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NOTE

Synthesis, Characterization and ESR Study of Copper(II)-Schiff Base Complex

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Bioactive behaviour of chloroaniline, vanillin and copper is well known. The present communication reports the synthesis and spectral properties of a Cu(II) complex with Schiff-base derived from vanillin and 4-chloroaniline.

All the chemicals were of A.R. grade. The ligand vanillidene-4-chloroaniline (Schiff base) was synthesized by adding the methanolic solution of vanillin (0.01 mole) to the methanolic solution of 4-chloroaniline (0.01 mole) in 1:1 ratio followed by refluxation on a water bath for about 3–4 h.

A methanolic solution of the cupric chloride salt (0.01 mole) was added to the methanolic solution of the Schiff base (0.01 mole) in 1:1 ratio. The resulting mixture was refluxed on a water bath for about 4 h. The complex was separated on concentrating and cooling the refluxate to a small volume for obtaining the complex. The precipitated black coloured complex was washed with ethanol followed by ether and was dried under reduced pressure over anhydrous $CaCl_2$ in a desiccator. The complex is air-stable in methanol and $CaCl_2$ (yield: 60%).

The analytical data of the complex show that the complex has metal to ligand stoichiometry in 1:1, the molar conductance value of the complex comes to be 128.2 $ohm^{-1}\ cm^2\ mol^{-1}$ (in methanol) indicating a uni-univalent electrolytic nature[1, 2]. The magnetic moment value is found to be 1.78 B.M.[5]

The IR spectrum of the ligand exhibited a broad band at *ca.* 3380 cm^{-1} which has been assigned to the stretching vibration of the phenolic—OH group and a sharp band at 1360 cm^{-1}, may be due to phenolic —OH deformation. These bands disappear in the complex spectra. An intense band at 1240 cm^{-1} (ν(C—O)) in the ligand shifts to higher frequency by 40 cm^{-1} in the complex. These observations are in favour of deprotonation of the phenolic —OH after its chelation with the metal ion. The band due to >C=N— (azomethine group) appearing at 1620 cm^{-1} in free ligand shifts to lower frequency *i.e.* 1580 cm^{-1} in the complex indicating coordination through the azomethine nitrogen. The Schiff base behaves as an anionic bidentate chelating through N and O. The spectra of complex

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exhibited new bands around 3480 cm^{-1} and 730 cm^{-1} which have been credited to coordinated water molecules. The ν(Cu—O) and ν(Cu—N) vibrations have been verified to exist by the appearance of new bands in the spectra of complex at 520 cm^{-1} and 460 cm^{-1} respectively. [3,4,7–8]

The electronic spectrum of the complex shows two bands at 12,987 cm^{-1} and 18,518 cm^{-1} assignable to $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions respectively. These findings suggest the square-planar geometry for the complex[5,6].

The ESR spectrum (in solid state) of the complex has been recorded at temperature 30°C on the X-band at frequency 9.5 GHz under the magnetic field strength of 4000 ± 2000 gauss[10–12].

ESR spectrum of the complex exhibits Lorentzian type of peaks. The values of ESR parameters *viz.* $g_{||}$, $g_{\perp}$, g_{av}, g and Δg, are as 2.2282, 2.0898, 2,1359, 2.5412 and 0.1384 respectively.

The value of $g_{||} = 2.2282$ indicate the prevalence of covalent character in the metal ligand bond. The value of axial symmetry parameter G for this complex is appreciably less than 4; this suggests about the interaction between the copper centres in solid state, (which is further supported by lowering μ_{eff} value). The value of G also indicates the medium or strong field nature of the used ligand.

The measure of the difference between $g_{||}$ and $g_{\perp}$ has been taken as an anisotropy parameter. The theoretical correlation $g_{||} > g_{\perp} > 2$ is also applicable to this complex suggesting a tetragonally elongated or square-planar copper(II) complex with a ground state $d_{x^2-y^2}$.

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