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## Bis-(3,5- dimethoxy salicylidine)-ethylenediamine as a gravimetric reagent for Cu(II)

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**Abstract:** Complex of Cu(II) with bis-(3,5-dimethoxy salicylidine)-ethylenediamine was synthesized and was characterized by elemental analysis, melting point determination, conductivity measurement, magnetic property studies and spectroscopic studies. Molecular formula of the newly prepared complex was determined as  $C_{20}H_{22}N_2O_6Cu$  and the probable geometry has been suggested as square planar. Gravimetric estimation of Cu(II) was made with bis-(3,5-dimethoxy 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 highly satisfactory and at par with the previously reported result of estimation of Cu(II) iodometrically .**

**Key words:** Bis-(3,5-dimethoxy salicylidine)-ethylenediamine, with bis-(3,5-dimethoxy salicylidine)-ethylenediamine Cu(II) complex.

**Introduction:** Synthesis and characterization of Cu(II) complex with bis-(3,5-dimethoxy salicylidine)-ethylenediamine ligand was done with a view to gravimetric estimation of Cu(II). Hypothesis behind this work is that the reagent bis-(3,5-dimethoxy salicylidine)-ethylenediamine may prove better reagent for the gravimetric estimation of Cu(II). Schiff base compounds have been extensively used in the analytical determination of the metals since long<sup>1-29</sup>. Present investigation is an extension of pioneer work done by Dubsy and Sokol<sup>30</sup>. 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 :** All the chemicals used under present investigation were of AR quality.

**Preparation of Bis-(3,5-dimethoxy salicylidine)-ethylenediamine:** 3,5-dimethoxy salicylaldehyde and ethylenediamine were taken in 2:1 molar ratio in a conical flask in methanol. The mixture was stirred well, 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.

**Preparation of Bis-(3,5-dimethoxy salicylidine)-ethylenediamine Cu(II) complex:** A deep blue ammonical solution of the copper(II) sulphate was treated with an alcoholic solution of the ligand Bis-(3,5-dimethoxy salicylidine)-ethylenediamine in 1:1 molar ratio. A grey green precipitate was separated out. This was digested on the steam bath for an hour and then left to stand for half an hour, filtered, washed with water and dried in air.

**Characterization of the ligand bis-(3,5-dimethoxy salicylidine)- ethylenediamine and its Cu(II) complex:** The ligand bis-(3,5-dimethoxy 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-dimethoxy salicylidine)-ethylenediamine was soluble in alcohol and acetone. However, it is highly soluble in dioxan, pyridine and dimethyl formamide but insoluble in water. It decomposes at 172°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°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.

## Results and Discussion:

**Molar conductance:** Its molar conductance in 10<sup>-3</sup>M solution in DMF was found to be 14 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> indicating its non-electrolytic nature.

**Magnetic susceptibility:** The observed values of magnetic moment for complexes are generally diagnostic of the coordination geometry about the metal ion. The magnetic moment of the Cu(II) complex was found to be  $\mu_{\text{eff}} = 1.78$  B.M. On the basis of studies of several Cu(II) complexes, Ray and Sen<sup>31</sup> have categorised them into two subgroups- (i) complexes having magnetic moments between 1.73 and 1.84 and (ii) complexes having magnetic moments between 1.94 and 2.20 B.M. They assigned the former to be square planar with dsp<sup>2</sup> hybridisation and later tetrahedral sp<sup>3</sup> or octahedral with sp<sup>3</sup>d<sup>2</sup> hybridisation. The absence of orbital contribution in former category has been explained by the authors<sup>31</sup> on the assumption of greater quenching effect of the orbital moment. The Pauling's valence bond theory<sup>32</sup> 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.<sup>33</sup> and Kettle<sup>34</sup> 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 magnetic moment value 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 32000 cm<sup>-1</sup> is assigned to the phenolic –OH group. This band is completely disappeared in the complex suggesting the deprotonation<sup>35</sup> of phenolic –OH and the coordination of the ligand to metal through the oxygen atom. A strong band at 1250 cm<sup>-1</sup> observed in the infrared spectra of the ligand is attributed to C – O stretching frequency. This band is shifted by 45 cm<sup>-1</sup> and appeared at 1295 cm<sup>-1</sup> in the complex, which also support the fact that chelation of the ligand

to metal occurs through oxygen atom. The bands at  $3060\text{ cm}^{-1}$  and  $3010\text{ cm}^{-1}$  are due to C – H and aromatic C – H stretching vibrations respectively. The bands at  $1625\text{ cm}^{-1}$ ,  $1590\text{ cm}^{-1}$  and  $1325\text{ cm}^{-1}$  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  $20\text{-}25\text{ cm}^{-1}$  in the complex suggesting the coordination of the ligand to metal through nitrogen atom of C = N group. The band at  $1050\text{ cm}^{-1}$  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 suggesting the complexation through O-atom by deprotonation. 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  $530\text{ cm}^{-1}$  and is assigned to metal nitrogen stretching<sup>36</sup> as well as N – M – N bending<sup>37</sup> mode of vibrations. Another new band in the spectrum of the complex at  $560\text{ cm}^{-1}$  is attributed to the M – O bond<sup>38</sup>.

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

**Electronic spectra:** Sacconi<sup>33</sup> and Meek et. al.<sup>39</sup> have observed that square planar complexes have a complex broad band of relatively higher frequencies ( $16000\text{ cm}^{-1}$ ). The regular tetrahedral complexes of Cu(II) show no d-d absorption band in the region  $10,000\text{ cm}^{-1}$  –  $20,000\text{ cm}^{-1}$ . The prepared complex of Cu(II) shows one broad band in the visible spectrum at  $16340\text{ cm}^{-1}$  which may be assigned to combination of  ${}^2B_{1g}$ ,  ${}^2A_{1g}$ ,  ${}^2B_{1g}$  and  ${}^2B_{2g}$  and  ${}^2E_g$ . Thus, the observed electronic band positions suggest the square planar geometry of the complex. →

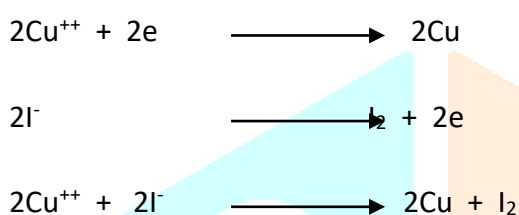
**Structure and bonding:** On the basis of the above facts the structure of the complex can be drawn as in Fig.-1.

**Gravimetric Estimation of Cu(II) with the help of bis-(3,5-dimethoxy salicylidine)-ethylenediamine:** 3.930 gms. of copper sulphate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) AnalR grade was taken in a 1000 ml measuring flask and dissolved in distilled water. One to two ml of conc.  $\text{H}_2\text{SO}_4$  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 gms. of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  contains one gm 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.  $\text{NH}_3$  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  $\text{BaCl}_2$  solution. The precipitate was dried to constant weight in hot air oven  $110^\circ\text{C}$  and

weighed as  $C_{20}H_{22}N_2O_6Cu$  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-dimethoxy 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:



The amount of iodine liberated was titrated using standard N/100 sodium thiosulphate solution<sup>40</sup> 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.

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

**Table-1**

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

Compound	Colour	m.p./ decomp/ trans. temp. °C	% analysis, found/(calcd)				Conductivity (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )
			C	H	N	Cu	
Bis-(3,5-dimethoxy salicylidine)-ethylenediamine	Yellow	172	61.55 (61.82)	6.00 (6.23)	7.10 (7.21)	-	-
Bis-(3,5-dimethoxy salicylidine)-ethylenediamine Cu(II) complex	Grey-green	>300	53.00 (53.37)	4.51 (4.93)	6.00 (6.23)	14.00 (14.12)	14

Table-2

## Selected IR bands of ligand bis-(3,5-dimethoxy salicylidine)-ethylenediamine and its Cu(II) complex

Compound	$\nu$ (-OH)	$\nu$ (C - H)	$\nu$ (C = N)	$\nu$ (C - O)	$\delta$ (C - N)	$\delta$ (-O -H)	$\nu$ (M - N)	$\nu$ (M-O)
Bis-(3,5-dimethoxy salicylidine)-ethylenediamine	3200b	3060, 3010	1625, 1590	1250	1325	1050	-	-
Bis-(3,5-dimethoxy salicylidine)-ethylenediamine Cu(II) complex	-	3060, 3010	1600, 1565	1295	1305	-	530	460

Table-3

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

Amount of metal (mg)	Mean value of the Weight of the complex (mg)	Expected weight of the complex	Error (mg)
10	70.7	70.8	0.1
15	106.1	106.2	0.1
20	141.4	141.6	0.2
25	176.8	177.0	0.2
30	212.2	212.4	0.2
35	247.6	247.8	0.2
40	283.0	283.2	0.2
45	318.4	318.6	0.2
50	353.8	354.0	0.2
55	389.2	389.4	0.2
60	424.5	424.8	0.3
65	459.9	460.2	0.3
70	495.3	495.6	0.3
75	530.0	531.0	0.1
80	566.3	566.4	0.1
85	601.6	601.8	0.2
90	637.0	637.2	0.2
95	672.4	672.6	0.2
100	707.7	708.0	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 <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (N/100) solution	Experimental volume of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (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	10.2
100	0.008	11.68	11.7
100	0.009	13.14	13.1
100	0.01	14.60	14.6

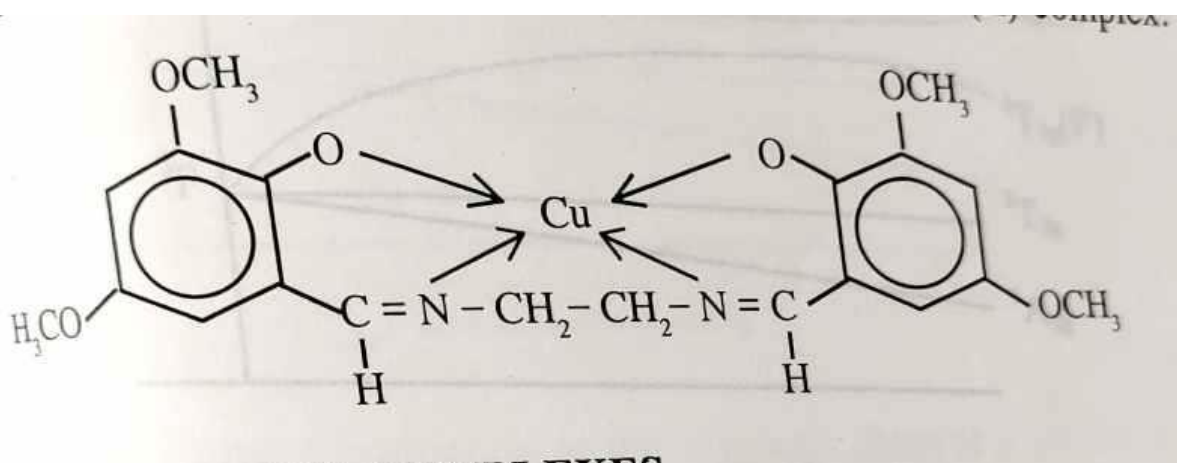


Fig.-1. Bis-(3,5-dimethoxy salicylidine)- ethylenediamine Cu(II) complex

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