 M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abs. of complexes</td>
<td>Fe(III) (411 nm)</td>
</tr>
<tr>
<td>Fe(III) (411 nm)</td>
<td>0.071</td>
</tr>
<tr>
<td>1:2.5</td>
<td>0.118</td>
</tr>
<tr>
<td>1:5</td>
<td>0.168</td>
</tr>
<tr>
<td>1:7.5</td>
<td>0.252</td>
</tr>
<tr>
<td>1:1</td>
<td>0.246</td>
</tr>
<tr>
<td>1:12.5</td>
<td>0.327</td>
</tr>
<tr>
<td>1:15</td>
<td>0.499</td>
</tr>
</tbody>
</table>
Table III
Metal : Ligand ratios ,Stability constant values and Molar Conductivity of the complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>pH</th>
<th>( \lambda_{\text{max}} ) (nm)</th>
<th>Metal :Ligand</th>
<th>( \beta )</th>
<th>\log ( \beta )</th>
<th>Conductivity ( \text{s.mol}^{-1}.\text{cm}^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(III)- BHPAT</td>
<td>7</td>
<td>411</td>
<td>2:1</td>
<td>( 0.133 \times 10^8 )</td>
<td>7.123</td>
<td>10</td>
</tr>
<tr>
<td>Co(III)- BHPAT</td>
<td>7</td>
<td>411</td>
<td>2:1</td>
<td>( 1.378 \times 10^8 )</td>
<td>8.139</td>
<td>12</td>
</tr>
</tbody>
</table>

Stability constants are obtained spectrophotometricaally by measuring the absorbance of solutions of ligand and metal mixture at fixed wavelength \( \lambda_{\text{max}} \) and pH values. The degree of formation of the complexes is obtained according to the relationship \( \beta = (1 - \alpha) / (4\alpha^3 \cdot c^2) \), and \( \alpha = (A_\text{m} - A_\text{s})/A_\text{m} \), where \( A_\text{s} \) and \( A_\text{m} \) are the absorbance of the partially and fully formed complex respectively at optimum concentration\[20,21\]. The calculated \( \beta \) and \( \log \beta \) values for the prepared complexes are shown in the table above.

**IR spectra**

The wave numbers of some characteristic bands in the IR spectra of ligand, The stretching vibration of OH groups at (3429 cm\(^{-1}\)) and other vibration at (1112-1040 cm\(^{-1}\))[22,23], The \( \nu(\text{N}=\text{N}) \) stretching vibration appears (symmetrical) at (1404 -1473 cm\(^{-1}\)) \[15\], The asymmetrical (N\(=\)N) band usually overlaps with the bands of the aromatic rings hence is difficult to identify[24-26] in the free ligand spectra,The infrared band assignments of the ligand complexes of Fe(III), Co(III) ions (Table4). this band to vanish in the spectra of complexes [27]. The broad band at (3388,3365 cm\(^{-1}\)) in of the ligand complexes of Fe(III), Co(III) ions which assigned to \( \nu(\text{-OH (stretching)}) \) free Fig.(4,5). about involvement of phenol group in coordination with metal ions via oxygen group . New bands in the region (1390 cm\(^{-1}\)) to (N=O) from NO\(_3\) group[17] Fig.(5) and (821 cm\(^{-1}\)) to (OH) in group water coordination[28,29] Fig.(4) These were assigned in the spectra of metal complexes. These bands were not present in the spectrum of ligand, and they due to \( \nu(\text{M─N})\) and \( \nu(\text{M─O}) \) vibrations respectively . The appearance of these bonds support the involvement of azomethine and hydroxyl groups via nitrogen and oxygen atoms in complexation.

**Table IV**

FTIR to Ligand and complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>(O-H) coord.</th>
<th>(O-H) free</th>
<th>(N=\text{N})</th>
<th>(N=O) in NO(_3)</th>
<th>(O-H) in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>BHPAT</td>
<td>3429</td>
<td>Overlap</td>
<td>1404-1473</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>BHPAT- Fe</td>
<td>-----</td>
<td>3388</td>
<td>1454</td>
<td>-----</td>
<td>821</td>
</tr>
<tr>
<td>BHPAT- Co</td>
<td>-----</td>
<td>3365</td>
<td>1452</td>
<td>1390</td>
<td>-----</td>
</tr>
</tbody>
</table>
Fig. 4. IR spectrum to O-Tolidine

Fig. 5. IR spectrum to (BHPAT)

Fig. 6. IR spectrum to complex Fe(III)
Electronic spectra

The electronic spectral data of the ligand and its complexes were recorded in ethanol and their assignments are listed in (table 4). The UV-Visible spectrum of the ligand, Fig.(8) shows absorption peak at (443 nm) and (297 nm) assigned to (n→π*) and (π→π*) transitions respectively[30,31]. While the electronic spectra of the complexes Figs.(9,10) exhibited that the electronic transitions blue shift[32,33] (411 nm) to Fe(III) complex and (411 nm) to Co(III) complex.

The \( \lambda_{\text{max}} \) of complexes were slightly blue shifted which arise from the energy change of intense (n→π*) transition of the conjugated chromophore due the chelation between metal ions and azo ligand. The complexation of the dye with the metal ion was responsible for a significant hypochromic shift at(n→π*) transition region[34-37] Table (V).

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \lambda ) nm</th>
<th>( \lambda ) cm(^{-1} )</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>BHPAT</td>
<td>443</td>
<td>22573.363</td>
<td>n→π*</td>
</tr>
<tr>
<td></td>
<td>297</td>
<td>33670.034</td>
<td>π→π*</td>
</tr>
<tr>
<td>BHPAT-Fe</td>
<td>411</td>
<td>24330.9</td>
<td>Ligand field</td>
</tr>
<tr>
<td></td>
<td>907</td>
<td>11025.358</td>
<td>d-d transition</td>
</tr>
<tr>
<td></td>
<td>788</td>
<td>12690.355</td>
<td></td>
</tr>
<tr>
<td>BHPAT-Co</td>
<td>411</td>
<td>24330.9</td>
<td>Ligand field</td>
</tr>
<tr>
<td></td>
<td>907</td>
<td>11025.358</td>
<td>d-d transition</td>
</tr>
<tr>
<td></td>
<td>787</td>
<td>12706.48</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 9. UV-Vis. spectrum to complex Fe(III)

Fig. 10. UV-Vis. spectrum to complex Co(III)
Suggested chemical structure formula for the complexes

According to these results (FTIR, U.V.-Vis., molar conductivity and mole ratio) the structural formula of prepared complexes may be proposed in Fig. (11) and Fig. (12).

**Fig. 11. Suggested (BHPAT-Fe(III))**

**Fig. 12. Suggested (BHPAT-Co(III))**

**CONCLUSION**

1- prepared ligand coordinate with Fe(III) and Co(III) from type (bidentate).
2- Preparation the complexes were (1:2) (ligand : metal) from results (UV-Vis, FTIR, molar conductivity and mole ratio).
3- The electronic transitions blue shift to Fe(III) complex and Co(III) complex.

**REFERENCES**


