SPECTROPHOTOMETRIC STUDIES OF COPPER (II)---BIS-2-PYRIDYL GLYCOL COMPLEX

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ABSTRACT

An aqueous solution of bis-2-pyridyl glycol forms a deep blue water-soluble complex with an aqueous solution of copper (II) salts. The complex has an absorption maximum at 600-650 m\(\mu\) between pH range 3.0-8.7. The complex is stable for four days and obeys Lambert-Beer's law in the concentration range of 5.08-50.80 ppm. of copper (II) in solution. The optical density of the complex remains constant between pH 3.8-5.9. The molar composition as determined by the method of continuous variation and by the slope ratio method has been found to be 1:1. The limits of interference due to some foreign ions during the estimation of copper (II) have been determined.

INTRODUCTION

Ethylene glycol (I) has been used for the estimation of calcium\(^1\) and more recently its complexes with nickel, cobalt\(^2\) and germanium\(^3\) have been studied. The metal complexes of ethylene glycol are generally water-soluble. The present investigation deals with the studies regarding the metal complexes of bis-2-pyridyl glycol (II). \(\alpha\)-Pyridoin (III) which is structurally related to the present reagent has already been used for the gravimetric determination of molybdenum and tungsten.\(^4\)

Bis-2-pyridyl glycol (C\(_{12}\)H\(_{12}\)O\(_2\)N\(_2\)) is a white crystalline substance, m.p. 156\(^\circ\)C., sparingly soluble in cold water and non-aqueous solvents but possessing increased solubility in hot water and hot organic solvents. In addition to the
glycolic group the two pyridine rings on either side (II) would greatly enhance its capacity for complex formation as is shown by the large number of metal complexes that it has been observed to form.

Aqueous bis-2-pyridyl glycol solution forms water-soluble complexes with copper (II), iron (III), nickel (II), cobalt (II), manganese (II) and thorium (IV) while the complexes formed with uranium (VI), aluminium (III), beryllium (II) and cerium (IV) are insoluble in water. This reagent has already been used for the gravimetric determination of uranium, aluminium and beryllium and for the spectrophotometric determination of iron. The present studies deal with the spectrophotometric investigation of copper (II)-bis-2-pyridyl glycol complex.

**EXPERIMENTAL**

*Reagents.*—Bis-2-pyridyl glycol was obtained from F. Raschig GmbH, Ludwigshafen and its $10 \times 10^{-8}$ M aqueous solution was used. Standard solution of copper (II): A $10 \times 10^{-8}$ M CuSO$_4$·5H$_2$O (BDH A.R.) was used. A 2·5 M KNO$_3$ (BDH A.R.) was used for maintaining a constant ionic strength.

*Apparatus.*—Spectrophotometric measurements were carried out with a Unicam Spectrophotometer SP 600, using 10 mm. wide absorption cells. The cells could not be thermostated but all the solutions were brought to a constant temperature $21^\circ$ C. $\pm$ 0·05$^\circ$ C. in a thermostat before measuring the optical density. Beckman pH meter model H-2 was employed for pH measurements.

*Absorption spectra.*—The absorption spectra of the deep blue Cu (II)-bis-2-pyridyl glycol complex formed by mixing copper (II) salt and the reagent in the molar ratio of 1:4 were taken in the wavelength range of 380-1,000 m$\mu$ at pH 3·0-8·7 (Fig. 1). Absorption spectrum studies were also carried out when the molar ratio of copper to reagent was 1:1, 1:2 and 1:3. In each case the absorption maximum was observed in the range 600-650 m$\mu$. The absorption spectra studies of the above complex indicate that bis-2-pyridyl glycol like the amines in the cupramine complex produces a stronger electrostatic field which causes the absorption band to move from the far red to middle of the red region of the spectrum. During the subsequent studies the wavelength 625 m$\mu$ was; however, chosen as the copper sulphate exhibited a minimum absorption at this wavelength. The reagent, being colourless, did not show any absorption in this region.
Effect of pH on copper (II)-bis-2-pyridyl glycol complex.—The effect of pH on the complex was studied by taking its optical density measurements at various pH values from pH 2-11 at 625 m\(\mu\). It was found that the optical density remained constant and was maximum in the pH range 3·8-5·9 (Fig. 2). The pH of the solution was adjusted with dilute sodium hydroxide and hydrochloric acid solutions.

![Fig. 1](image1.png)

![Fig. 2](image2.png)

Minimum amount of reagent necessary for the determination of copper (II).—The optical densities at 625 m\(\mu\) of a series of solutions containing bis-2-pyridyl glycol and Cu (II) in the molar ratio of 0·25:1-8:1 were determined and are plotted in Fig. 3. It is observed that the excess of reagent has no effect on the optical density after the molar ratio of 1 is attained in each case. The nature of this curve suggests that there is only a minimum dissociation of the complex taking place. The molar ratio of the bis-2-pyridyl glycol to copper (II) was, however, maintained at 4 in subsequent studies.

Stability of the colour.—The colour of the complex was stable for four days at 10°-60° C. The complex could not be extracted with benzene, n-butanol, pentanol, chloroform, carbon tetrachloride, diethyl ether, ortho-dichloro-benzene and amyl alcohol.

Lambert Beer's law.—The complex formed at pH 5·2 was found to obey Lambert-Beer's law at 625 m\(\mu\) between the concentration 5·08-50·80 ppm. of copper (II).
Molar composition.—The molar composition of the complex was determined by Job's method of continuous variations as modified by Vosburg and Cooper.⁷

The optical densities at 625 mμ and pH 4.0–4.2 of the following two solutions prepared by mixing (a) x ml. of 10 × 10⁻³M of bis-2-pyridyl glycol solution with (10 − x) ml. of 10 × 10⁻³M of Cu (II) solution and (b) x ml. of 5 × 10⁻⁸M of bis-2-pyridyl glycol solution with (10 − x) ml. of Cu (II) solution of strength 5 × 10⁻⁸M (where x varies from 1 to 10) were determined employing water as reference solution. There was no absorption due to bis-2-pyridyl glycol at 625 mμ, while the absorption due to copper (II) solution at 625 mμ was quite negligible.

The function y defined as the difference between the optical density observed for a given mixture of the constituents and the corresponding optical densities of the respective components for no reaction, was taken in the present case as the optical density of the complex solution. The values of y are plotted against x in each case in Fig. 4 in which maxima are located when the molar ratio of bis-2-pyridyl glycol to copper (II) is 1:1. The complex, therefore, has the molar composition ML, where L is bis-2-pyridyl glycol.

The molar composition of copper (II) complex was also verified by slope-ratio method of Harvey and Manning.⁸ For this purpose two series of solutions were prepared employing 10 × 10⁻³M solutions of bis-2-pyridyl
glycol and copper (II). In one series the copper (II) concentration was varied maintaining the concentration of the bis-2-pyridyl glycol constant and in sufficient excess. In the other, the bis-2-pyridyl glycol concentration was varied maintaining the copper (II) concentration constant and in sufficient excess. The optical densities of the solutions of complex of both these series were determined at 625 m\(\mu\) and plotted as the Curves P and Q in Fig. 5. In the Curves P and Q the straight line portions AB and CD respectively were taken into account to find out the slope.

\[ \text{Slope of the Curve P} = \tan \theta_1 = 0.97 \]

\[ \text{Slope of Curve Q} = \tan \theta_2 = 1.06. \]

Molar composition of the complex = \(0.97/1.06\approx 1\) (approx.)

Thus the slope ratio of the two Curves indicates that the molar ratio of the bis-2-pyridyl glycol to copper (II) in the complex is 1, which confirms the results obtained by using Job’s method.

*Interference due to foreign ions.*—The interference due to the various cations and anions in the spectrophotometric determination of copper (II) with bis-2-pyridyl glycol was studied. A stock solution of the complex containing \(2 \times 10^{-3} \text{M}\) of copper (II) and three times the reagent was
used and an aliquot (1 ml.) of this solution was transferred to a 25 ml.
standard flask and mixed with a known amount of a foreign ion and the
volume made up to the mark with water. The pH of the complex, however,
was always maintained between 4.0-5.0. The concentration of foreign
salt in the complex was progressively increased till the optical density
changed by 2% of the theoretical value.

Table 1 gives the limits of interference due to foreign ions:

**TABLE 1**

<table>
<thead>
<tr>
<th>Foreign ions</th>
<th>Taken as</th>
<th>ppm. tolerated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citrate</td>
<td>Sodium citrate</td>
<td>96</td>
</tr>
<tr>
<td>Tartrate</td>
<td>Sodium tartrate</td>
<td>72</td>
</tr>
<tr>
<td>Oxalate</td>
<td>Sodium oxalate</td>
<td>60</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zinc sulphate</td>
<td>60</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Cadmium chloride</td>
<td>20</td>
</tr>
<tr>
<td>Nickel</td>
<td>Nickel sulphate</td>
<td>16</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Cobalt sulphate</td>
<td>12</td>
</tr>
<tr>
<td>Aluminium</td>
<td>Aluminium sulphate</td>
<td>3</td>
</tr>
<tr>
<td>Beryllium</td>
<td>Beryllium sulphate</td>
<td>3</td>
</tr>
</tbody>
</table>

Iron (II) & (III) and Ag (I) interfered in the above estimation as the reagent
formed a yellow complex with iron while the Ag (I) forms a black precipitate.

The copper (II)-bis-2-pyridyl glycol complex has been isolated in solid
state both from aqueous as well as methanolic solutions and investigations
on its structure are in progress.

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### References