Synthesis, structural, characterization, spectral studies and antimicrobial activities of Cobalt(II) and Nickel(II) complexes with azo dye ligand

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ABSTRACT

The solid complexes of Co(II) and Ni(II) with azo dye ligand derived by coupling of diazonium salt of sulfamethoxazole with 2-Ethyl-4-methyl phenol, have been synthesized and characterized by elemental analysis, conductometry, magnetic, IR, NMR, UV-Vis spectral studies and stepwise stability constants by Pθ metric method. From the analytical data the stoichiometry of the complexes has been found to be 1:2 (metal: ligand). The low conductance values suggest that the complexes are non-electrolytes. The physichemical data indicates tetragonal geometry for all the complexes. Complexes have been screened for antimicrobial activity against B.megaterium, B. subtilis, E.coli, P.fluorescens, A.awamori and A.niger.

INTRODUCTION

Metal complexes of biologically important ligands are sometimes more effective than the free ligands[1]. Azo dyes have been widely used in various fields and technologies like textiles, leather, plastics, paper, laser liquid crystalline displays and ink Jet printers[2-4]. They are also used in food[5], drug, cosmetic and photochemical production[6]. The pharmalogical and chemotherapeutical activity of azo dyes are well recognized as they possess antibacterial, antifungal, antiseptic, herbicidal, pesticidal and anticancerial properties[7]. Azo dyes are also used as indicators in chemistry. Keeping all these important properties of azo dyes in mind the synthetics organic chemists have been inspired to prepare broad spectrum drugs from the azo dyes obtained from aromatic and heterocyclic amines. We now focus our attention to the preparation of completely new azo dyes ligands and to study their complexation behavior with divalent transition metal ions. The present paper reports the synthesis of new azo dye ligand (Figure 1) and metal complexes.

The products have been evaluated for antimicrobial activity. Some compounds are found to have antimicrobial activity comparable to that of standard drugs, viz. sulfamethoxazole, and sulfadiazine. The product has also been characterized by elemental analysis, absorption spectra, conductivity measurements, molecular weight determination, magnetic moment measurements and stepwise stability constants by Pθ metric method. By using the results of above study, structure of metal complex is proposed.
EXPERIMENTAL

All the chemicals were of B.D.H. or E.Merck grade. Metal, carbon, hydrogen, nitrogen and sulphur were estimated by standard methods. Conductivity measurements in DMF was made using Toshniwal conductivity bridge using a dip type cell at room temperature. Magnetic moment was measured at room temperature on a Gouy balance using mercury (II) tetrachlorocyanate cobalt(II) as the calibrant. IR spectra were recorded using KBr disc on Nicolet Megna-IR550 SERIES II. Electronic spectra were recorded on Backman spectrometer using matched silica cells. NMR spectra were recorded on BRUKER spectrometer (300 MHz) in CDCl3. Mass spectra were recorded on a JEOL D-300 spectrometer at room temperature.

Preparation of the ligand

Preparation of 3-ethyl-2-hydroxy-5-methyl-4’-(5”-methyl-oxazol-3”-yl)-amino-sulphonyl azobenzene (Azo dye ligand). Sulfamethaxazole (0.025M) was taken in 10 ml HCl (0.055M) solution, and it was added to sodium nitrite solution 20ml (0.025M) and the mixture was cooled in icebath. (yields diazonium salt of sulfamethaxazole). In another flask 2-ethyl-4-methyl phenol (0.025M) dissolved in 10ml (0.025M) NaOH and cooled at 0°C. In situ diazonium salt of sulfamethaxazole was coupled with 2-ethyl-4-methyl phenol(in above solution) by adding dropwise at 0°C with constant stirring and keeping the pH of the solution neutral.

Earlier 2-ethyl-4-methyl phenol was prepared by clemmensen’s reduction of 2-acetyl-4-methyl phenol. 2-acetyl-4-methyl phenol was prepared by Fries migration of p-cresyl acetate. p-cresyl acetate was prepared by acetylation of p-cresol.

Preparation of the complexes

The complexes of cobalt(II) and Nickle(II) prepared by refluxing the mixture of alcoholic solution of azo dye ligand (2M) i.e.3-ethyl-2-hydroxy-5-methyl-4’-(5”-methyl-oxazol-3”-yl)-amino-sulphonyl azobenzene and metal salt solution (1M) for two hours in presence of excess of ammonium hydroxide (pH = 10.0). The complexes were recrystallised from alcohol.

RESULTS AND DISCUSSION

IR spectral data of the ligand

IR (KBr) cm⁻¹: 3432 (N-H str. Sym. & O-H str.), 3080 (=C-H str.), 2969 (C-H str.-CH₃), 2915 (C-H str.-CH₂), 2860 (C-H str.sym.), 1614 (-N=N- str.& N-H def.), 1580 (-C=C str.), 1467 (oxazole ring str.), 1417 (C-H def.asym., N=N def.), 1398 (O-H def.& C-H def.sym.), 1341 (S=O str.asym.), 1264 (C-H i.p. def. disub. benzene), 1177 (S=O str.sym.), 1140 (C-H i.p. oxazol), 1034 (ring skeletal oxazol), 900 (C-H o.o.p. oxazol), 755 (N-H wag.).

NMR spectral data of the ligand

¹H NMR (CDCl₃): 1.21-1.25 δ(3H, t,-CH₂-CH₃), 2.34-2.38 δ(6H, 2 x s, 2 x -CH₃), 2.64-2.71 δ(2H, q, -CH₂-CH₃), 6.28 δ(1H, s, = CH oxazol ring), 7.11 δ (1H, s, Ar-H), 7.54 δ (1H, s, Ar-H), 7.86-7.89 δ (2H, d, Ar-H), 7.96-7.98 δ (2H, d, Ar-H), 12.86 (1H, s, Ar- OH).

Mass spectra

(m/z): 401 (M⁺), 309, 287, 266, 239, 207, 154, 135, 120, 105, 91, 77, 69, 55, 41.

Absorption spectra


Antimicrobial activity

The testing were carried out by cup-plate method at a concentration of 50 µg using gram positive bacteria as B.megaterium and B. subtilis and gram negative bacteria as E. coli. And P. fluorescens and fungi as A. awamori and A.niger. Most of the compounds were moderately active against different strains of bacteria and fungi. However, comparatively significant was observed in compounds (along with zone of inhibition in mm) having azodye ligand -(18), Co(II) complex -(20), Ni(II) complex -(18) against B. mega, azodye ligand -
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Co(II) complex -(19), Ni(II) complex -(16) against B. subtilis, azodye ligand -(16), Co(II) complex -(16), Ni(II) complex -(22) against E. coli., azodye ligand -(18), Co(II) complex -(19), Ni(II) complex -(15) against A. aorgen, azodye ligand -(17), Co(II) complex -(17), Ni(II) complex -(17) against A. awamori, azodye ligand -(19), Co(II) complex -(15), Ni(II) complex -(16) against A. niger

**TABLE 1 : Some physical properties of metal complexes.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular weight</th>
<th>%found(calculated)</th>
<th>Conductivity</th>
<th>μ&lt;sub&gt;eff&lt;/sub&gt;</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>M</td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Found/ (Req.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co(C&lt;sub&gt;19&lt;/sub&gt;H&lt;sub&gt;19&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;N&lt;sub&gt;4&lt;/sub&gt;S)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>856.93</td>
<td>6.88</td>
<td>53.21</td>
<td>4.43</td>
</tr>
<tr>
<td></td>
<td>(845.85)</td>
<td>(6.89)</td>
<td>(53.22)</td>
<td>(4.45)</td>
</tr>
<tr>
<td>Ni(C&lt;sub&gt;19&lt;/sub&gt;H&lt;sub&gt;19&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;N&lt;sub&gt;4&lt;/sub&gt;S)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>856.71</td>
<td>6.85</td>
<td>53.23</td>
<td>4.43</td>
</tr>
<tr>
<td></td>
<td>(845.90)</td>
<td>(6.87)</td>
<td>(53.25)</td>
<td>(4.47)</td>
</tr>
</tbody>
</table>

**P<sup>H</sup>-metric measurements**

For the determination of stepwise stability constants an expanded scale systronic P<sup>H</sup> meter with accuracy ±0.02 units was employed. All experiments were carried out at 30 ± 0.2 °C and temperature was maintained constant using thermostat. The three sets acid, acid + ligand, acid + ligand + metal were prepared.

In each case total volume was made up to 40 ml by adding required amount of double distilled water or purified dioxane as the case may be. The ionic strength was maintained by adding appropriate amount of sodium nitrate (0.01M) and mixtures were titrated with standard NaOH solution. A modified form of Irving-Rossti<sup>[12]</sup> titration technique was used for calculating the stability constants. The P<sup>H</sup> meter was calibrated with aqueous buffers. In the calculations for pL the pH meter reading ‘B’ was used instead of converting it to true pH value (Corresponding to aqueous medium). The use of pH meter reading “B” instead of true pH values did not make any differences<sup>[13,14]</sup> in the calculation of free ligand concentration and was usually valid for water dioxane media.

**TABLE 2 : Stepwise stability constants of metal complexes of 3-ethyl-2-hydroxy-5-methyl-4-’(5”-methyl-oxazol-3”-yl)- amino-sulphonyl azobenzene in (60: 40) Dioxane: Water, μ =0.1M, Temp 30 ± 0.2 °C.**

<table>
<thead>
<tr>
<th>Ligand</th>
<th>logK&lt;sub&gt;1&lt;/sub&gt;&lt;sup&gt;H&lt;/sup&gt;</th>
<th>logK&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;H&lt;/sup&gt;</th>
<th>logB&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;H&lt;/sup&gt;</th>
</tr>
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<tbody>
<tr>
<td>C&lt;sub&gt;19&lt;/sub&gt;H&lt;sub&gt;20&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;N&lt;sub&gt;4&lt;/sub&gt;S</td>
<td>10.622</td>
<td>3.703</td>
<td>14.365</td>
</tr>
<tr>
<td>Complex Co (C&lt;sub&gt;19&lt;/sub&gt;H&lt;sub&gt;19&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;N&lt;sub&gt;4&lt;/sub&gt;S)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>6.7019</td>
<td>4.0221</td>
<td>10.7240</td>
</tr>
<tr>
<td>Ni (C&lt;sub&gt;19&lt;/sub&gt;H&lt;sub&gt;19&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;N&lt;sub&gt;4&lt;/sub&gt;S)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>7.6232</td>
<td>4.4043</td>
<td>12.0275</td>
</tr>
</tbody>
</table>

**Conductance measurements**

Molar conductance values of all the complex in 10<sup>-3</sup> M DMF solutions are given in TABLE 1. These values are consistent with the non-electrolytic<sup>[15]</sup> nature of this complex.

**Magnetic measurements**

The observed magnetic moments of the resulting complex are given in TABLE 1. This value shows that Co(II) complex is paramagnetic nature with one unpaired<sup>[16,17]</sup> electron and. Ni(II) complex is diamagnetic.

**UV and visible spectra**

The spectra of Cobalt(II) complex (D<sub>4</sub>h) show a band at 768 nm along with ligand bands. The transition corresponding to 2<sup>A</sup>1<sub>g</sub> → 2<sup>B</sup>1<sub>g</sub> and 2<sup>A</sup>1<sub>g</sub> → 2<sup>E</sup>1<sub>g</sub> are expected. Here only one absorption maxima is observed at 768 nm which can be attributed to 2<sup>A</sup>1<sub>g</sub> → 2<sup>B</sup>1<sub>g</sub>. The spectra of Nickel(II) complex two Absorption bands are expected corresponding to 3<sup>B</sup>1<sub>g</sub> → 1<sup>A</sup>1<sub>g</sub> at 685 nm and 1<sup>A</sup>1<sub>g</sub> → 1<sup>E</sup>1<sub>g</sub> at 360 nm. Hence it is concluded that the nickel complex is having tetragonal symmetry.

**Potentiometric study**

The P<sup>H</sup> metric studies of the metal complex show the n values as 1.78 and 1.70 for Co(II) and Ni(II) respectively, indicating two ligands per metal ion, the stepwise stability constants (TABLE 2) follow the Irving-Williams order.

**CONCLUSION**

Basing upon the above observation, the Co(II) and Ni(II) complexes structure have been proposed as under (Figure 2). The complexed are biologically active since they exhibit enhanced antibacterial activities com-
pared to their parent ligands.

\[ \text{Figure 2: } M = \text{Co(II)} & \text{Ni(II)} \]

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REFERENCES