

Synthesis and characterization of Cu(II) complex with Bis-(3,5-dimethoxy salicylidine)- ethylenediamine

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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.

(Keywords : Bis-(3,5-dimethoxy salicylidine)-ethylenediamine, Complex Cu(II) with bis-(3,5-dimethoxy salicylidine)-ethylenediamine)

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 long¹⁻²⁹. Present investigation is an extension of pioneer work done by Dubsky and Sokol³⁰. 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.

Experimental

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.

Molar conductance: Its molar conductance in 10^{-3} M solution in DMF was found to be $14 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ 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 $\mu_{\text{eff}} = 1.78 \text{ B.M.}$ On the basis of studies of several Cu(II) complexes, Ray and Sen³¹ 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^2 hybridisation and later tetrahedral sp^3 or octahedral with sp^3d^2 hybridisation. The absence of orbital contribution in former category has been explained by the authors³¹ on the assumption of greater quenching effect of the orbital moment. The Pauling's valence bond theory³² 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.*³³ and Kettle³⁴ 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 3200 cm^{-1} is assigned to the phenolic -OH group. This band is completely disappeared in the complex suggesting the

deprotonation³⁵ of phenolic -OH and the coordination of the ligand to metal through the oxygen atom. A strong band at 1250 cm^{-1} observed in the infrared spectra of the ligand is attributed to C - O stretching frequency. This band is shifted by 45 cm^{-1} and appeared at 1295 cm^{-1} in the complex, which also support the fact that chelation of the ligand to metal occurs through oxygen atom. The bands at 3060 cm^{-1} and 3010 cm^{-1} are due to C - H and aromatic C-H stretching vibrations respectively. The bands at 1625 cm^{-1} , 1590 cm^{-1} and 1325 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 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 cm^{-1} and is assigned to metal nitrogen stretching³⁶ as well as N - M - N bending³⁷ mode of vibrations. Another new band in the spectrum of the complex at 560 cm^{-1} is attributed to the M - O bond³⁸.

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:

Sacconi³³ and Meek *et. al.*³⁹ have observed that square planar complexes have a complex broad band of relatively higher frequencies (16000 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 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 Fig.-1.

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. $^{\circ}\text{C}$	% analysis, found/(calcd)				Conductivity (ohm $^{-1}$ cm ^{2} mol $^{-1}$)
			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	ν (-OH)	ν (C - H)	ν (C = N)	ν (C - O)	δ (C - N)	δ (-O - H)	ν (M - N)	ν (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

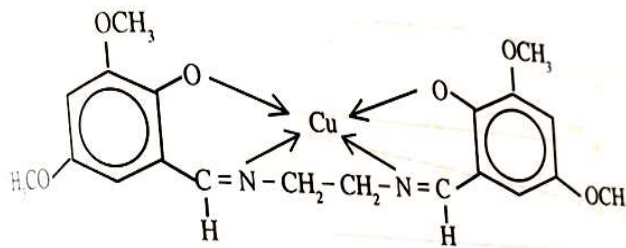


Fig.-1. Bis-(3,5-dimethoxy salicylidine)- ethylenediamine Cu(II) complex

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