

## Structural Studies of Cu(II) & Ni(II) Complexes with a Chiral Schiff Base

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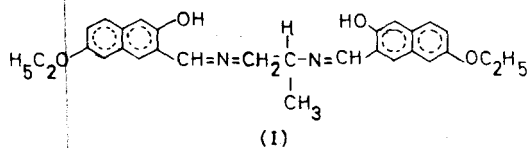
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Cu(II) and Ni(II) complexes of the schiff base derived from 6-ethoxy-2-hydroxynaphthaldehyde and isopropylenediamine [N,N'-bis(6-ethoxy-2-hydroxynaphthalidene)isopropylenediamine] have been prepared and characterised by elemental analysis, magnetic and spectral data. Circular dichroism spectral data show that the Cu(II) complex has a non-planar structure and the Ni(II) complex has a planar structure.

Investigations on metal complexes of chiral schiff bases have got a boost due to the fast development of circular dichroism and other spectrophotometric techniques. Divalent metal ion complexes of quadridentate schiff base ligands derived from the reaction of diamines with 2,5-dihydroxyacetophenone, 2,5-dihydroxypropiophenone and 2,5-dihydroxybenzophenone were assigned square-planar structure<sup>1,2</sup>. If the diamine involved in the schiff base condensation is made optically active  $\pi \rightarrow \pi^*$  transitions in the chromophoric part of the ligands may couple and produce exciton components of opposite handedness in case of deviation from planarity of the coordination sphere in the complexes<sup>3-5</sup>. Circular dichroism spectral studies on Cu(II) complexes of the above ligands show that they have got a pseudotetrahedral structure<sup>6</sup>. This prompted us to undertake synthesis and characterization of Cu(II) and Ni(II) complexes of the chiral schiff base N,N'-bis(6-ethoxy-2-hydroxynaphthalidene)isopropylenediamine(I).

Isopropylenediamine was resolved by standard procedure described by Dwyer *et al.*<sup>7</sup> This was treated with 6-ethoxy-2-hydroxynaphthaldehyde when yellow crystalline schiff base was instantaneously obtained. It is soluble in almost all common organic solvents. It was recrystallised from chloroform (m.p. 93°C).



The metal complexes were prepared by mixing hot equimolar solutions of ligand in methanol and copper nitrate/nickel nitrate in water. The Ni(II) complex was formed at  $pH \approx 6$ . The complexes were digested on a waterbath and extracted several times with chloroform. Finally, the complexes were recrystallised from chloroform. The copper complex is dark-green in colour while the nickel complex is reddish-yellow.

Carbon, hydrogen and nitrogen were estimated by micro-analytical methods. Copper and nickel were estimated gravimetrically as CuO and Ni(DMG)<sub>2</sub>. Analytical data: Cu(II) complex: Found: C, 64.95; H, 5.23; N, 5.29; Cu, 12.00. Calc.: C, 65.46; H, 5.30, N, 5.26; Cu, 11.94%; Ni(II) complex: Found: C, 65.81; H, 5.29; N, 5.24; Ni, 11.13. Calc.: C, 66.06; H, 5.35; N, 5.32; Ni, 11.14%.

Elemental analyses show that the complexes have 1:1 (M:L) ratio. Thus, the ligand behaves in a quadridentate dibasic manner. Molecular weights of the complexes determined ebullioscopically in chloroform revealed their monomeric nature. Conductivity measurements showed the covalent nature (2.2-2.7 mhos  $cm^2 mol^{-1}$ ) of these complexes.

Room temperature magnetic moment obtained using Gouy method for Cu(II) complex was found to be 2.2 B.M. The excess over that required for one unpaired electron may be due to spin-orbit coupling. The Ni(II) complex was found to be diamagnetic.

IR spectra of both the complexes are similar. A band observed at  $3480 cm^{-1}$  in the spectrum of ligand, assigned to  $\nu O-H$ , is not observed in the spectra of the complexes suggesting the involvement of oxygen atom of the hydroxyl group in coordination after deprotonation of OH. The band observed at  $1580 cm^{-1}$  in the ligand spectrum due to  $\nu C=N$  is shifted to  $1630 cm^{-1}$  in the complexes suggesting the involvement of the azomethine group ( $>C=N$ ) in complexation through the nitrogen atom.  $\nu M-N$  and  $\nu M-O$  modes were observed at 530 and  $420 cm^{-1}$  respectively.

The absorption spectrum of the Cu(II) complex showed only one band at 562 nm which is typical of square-planar complexes. The spectrum of the Ni(II) complex showed three weak bands<sup>8</sup> at 557, 686 and 712 nm due to the transitions  ${}^1E_g \leftarrow {}^1A_{1g}$ ,  ${}^1A_{2g} \leftarrow {}^1A_{1g}$  and  ${}^1B_{1g} \leftarrow {}^1A_{1g}$  respectively.

Polycrystalline state EPR spectrum of the Cu(II) complex showed the anisotropic character of the

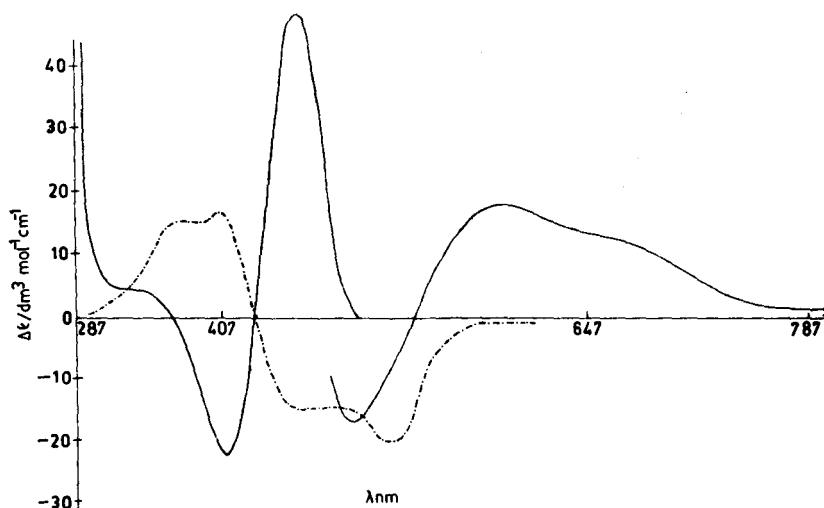


Fig. 1—CD Spectrum of Cu(II) complex (—) in chloroform and of the ligand (-----) in chloroform

complex. The solution spectrum in a mixture of  $\text{CHCl}_3$  and acetone at room temperature showed four  $g_{\text{iso}}$  bands. The two bands at higher field showed superhyperfine splitting due to nitrogen.  $g_{\text{iso}}$  and  $A_{\text{iso}}$  values have been calculated to be 2.092 and 89.13G respectively. The solution spectrum at liquid nitrogen temperature gave three values for the  $g$ -tensor,  $g_x$  (2.02),  $g_y$  (2.07) and  $g_z$  (2.185). The  $g_{\text{av}}$  value calculated was found to be exactly the same as the  $g_{\text{iso}}$  value (2.092) obtained from room temperature spectrum. The first band in the  $g_{\parallel}$  region showed the splitting due to nitrogen.  $A_{\parallel} = 200\text{G}$ ,  $A_{\perp} = 89.13\text{G}$ ,  $A_x^{\text{Cu}} = 7.0\text{G}$  and  $A_y^{\text{Cu}} = 9.0\text{G}$  were also calculated from the spectra. Since three  $g$ -factors are observed, the molecule is rhombic with the unpaired electron in the  $d_{x^2-y^2}$  orbital with the ground state term  ${}^2B_{1g}$ . The values  $g_{\parallel}/A_{\parallel} = 109.25$  and  $A_{\parallel}$  are in the range expected for square planar complexes.

NMR spectrum of the Ni(II) complex showed a signal at  $\tau$  8.6 which could be due to the two  $-\text{CH}_3$  groups in the ethoxy moiety attached to the naphthyl ring. The  $-\text{CH}_2$  groups attached to the  $-\text{CH}_3$  group broaden the  $-\text{CH}_3$  peak due to  $J$ - $J$  coupling. The signal due to  $-\text{CH}_2$  group was found at  $\tau$  3.7. This signal was deshielded by the presence of oxygen atom. The peak at  $\tau$  8.3 could be due to the  $-\text{CH}_3$  group attached to the asymmetric carbon atom of the diamine. This was not split, confirming that this  $-\text{CH}_3$  group is chemically isolated from other protons as is evident from the proposed structure. Two sharp peaks observed at  $\tau$  7.0 and 7.1 are assigned to the  $\text{>CH}$  group of the aldehyde through which the diamine

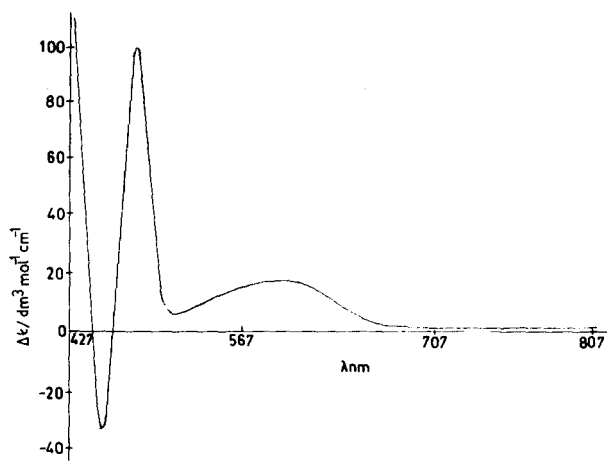


Fig. 2—CD spectrum of Ni(II) complex in chloroform

group is attached to the naphthyl ring. The  $-\text{CH}_2$  group in the diamine part gave a signal at  $\tau$  6.4. The signals due to aromatic protons were observed as strong peaks at  $\tau = 3.1, 2.65$  and  $2.80$ . The proton attached to the asymmetric carbon atom in the coordination sphere gave signal at  $\tau$  2.7. It is highly deshielded and this deshielding could be due to its position in the coordination sphere.

The circular dichroism (CD) spectrum of the ligand is typical of exciton coupling in a gauche conformation with negative optical factor for the low energy component. The observed fine structure in the CD spectrum could be due to an overlaid  $n \rightarrow \pi^*$  transition as shown below:



In the CD spectrum of the Cu(II) complex of the schiff base, transition region of the chromophore is observed at the same energy level as in the spectrum of schiff base (Fig. 1); furthermore, it exhibits a CD spectrum typical of exciton coupling. This indicates a tetrahedral distortion of the Cu(II) coordination sphere. The low energy exciton component of the complex has a positive optical factor whereas that of the ligand has a negative optical factor. This suggests that the absolute configuration of the ligand part in the complex is opposite to that of the free ligand. The CD spectrum of the complex shows an envelope in the  $\pi \rightarrow \pi^*$  region, indicating the copper complex to be non-planar. Hence the CD spectrum of the Cu(II) complex suggests a psuedotetrahedral, i.e., a deformed square-planar structure for the complex. However, the electronic and EPR spectra clearly point to a square-planar structure for Cu(II) complex. The distortion from square-planar towards tetrahedral structure suggested by the CD spectrum must, therefore, be small. In the spectrum of Ni(II) complex (Fig. 2), the transition regions of the chromophore of the ligand and the complex are at different energies suggesting the absence of tetrahedral distortion of the Ni(II) coordination sphere. There is no envelope in the  $\pi \rightarrow \pi^*$  region in the CD

spectrum suggesting a planar structure for Ni(II) complex. Like in the case of Cu(II) complex, the absolute configuration of the ligand part in the complex is opposite to that of the free ligand since the low energy exciton component of the complex has a positive optical factor whereas that of the ligand has a negative optical factor as is evident from the CD spectra of the two. Hence, it is concluded that the Ni(II) complex is square-planar.

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