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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, prepd. 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, ^{1}HNMR and spectrophotometric analysis. A photometric method for the determination of Cu(II) of its 5-(3-bromo phenyl)-4-{[(1E)-(4-methoxy phenyl) methelene]amino}-4H-1,2,4-triazole-3-thiol (SB_1) 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;
^{1}HNMR;
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 megnatic properties and relevant biological properties, the Schiff bases have been extensively studied[1-4]. A number of Schiff base complexes have been tested for antimicrobacterial activities and many of them have been found to exhibit bacteriostatic and fungistatic activities[5,6]. The formation of stable complexes have been facilitated by the presence of functional groups such as -SH sufficiently near to azomethine group[7] and electron donor atoms.

The metal complexes of schiff bases have been used as active drugs against tumor[8] and tuberculosis[9] and also as insect repellents[10] and fungicides[11]. Schiff bases derived from sulpha drugs and salicylaldehyde have been found to be good chelating agents[12-13]. Therefore Iron (III), Cobalt (II), Nickel (II), complexes of schiff bases derived from sulphadiazine with 5-nitro-salicylaldehyde have been reported[14]. 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[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[24].

Preparation of ligands

The 5-(3-bromo phenyl)-4-{[(1E)-(4-methoxy phenyl) methelene]amino}-4H-1,2,4-triazole-3-thiol (SB_1) and 5-(3-bromo phenyl)-4-{[(1E)-(4-methyl phenyl) methelene]amino}-4H-1,2,4-triazole-3-thiol (SB_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.

Gravimatric and photometric studies of metal complexes

A 1.0 % solution of the schiff base in dioxane was used. Copper sulphate solution (0.05 M, 10 ml) taken in a clean beaker was diluted to about 100 ml with distilled water and pH of the solution was adjusted to 2.5 to 6.0 using appropriate buffer solution. The solution was warmed at 60^0C and small excess of schiff base-SB_1 was added (1%, 30 ml). A buff precipitate obtained was digested on water bath for 60 minutes at 60^0C. The precipitate was filtered through a previously weighed sintered glass crucible (G_4) and washed with warm water, followed by 50% dioxane-ethanol to remove excess ofthereagent which might have precipitated on dilution. The chelate was dried to constant weight at 110-115^{0}C in hot air oven, cooled and weighed.

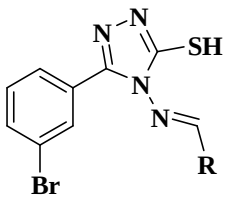
The experiment was repeated at different pH of solution. The experiment was also repeated with different aliquots keeping the optimum pH to evaluate its applicability. The results are given in TABLE 2.

Photometric study of cu(ii) complex

The Cu(II) -SB_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



R= 4-OCH_3-C_6H_4-

TABLE 2: Data of gravimetric analysis at different pH for Cu(II)

pH	Cu(II) complexin (g)	Cu(II) foundin (g)	Error in (g)	Error %
2.5	0.4077	0.03086	-0.00094	-2.9
2.5	0.4087	0.03094	-0.00086	-2.7
3.0	0.4094	0.03099	-0.00081	-2.5
3.0	0.4116	0.03116	-0.00064	-2.0
3.5	0.4140	0.03134	-0.00046	-1.44
3.5	0.4149	0.03141	-0.00039	-1.22
4.0	0.4157	0.03147	-0.00033	-1.03
4.0	0.4168	0.03155	-0.00025	-0.78
4.5	0.4176	0.03161	-0.00019	-0.59
4.5	0.4186	0.03169	-0.00011	-0.34
5.0	0.4198	0.03178	-0.00002	-0.062
5.0	0.4206	0.03184	+0.00004	+0.027
5.5	0.4221	0.03195	+0.00015	+0.47
5.5	0.4227	0.03200	+0.00020	+0.62
6.0	0.4239	0.03209	+0.00029	+0.91
6.0	0.4250	0.03217	+0.00037	+1.16

TABLE 1: The physical data of ligands

Schiff base	R	M.F.	M.W. Gm/mol	M.P. ^{0}C	Yield %	% of Nitrogen Calcd.	% of Nitrogen Found	Rf Value	Solvent system
SB_1	4-OCH_3-C_6H_4-	$C_{16}H_{13}BrN_4O$-S	389	213	60	14.39	14.31	0.42	S_1

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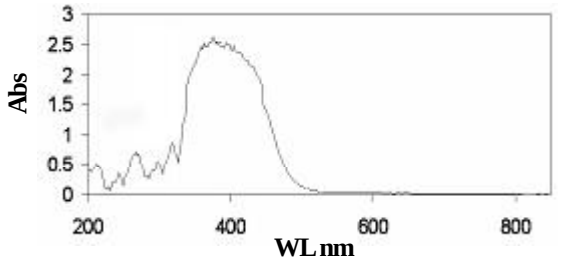


Figure 1: Absorption spectra of Cu(II)-SB_1 complex

TABLE 3 : Verification of Beer's Law

Cu(II) solution taken in ml	Cu(II) taken in ppm	Absorbance
0.3	3.81	0.0401
0.6	3.62	0.0802
0.9	11.43	0.121
1.2	15.24	0.159
1.5	19.05	0.198
1.8	22.86	0.237
2.1	26.67	0.281
2.4	30.48	0.317

TABLE 4 : Data of stability constants and difference of free energy

Method	E_M	Es	α	K_S
Job's	0.288	0.278	0.0347	8.0×10^6
Mole ratio	0.205	0.192	0.0634	2.3×10^6

Mean $K_S = 5.15 \times 10^6$; ΔG^O = -9.151 k.cal/mole

that the absorbance of the coloured solution of complex increases continuously towards the shorter wave length. A shoulder is observed at 410 nm and hence all the measurements were carried out at 410nm. 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 $CH_3COONa + CH_3COOH$ 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 10×10^2 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:

$$K_s = 1 - \alpha / 4c^2 \alpha^2$$

From mean Ks value, the standard free energy change ΔG^0 for the formation reaction of complex has been calculated at 25^0C using the formula:

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

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.

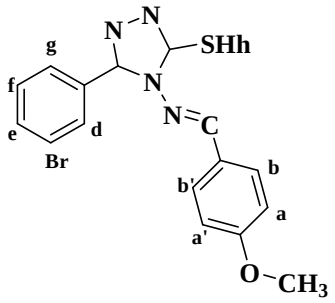
Infrared spectra

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 legands 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 MH_z) using $CDCl_3$ as a solvent and TMS as an internal standard. The PMR spectra of SB_1 exhibited signal at δ 7.01(s, 2H, Ar-Haa'), 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 δ3.89(s, 3H, $-OCH_3$).



RESULT AND DISCUSSION

Gravimetric determination was carried out at pH range 2.5-6.0 from this it is found that minimum error is obtain at 5 pH. Therefore photometric study was done at 5-pH. The absorption spectra of 5-(3-bromo phenyl)-4-{[(1E)-(4-methoxy phenyl) methelene] 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.

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