

New Antiferromagnetic Copper(II) Complexes with ONO Donor Schiff Bases

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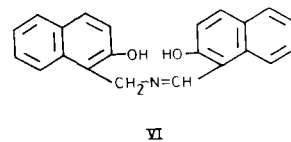
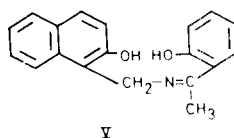
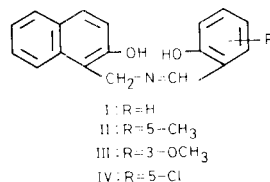
Copper(II) complexes of schiff bases derived from salicylaldehyde, 5-methylsalicylaldehyde, 5-chlorosalicylaldehyde, 3-methoxysalicylaldehyde, *o*-hydroxyacetophenone, 2-hydroxy-1-naphthaldehyde and 1-aminomethyl-2-naphthol have been synthesized. The elemental analyses indicate 1 : 1 stoichiometry. The complexes exhibit subnormal magnetic moments (1.46-1.39 B.M.) at room temperature due to antiferromagnetic exchange. The complexes exhibit one broad and two sharp intense electronic spectral bands in the ranges 600-630, 390-410 and 320 nm respectively. The ESR spectra of the complexes at room temperature resemble those of standard dimers. The schiff bases behave as tridentate dibasic ONO donor ligands giving the complexes of the type CuL where L is the dianion of the schiff base. On the basis of magnetic susceptibility, infrared, electronic spectra and ESR spectra, a dimeric structure with 1-aminomethyl-2-naphtholic oxygen atoms as the bridging atoms is suggested.

Copper acetate monohydrate and acetylacetonemono-(*o*-hydroxyanil)copper(II), the two distinct prototype dimers¹⁻³ with antiferromagnetic exchange, have stimulated much experimental and theoretical work⁴⁻⁶ directed towards the understanding of spin coupling in magnetically condensed dimers. There has been also much interest in the correlation between the structural features and the magnetic properties of bridged copper(II) dimers^{3,7,8} wherein spin pairing between the two adjacent copper atoms may occur via bridging oxygen atoms. In the synthesis of such dimers, the tri-dentate dibasic schiff bases obtained from *o*-hydroxyaldehyde or ketone and *o*-aminophenol or amino acid or ethanolamine or aroylhydrazide are the suitable ligands because they satisfy the charge of the bivalent metal ion but do not meet the coordination requirements of the metal ion and, therefore, force the bivalent metal ions to dimerize or polymerize resulting in complexes with unusual magnetic, thermal and structural properties^{9,10}.

Though much work has been done on the complexes of copper(II), considerably less is known about the dimeric complexes of copper(II) with ONO donor schiff bases. The present work describes the synthesis, spectral and magnetic properties of copper(II) complexes with the schiff bases I-VI.

Materials and Methods

Salicylaldehyde, *o*-hydroxyacetophenone and *o*-vanillin were SM, Aldrich and BDH reagents respectively. 2-Hydroxy-1-naphthyl methyl amine hydrochloride and 2-hydroxy-1-naphthaldehyde were prepared according to Duff's method¹¹. 5-Methylsalicylaldehyde and 5-chlorosalicylaldehyde were also prepared by Duff's method¹². Copper



chloride was an AR grade reagent. The schiff bases were prepared by the reaction of amine (0.1 M) with the corresponding aldehyde (0.1 M) in methanol and were recrystallized from methanol.

Preparation of complexes

To an ethanolic solution (0.1 M) of base hydrochloride and corresponding aldehyde (0.1 M), an alcoholic solution of NaOH (0.3 M) was added with vigorous stirring and the contents were boiled on a water-bath until a clear reddish-yellow solution was obtained. To this solution, an aqueous solution of copper chloride (0.1 M) was added slowly with constant stirring and the contents were again boiled on a water-bath for some time. The precipitated complex (pale green) was filtered and washed with ethanol and finally with ether and dried over anhydrous calcium chloride.

The copper in the complexes was estimated gravimetrically by a standard method¹³ and nitrogen was estimated by Kjeldhal's method.

The conductance measurements were done on an ELICO CM-82 conductivity bridge with a cell having

Table 1—Analytical, Electronic Spectral and Magnetic Moment Data of Copper(II) Complexes of Tridentate Dibasic Schiff Bases

Sl. No	Ligand used	Empirical formula	Found (Calc.) %		μ_{eff} (298°K) B.M.	Electronic spectra λ_{max} (nm)
			Cu	N		
1	I	(C ₁₈ H ₁₃ NO ₂)Cu	19.14 (18.76)	4.01 (4.13)	1.40	630, 390
2	II	(C ₁₉ H ₁₅ NO ₂)Cu	18.40 (18.02)	3.78 (3.97)	1.46	610, 400
3	III	(C ₁₉ H ₁₅ NO ₃)Cu	17.41 (17.05)	3.52 (3.75)	1.42	620, 410
4	IV	(C ₁₈ H ₁₂ NO ₂ Cl)Cu	17.49 (17.01)	3.61 (3.74)	1.45	620, 395
5	V	(C ₁₉ H ₁₅ NO ₂)Cu	17.56 (18.02)	4.00 (3.97)	1.43	600, 400
6	VI	(C ₂₂ H ₁₅ NO ₂)Cu	15.80 (16.36)	3.66 (3.60)	1.39	615, 405

a cell constant of 0.624 cm^{-1} . The magnetic measurements were made on a Gouy balance at room temperature using $\text{Hg}[\text{CO}(\text{SCN})_4]$ as a calibrant. The electronic spectra of complexes in nujol mull were recorded on a Backmann DMR-21 spectrophotometer in the region 300-1000 nm.

IR spectra were recorded on a Perkin-Elmer-257 spectrophotometer in KBr in the region $4000\text{--}650\text{ cm}^{-1}$ and in nujol mull on a Perkin-Elmer-577 grating spectrophotometer in the region $650\text{--}200\text{ cm}^{-1}$. The ESR spectra of the complexes at room temperature were recorded on a EPR-E-4 spectrometer operating in the X-band region with 100 KHz modulation frequency using diphenyl picryl hydrazyl free radical (DPPH) as the g-marker.

Results and Discussion

The complexes are amorphous, green solids insoluble in common organic solvents and melt or decompose above 250°C . They are soluble in DMF and DMSO to some extent. The results of elemental analyses (Table 1) show that the complexes have 1:1 (metal:ligand) stoichiometry indicating the tridentate dibasic behaviour of the ligands. The complexes are of the type CuL where L is the dianion of the schiff base.

The values of molar conductance of the complexes in DMF at the concentration 10^{-3} M are in the range $1\text{--}2\text{ mho mol}^{-1}\text{ cm}^{-2}$, indicating the nonelectrolytic nature of the complexes.

The magnetic moments of the complexes measured at room temperature are given in Table 1. The observed values (1.39-1.46 B.M.) are less than the spin-only value (1.73 to 2.20 B.M.) for copper(II) ($3d^9$) mononuclear complexes having no major interactions between two copper moieties¹⁴. A remarkable feature of the magneto-chemistry of bivalent copper complexes of dibasic tridentate schiff bases is the

frequency with which evidence of magnetic exchange is found, usually of the super-exchange type¹⁵⁻¹⁷. The low magnetic moments in copper(II) complexes are usually attributed to spin-coupling within the dimer brought about by the bridging of monomeric units of paramagnetic centres through the phenolic or enolic oxygen atoms^{8,18,19}. This oxygen bridging often leads to change in electronic structure of the attached atoms resulting in reduction of paramagnetism partially or completely of the metal atoms bridged. So the subnormal magnetic moments observed for the present copper(II) complexes may be accounted for by assuming dimeric structure in the solid state in which considerable antiferromagnetic exchange occurs through a super-exchange mechanism as there is little possibility of a direct interaction^{16,19}. However, in the absence of magnetic susceptibility data over a temperature range, no definite conclusions can be drawn.

Copper(II) is a $3d^9$ ion and hence the Jahn-Teller effect is operative. It has been well established that for an octahedral copper(II) complex, a ligand-field band appears around 800 nm due to the ${}^2E_g \rightarrow {}^2T_{2g}$ transition. This characteristic band shows a considerable blue shift as the J-T distortion leads, in extreme case, to square-planar structure; the band is often asymmetric or has a small shoulder suggesting the lowering of crystal field transition²⁰. Therefore, the position of this band is variable.

A band occurring in the range 375-400 nm is a subject of much controversy. Tsuchida and Yamada assumed this to be due to Cu-Cu linkage²¹. Basu *et al.*²² indicated it to be due to a ligand transition rather than $d\text{--}d$ transition²², whereas Graddon²³ assumed it to be due to $d_{xz} \rightarrow d_{x^2-y^2}$. Further, this band in copper(II) complexes is taken as an indicator of the presence of dimer with reduced magnetic moment²³. A

high intensity band occurring in the range 375-400 nm in binuclear copper(II) complexes has been assigned to the symmetry forbidden ligand-metal charge-transfer^{19,24}. In view of the above facts, the observed broad and medium intensity band in the range 600-630 nm and the high intensity band in the range 390-410 nm for the present complexes may be attributed to the characteristic copper(II) transition ${}^2E_g \rightarrow {}^2T_{2g}$ and the symmetry forbidden ligand-metal charge-transfer transition respectively. The third band observed for the present complexes around 320 nm may be due to $\pi \rightarrow \pi^*$ or $d \rightarrow \pi^*$ transition. In view of the above observations and the observed subnormal magnetic moments, we suggest a dimeric square-planar structure for these copper(II) complexes in which the two copper entities are linked through oxygen atoms.

The strong absorption band for the free ligands occurring around $1620\text{-}30\text{ cm}^{-1}$ is shifted to lower frequency region by $10\text{-}20\text{ cm}^{-1}$ in the complexes indicating the involvement of nitrogen atom of azomethine group in the coordination⁸. This is supported by the appearance of a band in the far IR region $510\text{-}540\text{ cm}^{-1}$ due to $\nu(\text{Cu}-\text{N})$ ²⁵. The absence of a weak broad band due to intramolecular hydrogen-bonded OH to the nitrogen atom of azomethine group in the region $2650\text{-}2700\text{ cm}^{-1}$ in the complexes indicates the deprotonation of both the replaceable hydrogen atoms and the dibasic character of schiff bases, leading to the involvement of both the phenolic oxygen atoms in the coordination²⁶. This is supported by the appearance of a band around 460 cm^{-1} due to $\nu(\text{Cu}-\text{O})$. The coordination effects are expected to be greater for bands associated with the bridging oxygen atoms. The ligands have two phenolic oxygen atoms (one belonging to the salicylaldehyde part of the molecule and the other to naphthyl methylamine part of the molecule). One of them may be involved in the oxygen bridge formation. The complexes prepared in alkaline medium usually prefer the oxygen atom of the amine substituent to that of the phenyl ring for the bridge formation and as such many complexes with iminoalcoholic and benzylamino phenolic oxygen bridges are reported²⁸. So we suggest the naphthyl-methylamino phenolic oxygen atoms as the bridging atoms.

A representative one-line ESR spectrum of copper complex obtained from 1-aminomethyl-2-naphthol and 2-hydroxy-1-naphthaldehyde is given in Fig. 1. The copper(II) ion ($3d^9$) with an effective spin of $\frac{1}{2}$ and ground state²⁹ $d_{(x^2-y^2)}$ has $g_{\parallel}=2.3$ and $g_{\perp}=2.07$. When the monomeric specie change into dimeric specie having axial symmetry and identical sites, the g -values also change due to the change in symmetry. The widths and shapes of the absorption lines offer a means of studying the magnetic coupling and exchange

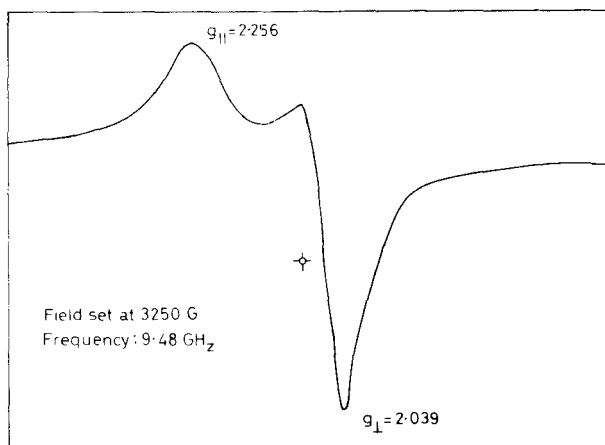


Fig. 1—ESR spectrum of Cu^{2+} schiff base 2-hydroxy-1-naphthaldehyde

interaction within the substance²⁹. Seven line solution ESR spectra of copper(II) chelates³⁰ and a forbidden $\Delta M = 2$ transition around 1600 gauss ($g \sim 4$) have been presented as the evidences for dimers in solution. The polycrystalline X-band ESR spectra of the present complexes are quite similar to those of representative chlorodimers. The anisotropy of the g -tensors is well resolved into $g_{\parallel}$ and $g_{\perp}$ with the numerical values 2.256 and 2.039 at room temperature respectively. These values closely agree with those of standard dimers. These observations are quite in agreement with the magnetic and IR results supporting the dimeric nature of the complexes.

All the above observations clearly suggest that the ligands exhibit diabasic tridentate behaviour in these copper(II) complexes as revealed by the analytical results that show 1:1 stoichiometry. The electronic spectral results suggest a square-planar configuration. The subnormal magnetic moments observed for these complexes at room temperature indicate significant spin exchange between the two adjacent copper atoms. The IR data show the presence of dimer with the naphthylmethylamino phenolic oxygen bridge suggesting the super-exchange type mechanism for the antiferromagnetic exchange present in the complexes. The ESR spectra also support the dimeric nature of the complexes. In view of the above facts and the common square-planar configuration known for the copper(II) complexes, a dimeric square-planar structure is proposed. However, the dimeric nature of the complexes cannot be substantiated by the molecular weight determination because of their insolubility in common organic solvents.

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