# Bis-(3,5-dimethyl salicylidine)-ethylenediamine as a Gravimetric Reagent for Cu(II)

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## ABSTRACT

Complex of Cu(II) with bis-(3,5-dimethyl salicylidine)-ethylenediamine was synthesized and characterized by elemental analysis, melting point determination, conductivity measurement, magnetic and spectroscopic studies. Molecular formula of the newly prepared complex was determined as $C_{20}H_{22}N_2O_2Cu$ and the probable geometry has been suggested as square planar. Gravimetric estimation of Cu(II) was made with bis-(3,5-dimethyl salicylidine)-ethylenediamine and the result was compared with the known method of estimation of Cu(II) iodometrically. It was found that the result of estimation with newly prepared reagent was as good as the reported result of estimation of Cu(II) iodometrically .

Keywords: Bis-(3,5-dimethyl salicylidine)-ethylenediamine, Bis-(3,5-dimethyl salicylidine)-ethylenediamine Cu(II) complex, Gravimetric Estimation of Cu(II).

## INTRODUCTION

Synthesis and characterization of Cu(II) complex with bis-(3,5-dimethyl salicylidine)-ethylnediamine ligand was done with a view to gravimetric estimation of Cu(II). Hypothesis behind this work is that the reagent bis-(3,5-dimethyl salicylidine)-ethylenediamine may prove better reagent for the gravimetric estimation of Cu(II). Shiff base reagents have been extensively used in the analytical determination of the metals since long1-38. Present investigation is an extension of pioneer work done by Dubsky and Sokol[39]. They reported the formation of inner complex salt using (Bis-salicylidine)-ethylenediamine with Ni(II) and Cu(II). We extended his work by preparing and using the similar ligand.

## MATERIALS AND METHODS

Chemicals used in the present investigation were of AR quality.

### Preparation of Bis-(3,5-dimethyl salicylidine)-ethylenediamine

3,5-dimethyl salicylaldehyde and ethylenediamine were taken in 2:1 molar ratio in a conical flask in methanol and the mixture was refluxed on steam bath for about four hours with constant stirring. Yellow coloured product was

obtained. It was cooled, filtered, crystallized from methanol and kept in a desiccator.

### Characterization of the ligand bis-(3,5-dimethyl salicylidine)-ethylenediamine and its Cu(II) complex

　　　　The ligand bis-(3,5-dimethyl salicylidine)-ethylenediamine and its Cu(II) complex were characterized by elemental analysis, melting point determination, conductivity measurement, magnetic property studies and spectroscopic studies. The ligand bis-(3,5-dimethyl salicylidine)-ethylenediamine was soluble in alcohol and acetone. However, it is highly soluble in dioxin, pyridine and dimethyl formamide but insoluble in water. It decomposes at 160$^0$C. The newly prepared complex of the ligand with Cu(II) is insoluble in water and methanol but slightly soluble in acetone and highly soluble in pyridine and DMF. It decomposed above 300$^0$C. Analytical data of the ligand and its Cu(II) complex is given in Table 1 and the spectroscopic data is given in Table 2.

**Table 1: Analytical data of the ligand bis-(3,5-dimethyl salicylidine)-ethylenediamine and its Cu(II) complex**

| Compound | Colour | m.p./decomp/ trans. temp.$^0$C | % analysis, found/(calcd) | | | | Conductivity Ohm$^{-1}$ cm$^2$ mol$^{-1}$ |
|---|---|---|---|---|---|---|---|
| | | | C | H | N | M | |
| Bis-(3,5-dimethyl salicylidine)-ethylenediamine | Yellow | 160 | 73.56 -74.03 | 7.29 -7.46 | 8.61 -8.64 | - | - |
| Bis-(3,5-dimethyl salicylidine)-ethylenediamine Cu(II) complex | Grey-green | 300 | 62 -62.23 | 5.7 -5.75 | 7.21 -7.26 | 16.29 -16.46 | 14 |

**Table 2: Selected IR bands of ligand bis-(3,5-dimethyl salicylidine)-ethylenediamine and its Cu(II) complex**

| Compound | $\vartheta$(-OH) | $\vartheta$(C - H) | $\vartheta$(C = N) | $\vartheta$(C-O) | $\vartheta$(C-N) | $\vartheta$(-O-H) | $\vartheta$(M-N) | $\vartheta$ (M-O) |
|---|---|---|---|---|---|---|---|---|
| Bis-(3,5-dimethyl salicylidine)-ethylenediamine | 3190b | 3050, 3000 | 1615, 1580 | 1240 | 1320 | 1025 | - | - |
| Bis-(3,5-dimethyl salicylidine)-ethylenediamine Cu(II) complex | - | 3050, 3000 | 1695, 1560 | 1275 | 1300 | - | 520 | 450 |

### Molar conductance

　　　　Its molar conductance in 10$^{-3}$M solution in DMF was found to be 14 Ohm$^{-1}$ cm$^2$ mol$^{-1}$ indicating its non-electrolytic nature.

### Magnetic susceptibility

　　　　Magnetic moments value of the complex compounds generally suggest the coordination geometry about the metal ion. The magnetic moment of the Cu(II) complex was found to be $\mu_{eff} =$ 1.78 B.M. On the basis of studies of several Cu(II) complexes, Ray and Sen[31] have categorised them into two subgroups-(i) complexes having magnetic moments between 1.73 to 1.84 and (ii) complexes having magnetic moments between 1.94 to 2.20 B.M. They assigned the former to be square planar with dsp$^2$ hybridisation and later tetrahedral sp$^3$ or octahedral with sp$^3$d$^2$ hybridisation. The absence of orbital contribution in former category has been explained by the authors[40] on the assumption of greater quenching effect of the orbital moment. The Pauling's valence bond theory[41] assumed that the tetrahedral complexes of Cu(II), owing to their own symmetry, have a greater orbital contribution to the magnetic moments than the square one. Sacconi *et al.,*[42] and Kettle[43] suggested that square planar Cu(II) complexes have magnetic moment in the range of 1.73–1.86 B.M. whereas a distorted tetrahedral configuration, the moments will be larger than 2.00 B.M. In the present investigation the value of magnetic moment of the complex lies in between 1.73 to 1.86 B.M. suggesting them to have a square planar structure.

### IR-spectra

　　　　The broad band observed in the infrared spectra of the ligand at 3190 cm$^{-1}$ is assigned to the phenolic –OH group. This band is completely disappeared in the complex suggesting the deprotonation[44] of phenolic –OH and the coordination of the ligand to metal through the oxygen atom. A strong band at 1240 cm$^{-1}$ observed in the infrared spectra of the ligand is attributed to C–O stretching frequency. This band is shifted by 35 cm$^{-1}$ and appeared at 1275 cm$^{-1}$ in the complex, which also support the fact that chelation of the ligand to metal occurs through oxygen atom. The bands at 3050 cm$^{-1}$ and 3000 cm$^{-1}$ are due to C–H and aromatic C–H stretching vibrations respectively. The bands at 1615 cm$^{-1}$, 1580 cm$^{-1}$ and 1320 cm$^{-1}$ observed in the spectra of the ligand are assigned to stretching C=N and bending C–N frequencies and these bands are shifted to lower frequencies by 20 cm$^{-1}$ in the complex suggesting the coordination of the ligand

to metal through nitrogen atom of C=N group. The band at 1025 cm$^{-1}$ in the spectrum of the ligand is assigned to the bending –OH frequency and this band is completely disappeared in the spectrum of the complex. These features clearly suggest that the coordination of the ligand to metal is through nitrogen and oxygen atom of the ligand. The new band observed in the spectrum of the complex at 520 cm$^{-1}$ is assigned to metal nitrogen stretching[45] as well as N–M–N bending[46] mode of vibrations. Another new band in the spectrum of the complex at 450 cm$^{-1}$ is attributed to the M–O bond[47].

Thus, it is clear that the ligand behaves as a tetradentate ligand, coordinating through two nitrogen atoms (Schiff residue) and two oxygen atoms by the deprotonation of phenolic hydrogen atoms.

### Electronic spectra

Sacconi[42] and Meek *et al.*,[48] have observed that square planar complexes have a complex broad band of relatively higher frequencies (16000 cm$^{-1}$). The Cu(II) complexes having regular tetrahedral geometry show no d-d absorption band in the region 10,000 cm$^{-1}$ –20,000 cm$^{-1}$. The prepared complex of Cu(II) shows one broad band in the visible spectrum at 16260 cm$^{-1}$ which may be assigned to combination of $^2B_{1g}{\rightarrow}^2A_{1g}$, $^2B_{1g}{\rightarrow}^2B_{2g}$ and $^2B_{2g}{\rightarrow}^2E_g$. Thus, the observed electronic band positions suggest the square planar geometry of the complex.

### Structure and bonding

On the basis of the above facts the structure of the complex can be drawn as in Figue 1.
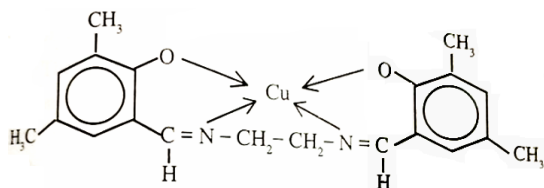


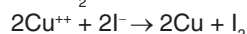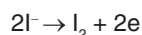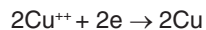**Fig. 1. Bis-(3,5-dimethyl salicylidine)-ethylenediamine Cu(II) complex**

### Gravimetric Estimation of Cu(II) with the help of bis-(3,5-dimethyl salicylidine)-ethylendiamine

3.930 g of copper sulphate pentahydrate (CuSO$_4$.5H$_2$O) AnalR grade was taken in a 1000 mL measuring flask and dissolved in distilled water. One to two mL of conc. H$_2$SO$_4$ was added. The volume was made up to the mark with occasional shaking and left to stand for about an hour to ensure that the solution has become homogeneous. Since 3.930 g of CuSO$_4$.5H$_2$O contains one g of the metal, each mL of prepared solution contains one milligram of Cu(II). From this solution, 10 mL, 15 mL, 20 mL, 25 mL, ………………..100 mL were taken out by means of a pipette and added in a beaker. After that each set was diluted by distilled water to make the volume to 100 mL and conc. NH$_3$ was added till solution is clear. Now one percent solution of the ligand was prepared in alcohol. To 100 mL of the metal solution prepared above, alcoholic solution of the ligand was added slowly with continuous stirring. Precipitation (grey green) started immediately. After the addition of the ligand solution, the whole mass was digested on steam bath for about an hour and then left for about an hour to settle. The complete precipitation was tested with the supernatant liquid. Use of excess of ligand was avoided. Finally the complex was filtered through a previously washed, dried and weighed sintered glass crucible (G$_3$, G$_4$). The precipitate was washed several times with cold water till the final washings failed to produce turbidity with BaCl$_2$ solution. The precipitate was dried to constant weight in hot air oven 110$^0$C and weighed as C$_{20}$H$_{22}$N$_2$O$_2$Cu to constant weight. Similar experiment was performed for each solution and for higher accuracy triplicate experiments for each set were done. The result of the experiment is given in Table 3.

Comparison of the result of estimation of Cu(II) obtained with the newly prepared reagent bis-(3,5-dimethyl salicylidine)-ethylenediamine to the result obtained iodometrically using standard solution of thiosulphate volumetrically: Comparison of result was done by determining the Cu(II) as follows.

Determination of Cu(II) iodometrically using standard solution of thiosulphate volumetrically: Cu(II) in solution is usually determined quantitatively by volumetric methods. The Cu(II) solution was treated with 6N ammonia till the solution has blue colour. The solution was then treated with 6N acetic acid till the blue colour discharged and the solution has a permanent faint blue colour. Such treatment is essential for the complete precipitation of iodine from iodide as represented by the redox reaction.

$$2Cu^{++} + 2e \rightarrow 2Cu$$
$$2I^- \rightarrow I_2 + 2e$$
$$2Cu^{++} + 2I^- \rightarrow 2Cu + I_2$$

The amount of iodine liberated was titrated using standard N/100 sodium thiosulphate solution49 using starch as indicator. The solution of Cu(II) with varying concentration were used for the iodometric determination of the metal. The result is tabulated in Table 4.

**Table 3: Gravimetric Estimation of Cu(II) with the help of  bis-(3,5-dimethyl salicylidine)-ethylendiamine**

| Amount of metal (mg) | Mean value of the Weight of the complex (mg) | Expected weight of the complex | Error (mg) |
|---|---|---|---|
| 10 | 60.6 | 60.7 | 0.1 |
| 15 | 90.9 | 91.0 | 0.1 |
| 20 | 121.3 | 121.4 | 0.1 |
| 25 | 151.6 | 151.7 | 0.1 |
| 30 | 182.0 | 182.1 | 0.1 |
| 35 | 212.2 | 212.4 | 0.2 |
| 40 | 242.6 | 242.8 | 0.2 |
| 45 | 272.9 | 273.1 | 0.2 |
| 50 | 303.3 | 303.5 | 0.2 |
| 55 | 333.5 | 333.8 | 0.3 |
| 60 | 364.0 | 364.2 | 0.2 |
| 65 | 394.3 | 394.5 | 0.2 |
| 70 | 424.6 | 424.9 | 0.3 |
| 75 | 454.9 | 455.2 | 0.3 |
| 80 | 485.4 | 485.6 | 0.2 |
| 85 | 515.8 | 515.9 | 0.1 |
| 90 | 546.0 | 546.3 | 0.3 |
| 95 | 576.3 | 576.6 | 0.3 |
| 100 | 606.7 | 607.0 | 0.3 |

**Table 4: Determination of Cu(II) iodometrically using standard solution of thiosulphate volumetrically**

| Volume of Cu(II) solution (mL) | Concentration of Cu(II) per 100 mL of the solution (gm) | Expected volume of $Na_2S_2O_3$ (N/100) solution | Experimental volume of $Na_2S_2O_3$ (N/100) solution |
|---|---|---|---|
| 100 | 0.003 | 4.38 | 4.4 |
| 100 | 0.004 | 5.88 | 5.9 |
| 100 | 0.005 | 7.30 | 7.4 |
| 100 | 0.006 | 8.76 | 8.8 |
| 100 | 0.007 | 10.22 | 1.02 |
| 100 | 0.008 | 11.68 | 11.7 |
| 100 | 0.009 | 13.14 | 13.1 |
| 100 | 0.01 | 14.60 | 14.6 |

Thus, it is obvious from the comparison of the result that the newly employed reagent bis-(3,5-demethyl salicylidine)-ethylenediamine is as good as the result obtained by the known method.

## CONCLUSION

Thus, it is obvious from the comparison of the result that the newly prepared reagent bis-(3,5-demethyl salicylidine)-ethylenediamine is as good as and an alternative reagent for the estimation of copper in comparison to the previously employed known reagent.

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**Conflict of Interest**
There is no any conflict of interest.

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