Complexation of zinc and copper with 4-4’diaminodiphenyl sulfone (Dapsone)

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ABSTRACT

Transition metal complexes of Cu(II) and Zn(II) have been synthesized with the drug Dapsone that is 4-4’diaminodiphenyl sulfone. Conductometric studies and elemental analysis suggest the ML2 stoichiometry. Molar conductance values indicate the non-electrolytic nature of the complexes. The ligand behaves as bidentate and forms co-ordinate bond through azomethine nitrogen. The structure assigned to the complexes, synthesized via Schiff base formation is supported by infrared spectral studies.

Key words: Schiff base, antibacterial, Dapsone, and Infrared spectroscopy.

INTRODUCTION

Schiff base metal chalets are widely applicable because of their industrial and biological importance and hence have well been studied in past.¹⁴ Survey of literature reveals that some studies on pharmacological activities of metal complexes of Schiff base. We report herein the synthesis and characterization of some transition metal ion chelates of Dapsone – Schiff base. In continuation of our previous work on metal complexes of established drugs.⁵⁻¹⁰ The synthesis and structural studies of Dapsone – Cu(II) and Zn(II) complex is described below.

EXPERIMENTAL

Pure sample of Dapsone (DPN), molecular formula C₁₂H₁₂N₂O₂S, molecular wt. 248.30, was obtained from Bengal Chemicals private limited, Kolkata. Metal salts were of Qualigen chemicals. Solvents used were absolute alcohol is of analytical grade.

Equimolar solutions of pure drug (0.01M) and salicyldehyde (0.01M) were taken in absolute alcohol. Both the solutions were mixed and refluxed for ½ an hour. While heating light yellow crystals of Dapsone- Schiff base were formed in the reaction mixture, which was washed with absolute alcohol, filtered, dried and weighted. Melting point was recorded.

Ligand-Metal ratio and stoichiometry

To confirm the ligand metal ratio, conductometric titrations using monovariation method were carried out on Systronics conductometer and dip type electrode. Titrations were carried out at 21°C ±1 C.

0.01M solution of Dapsone-Schiff base was prepared in 60% acetone and diluted to 200 ml with same solvent. This Schiff base solution was titrated against 0.02M metal solutions using monovariation titration. After making volume corrections the results were plotted in from of a
graph which shows the ligand metal ratio for Cu and Zn as 2:1. Formation of 2:1 complex was further confirmed by job’s method of continuous Variation\textsuperscript{12}, modified by Turner and Anderson\textsuperscript{13}. The stability constants and free energy changes were calculated.

**Synthesis of Complexes**

For the synthesis of complexes the drug Dapsone, in two molar ratios was allowed to react with one molar cupric chloride and zinc chloride saturated solutions separately. The saturated solutions mixtures of the drugs with copper and zinc solutions were refluxed for more than three hours and were allowed to cool and kept to for two days, whereupon solid crystalline complexes of copper and zinc were obtained in the form of fine crystals. The yield of two complexes was 40 % and 32 % respectively for copper and zinc. The complexes were washed with 60 % acetone, filtered, dried and weighed.

Melting points were recorded in open capillaries and are uncorrected.

**RESULTS AND DISCUSSION**

Conductometric studies, monovariation method and job’s method of continuous variation modified by Turner and Anderson\textsuperscript{10-11} indicate the formation of 2:1 (L:M) complexes of Schiff base of Dapsone with Cu(II) and Zn(II) complexes. Analytical data of these complexes are in agreement with the composition \((C_{19}H_{19}N_{2}O_{3}S)_{2}M\).

Proposed structure was further confirmed by IR spectral data\textsuperscript{12-16}. Bands observed at 1173 cm\(^{-1}\) and 1143 cm\(^{-1}\) characteristic of SO\(_2\)-N group. Absorption band at 1413 cm\(^{-1}\) shows chelate ring. Frequency at 892 cm\(^{-1}\) is characteristic of M-O linkage. Bands at 709 cm\(^{-1}\) and 715 cm\(^{-1}\) are characteristic of M-N linkage. Frequencies at 1362 cm\(^{-1}\) and 1212 cm\(^{-1}\) indicate the S-N linkage. Absorption band at 1004 cm\(^{-1}\) and 974 cm\(^{-1}\) shows the presence of sulphur in heterocyclic ring. The disappearance of frequencies of phenolic –OH in complex supports its involvement in complexation.

**Table 1: Synthesis and Physiochemical Characteristics of Complexes**

<table>
<thead>
<tr>
<th>Ligand/Complex</th>
<th>Ligand/Metal Ratio</th>
<th>Colour</th>
<th>% Yield</th>
<th>Stability Constant logK (L/mole)</th>
<th>Free energy change “ F” (K.Cal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPN-SB</td>
<td>-</td>
<td>Lt. yellow crystals</td>
<td>65</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(DPN-SA)(_2)Cu</td>
<td>2:1</td>
<td>Green crystals</td>
<td>40</td>
<td>9.59</td>
<td>-16.4849</td>
</tr>
<tr>
<td>(DPN-SA)(_2)Zn</td>
<td>2:1</td>
<td>Yellow crystals</td>
<td>32</td>
<td>9.32</td>
<td>-11.456</td>
</tr>
</tbody>
</table>

**Table 2: Analytical data of Complex**

<table>
<thead>
<tr>
<th>Complex</th>
<th>Elemental analysis</th>
<th>Found (Calculated)</th>
<th>m.p.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td></td>
<td>(64.0)</td>
<td>(5.01)</td>
<td>(8.00)</td>
</tr>
<tr>
<td>((C_{19}H_{19}N_{2}O_{3}S)_{2}Cu)</td>
<td>(64.77)</td>
<td>(4.54)</td>
<td>(7.95)</td>
</tr>
<tr>
<td></td>
<td>(36.98)</td>
<td>(2.5)</td>
<td>(15.69)</td>
</tr>
<tr>
<td></td>
<td>(36.00)</td>
<td>(2.91)</td>
<td>(16.67)</td>
</tr>
<tr>
<td>((C_{19}H_{19}N_{2}O_{3}S)_{2}Zn)</td>
<td>(36.98)</td>
<td>(2.5)</td>
<td>(15.69)</td>
</tr>
<tr>
<td></td>
<td>(36.00)</td>
<td>(2.91)</td>
<td>(16.67)</td>
</tr>
</tbody>
</table>
(I) (III) Dapsone (DPN)

(II) Dapsone Salicyldiamine

(III) Dapsone Salicyldiamine metal complex

REFERENCES