Synthesis, characterization and photometric studies of Cu(II) complex with bidentate Schiff base derived by S-triazole

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ABSTRACT
The reactions of Schiff base ligands, prep'd. by the condensation of 4-amino-5-(3-bromo phenyl)-4H-1,2,4-triazole-3-thiol with aromatic aldehyde like 4-methoxy benzaldehyde was studied with Cu(II). This complex was characterized from IR, 1HNMR and spectrophotometric analysis. A photometric method for the determination of Cu(II) of its 5-(3-bromo phenyl)-4-{[(1E)-(4-methoxy phenyl)methene]amino}-4H-1,2,4-triazole-3-thiol (SB₁) complex is described. The insoluble colored complex of Cu(II) was extracted in chloroform and the absorbance is measured at 410 nm. Beer’s law is obeyed up to 30.48 ppm for Cu(II) complex. The interference of diverse ions has also been investigated.

KEYWORDS
Schiff base; Complexes; Cu(II); IR; 1HNMR; Photometry; S-triazole.

INTRODUCTION
Schiff bases play the role of an important class of legands in the formation of metal coordination compounds. Owing to certain reasons like, manifestation of novel structural features, thermal stabilities, abnormal magnetic properties and relevant biological properties, the Schiff bases have been extensively studied[14-1]. A number of Schiff base complexes have been tested for antimicrobial activities and many of them have been found to exhibit bacteriostatic and fungistatic activities[56]. The formation of stable complexes have been facilitated by the presence of functional groups such as -SH sufficiently near to azomethine group[77] and electron donor atoms.

The metal complexes of schiff bases have been used as active drugs against tumor[88] and tuberculosis[99] and also as insect repellents[100] and fungicides[111]. Schiff bases derived from sulphur drugs and salicylaldehyde have been found to be good chelating agents[112-13]. Therefore Iron (III), Cobalt (II), Nickel (II), complexes of schiff bases derived from sulphadiazine with 5-nitrosalicylaldehyde have been reported[114]. The formation of co-ordination compounds of metal ions with organic reagent has been extensively used in analytical methods. Large number of organic compounds has been used for the analytical determination of various metal ions. Most of the applications are based on complex formation reaction. The introduction of modern instruments and advanced techniques such as spectrophotometry, polarographic determinations and atomic absorption has changed the face of rapidly expanding field of analytical chemistry. More and more researches have been done to look for more sensitive reagents which would be extremely selective and sensitive for metal ions.
The corrosion inhibition activity of Schiff bases have extensively been studied and reported\textsuperscript{15-23}.

**Material**

Analytical grade chemicals were used for the whole work. 3-bromo methyl benzoate, Hydrazine hydrate, 4-methoxy benzaldehyde and carbon disulphide were purchased from Sisco chem. The metal salts were purchased from Ranbaxy Mumbai and metal contents were estimated by using standard methods\textsuperscript{24}.

**Preparation of ligands**

The 5-(3-bromo phenyl)-4-\{(1E)-(4-methoxy phenyl) methlene\}amino\}-4H-1,2,4-triazole-3-thiol (SB\textsubscript{1}) and 5-(3-bromo phenyl)-4-\{(1E)-(4-methyl phenyl) methlene\}amino\}-4H-1,2,4-triazole-3-thiol (SB\textsubscript{2}) were prepared as follows:

To a solution of triazole in 10 mL DMF, aldehydes were added with constant stirring. To this mixture 1.0 ml glacial acetic acid was added as a catalyst. The reaction mixture was refluxed for 8 hrs. The content was cooled and poured on to crushed ice and triturated with sodium bisulphate solution. The product was isolated and crystallized from methanol. The physical data are reported in TABLE 1.

**Photometric study of Cu(II) complex**

The Cu(II) -SB\textsubscript{1} complex has been found to be soluble in chloroform, benzene, carbon tetrachloride, DMF, ethyl acetate. This enabled to verify the Beer’s law and its application for photometric determination.

**Absorption spectra**

Absorbance was measured using shimanzu-UV-160-A spectrophotometer, 5 mg of complex was dissolved in 25 ml of dioxane and absorbance of this solution was measured at different wave length in the range of 350-600 nm. The absorbance was plotted against wave length to get absorption spectra. It was observed

<table>
<thead>
<tr>
<th>pH</th>
<th>Cu(II) complex (g)</th>
<th>Cu(II) found (g)</th>
<th>Error (in g)</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>0.4077</td>
<td>0.03086</td>
<td>-0.00094</td>
<td>-2.9</td>
</tr>
<tr>
<td>2.5</td>
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<td>0.03094</td>
<td>-0.00086</td>
<td>-2.7</td>
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<tr>
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<td>0.03099</td>
<td>-0.00081</td>
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<td>3.0</td>
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<td>0.03116</td>
<td>-0.00064</td>
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<tr>
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<td>-0.00046</td>
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<tr>
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<td>0.4149</td>
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<td>-0.00039</td>
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<tr>
<td>4.0</td>
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<td>0.03147</td>
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<tr>
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<tr>
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<tr>
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<td>-0.00011</td>
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<td>0.03217</td>
<td>+0.00037</td>
<td>+1.16</td>
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</table>

**TABLE 1: The physical data of ligands**

<table>
<thead>
<tr>
<th>Schiff base</th>
<th>R</th>
<th>M.F.</th>
<th>M.W. Gm/mol</th>
<th>M.P. ºC</th>
<th>Yield %</th>
<th>% of Nitrogen</th>
<th>Rf Value</th>
<th>Solvent system</th>
</tr>
</thead>
<tbody>
<tr>
<td>SB\textsubscript{1}</td>
<td>4-OCH\textsubscript{3}-C\textsubscript{6}H\textsubscript{4}-</td>
<td>C\textsubscript{16}H\textsubscript{13}BrN\textsubscript{4}O-S</td>
<td>389</td>
<td>213</td>
<td>60</td>
<td>14.39</td>
<td>14.31</td>
<td>0.42</td>
</tr>
</tbody>
</table>
that the absorbance of the coloured solution of complex increases continuously towards the shorter wavelength. A shoulder is observed at 410 nm and hence all the measurements were carried out at 410 nm. Absorption spectrum is given in figure 1.

**Verification of beer’s law**

To 5 ml of solution (0.01 M) of the Schiff base-SBI, varying amounts of the metal ion solution (0.005 M) were added and the pH was adjusted to 5.0 using CH$_3$COONa + CH$_3$COOH buffer. The insoluble complex precipitated was extracted in chloroform using three 5 ml portions of chloroform and final volume of the chloroform extract was adjusted to 25 ml. The absorbance of these solutions was measured at 410 nm against chloroform as the blank. Absorbance values were plotted against the metal concentration expressed in ppm. A straight line passing through the origin, indicating the obeyance of Beer’s law as was obtained upto 30.48 ppm of Cu(II). The standard graph thus obtained may be used for the determination of copper in a unknown solution using Schiff base-SB$_1$. The results are tabulated in TABLE 3. Molar absorptivity calculated from Beer’s law plot was found to be 10$\times$10$^2$ lit.mol$^{-1}$ cm$^{-1}$ for Cu(II)-SB$_1$ reagent at 410 nm.

**Composition of complex**

The composition of Cu(II) complex with the Schiff base SB$_1$ has been determined on the basis of (i) Job’s method of continuous variation, and (ii) Yoe and Jones mole ratio method. From these methods it is found that the composition of Cu(II)-SB$_1$ was 1:2,$^{[25,26]}$

**Calculation of stability constant**

The stability constant is calculated by the equation:

$$K_s = 1 - \frac{\alpha}{4c^2} \alpha^2$$

From mean $K_s$ value, the standard free energy change $\Delta G^0$ for the formation reaction of complex has been calculated at 25°C using the formula:

$$\Delta G^0 = -RT\ln K_s$$

**Effect of diverse ions**

To study the effect of foreign ions on gravimetric determinations of Cu(II), 8-10 mg of various cations were added to a known amount of Cu(II) solution at pH 5.0 and gravimetric estimations were done. It was observed that Ba(II), Sr(II), Mg(II), Mn(II), do not interfere at this pH, but Fe(III), Co(II), Pd(II) interfere seriously. Many common anions like chloride, bromide, iodide, nitrate, nitrite, sulphate were not found to interfere.

**Infrared spectra**

IR spectral data have been interpreted on the basis of reported literature$^{[27-29]}$. IR spectra of the Schiff base and metal complex were recorded in the region 4000-400 cm$^{-1}$ (KBr disc.) using a SHIMANDZU-FT-IR 8400 spectrophotometer. A strong band observed around 959 cm$^{-1}$ in the spectrum of free ligand is assign to (C-S). In the metal complex a new bond was observed at 730 cm$^{-1}$ in the spectrum of metal complex is assign to (C-S). The bands at 1660-1580 cm$^{-1}$ assign to (N=CH) for the free ligands shifted to lower region in the range 1610-1595 cm$^{-1}$. This indicated the coordination of the azomethine nitrogen to metal atom$^{[30]}$. The new bands observed at 468 cm$^{-1}$ and 512 cm$^{-1}$ may be due to (M-S) and (M-N) linkages respectively$^{[31-33]}$.

**NMR spectra**

NMR Spectra of the legand was recorded on a
BRUKER Spectrometer (300 MHz) using CDCl₃ as a solvent and TMS as an internal standard. The PMR spectra of SB₃ exhibited signal at δ 7.01 (s, 2H, Ar-Ha’), δ 7.83 (d, 2H, Ar-Hbb’), δ 7.99 (s, 1H, Ar-Hd), δ 7.88 (d, 1H, Ar-He), δ 7.45 (d, 2H, Ar-Hfg), δ 9.76 (s, 1H, -N=CHC), δ 14.00 (s, 1H, SHh) and δ 3.89 (s, 3H, -OCH₃).

RESULT AND DISCUSSION

Gravimetric determination was carried out at pH range 2.5-6.0 from this it is found that minimum error is obtained at 5 pH. Therefore photometric study was done at 5-pH. The absorption spectra of 5-(3-bromo phenyl)-4-[(1E)-(4-methoxy phenyl) methylene] amino]-4H-1,2,4-triazole-3-thiol-copper(II) complex was measured against reagent blank. Copper(II) complex absorbs strongly at 410 nm. It was observed that Ba(II), Sr(II), Mg(II), Mn(II), do not interfere at this pH, but Fe(III), Co(II), Pd(II) interfere seriously. Many common anions like chloride, bromide, iodide, nitrate, nitrite, sulphate were not found to interfere.

REFERENCES

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