SHORT COMMUNICATIONS

ESR STUDIES ON SOME SCHIFF BASE COPPER(II) COMPLEXES IN DIFFERENT SOLVENTS

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THE characterization by spectroscopic and magnetic techniques was caried out for: 1, N,N'-hexamethylene-bis-(2,5-dihydroxyacetophenoneiminato) copper(II)[1]; 2, N,N'-tetramethylenebis-(2,5-dihydroxyacetophenoneiminato)copper(II)[2]; and 3, N,N'-ethylene-bis- (2,5-dihydroxyacetophenoneiminato) copper(II)[3]. The studies showed interesting results that the size of the methylene bridge did not affect the stereochemistry of the complexes. The present study describes the ESR and optical absorption studies on these complexes in different solvents. Various bonding and magnetic parameters are computed and discussed.

The complexes 1, 2 and 3 were prepared by the methods reported earlier[1-3]. The ESR spectra of the complexes were recorded on a Varian E-4 X-band spectrometer at room temperature and liquid nitrogen temperature using the solvents chloroform (Cf), dimethylsulphoxide (DMSO), dimethylformamide (DMF) and pyridine (Py). A few typical spectra are shown in figure 1. The optical absorption spectra were recorded on a Spectronic-20 spectrophotometer.

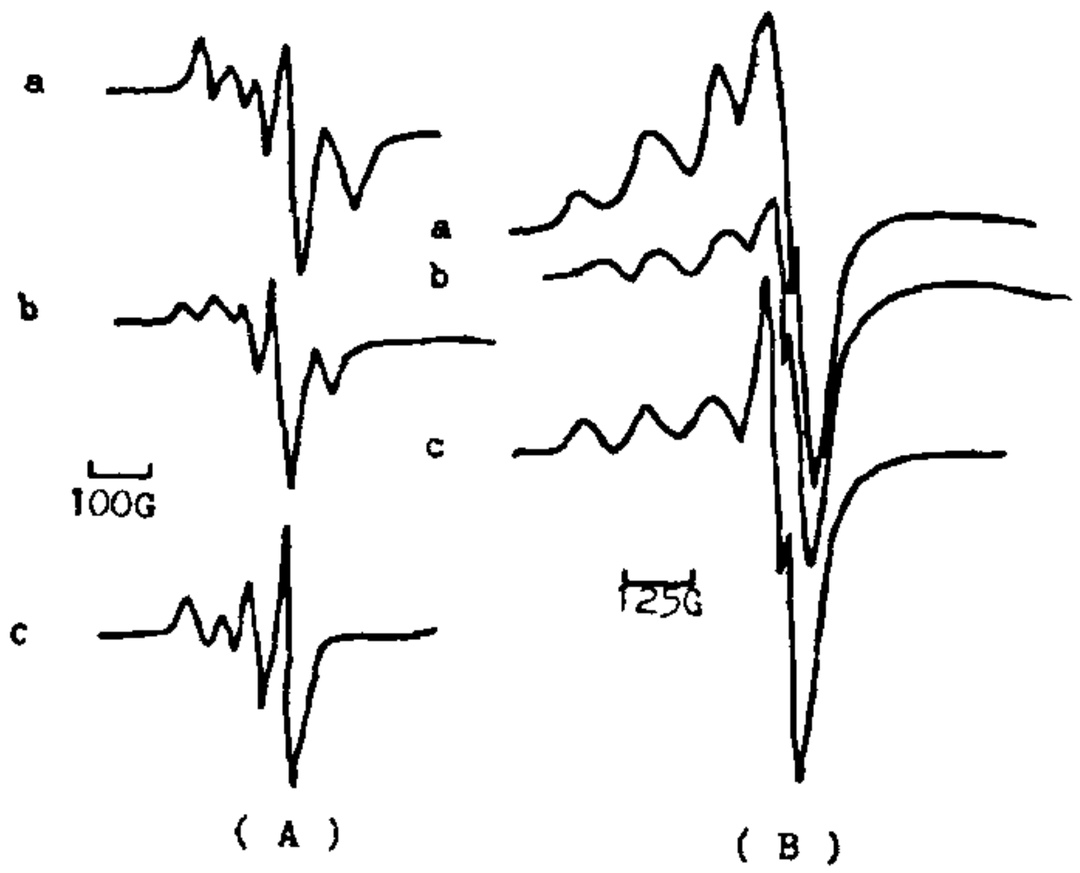

Figure 1. ESR spectra of (a) complex No. 1 (b) complex No. 2 and (c) complex No. 3 in pyridine solution at (A) room temperature and (B) liquid nitrogen temperature.

The room temperature ESR spectra of the complexes in solution show spin-dependent hyperfine line. The absence of any $M_S = \pm 1/2$ transition at half field, rules out any Cu–Cu interaction. The ESR spectra were analysed by the method of Kneubuhl[4], Sands[5] and Garman *et al*[6]. The average g_0 and A_0 values of the complexes are given in table 1. The spectra at liquid nitrogen temperature gave rise to well resolved hyperfine lines on g_{11} with no resolution on g_1 line suggesting that the e_1 and e_2 are the same or nearly the same. The $g_\perp$ and A_{11}

Table 1 *ESR data at room and liquid nitrogen temperatures with E values in different solvents*

	Room temperature data			Liquid nitrogen temperature			
Complex (solvents)	g_0	$A_0 \times 10^4 (cm^{-1})$	ΔE (cm^{-1})	g_{11}	$g_\perp$	$A_{11} \times 10^4$ cm^{-1}	$A_\perp \times 10^4$ cm^{-1}
1 (Cf)	2 088	60 17	18020	2 134	2 046	136	22
1 (DMSO)	2 104	54.72	15870	2 157	2 053	145	10
1 (DMF)	2 114	51 27	15630	2.162	2.058	127	13
1 (Py)	2.126	48 50	13890	2 238	2 050	127	11
2 (Cf)	2.088	59 24	17860	2 137	2 043	147	15
2 (DMSO)	2 106	53 69	13510	2 217	2 048	138	12
2 (DMF)	2.115	50 60	13440	2 223	2 050	127	13
2 (Py)	2 122	49 01	13160	2 225	2 053	127	10
3 (Cf)	2 091	57.54	17700	2 141	2 046	138	18
3 (DMSO)	2 109	51 84	13090	2 231	2.048	134	11
3 (DMF)	2 119	48.39	13160	2 236	2 040	120	12
3 (Py)	2.124	48 60	12990	2.257	2 043	125	11

parameters were obtained from the spectra at liquid nitrogen temperature[7]. The values of $A_\perp$ were obtained from equation 1 and are listed in table 1. The spin-Hamiltonian parameters are also presented in table 1.

$$A_0 = (A_{11} + 2A_\perp)/3 \tag{1}$$

The complexes possess [2N, 2O] coordination in the equitorial plane with two azomethine nitrogen and two phenolic oxygen at cis position[3]. The g_0 value increases in the order Cf → DMSO → DMF → Py corresponding to the increased axial interaction with these solvent molecules. Further, the g_0 value is maximum for the complex 3 and minimum for the complex 1. This indicates that the axial interaction with solvent molecule is hindered if the size of the methylene bridge increases. The A_0 values of the complexes fall in the order Cf → DMSO → DMF → Py, indicating that stronger the solvated complex, the smaller is the value of unpaired electron's wave function at the nucleus. Apparently, the bonding solvents pull the electron away from the copper. The g_{11} values for the complex 1 (table 1) in chloroform, DMSO and DMF, suggest no apparent change in coordination or a weak axial interaction; but the value in pyridine shows solvated effect. Further, the g_{11} values for the complexes 2 and 3 in DMSO, DMF and pyriding indicate the participation of the solvent molecule in coordination.

The electronic spectra of the complexes in chloroform exhibit absorption bands in the region 18020–17700 cm^{-1} attributable to $^2B_{1g} \rightarrow {}^2E_g$ transition. It has been observed that this transition, ΔE (table 1), is lowered in DMSO, DMF and pyridine suggesting the axial interaction of the solvent molecule. The extent of axial interaction falls in the order DMSO < DMF < Py.

The parameters α^2 and β^2, in-plane α-bonding and π-bonding respectively, were obtained from equations 2 and 3 and the values are listed in table 2. In these equations $p(=0.036)$, K(0.43) and Σ ($-830\ cm^{-1}$) are respectively the free ion dipole term, Fermi constant term and spin-orbit coupling constant term.

$$\alpha^2 = \frac{A_0}{pK} + \frac{g_0 - 2.0023}{K} \tag{2}$$

$$g_{11} = 2.0023 - \frac{8\Sigma\alpha^2\beta^2}{\Delta E} \tag{3}$$

The values of α^2 and β^2 (table 2) indicate that the σ-bonding is stronger as compared to π-bonding in all the solvents. This weak in-plane π-bonding suggests a greater degree of axial bonding supporting larger g_{11} inference (table 1). The strength of σ-bonding decreases with the increase in the degree of order of basicity of the solvent molecule. The strength of in-plane π-bonding, increases with the increase in the size of the methylene bridge and the strength of the σ-bonding increases with the decrease in the size of the methylene bridge. This supports a stronger participation of the solvent molecules in axial bonding if the size of the methylene bridge is small.

The values for paramagnetic susceptibility (χ_M), magnetic moment (μ_{eff}) and the Fermi constant term (K) were calculated from (4), (5) and (6).

$$\chi_M = N\beta^2 g_0^2 S(S+1)/3KT \tag{4}$$

$$\mu_{eff} = g_0[S(S+1)]^{1/2} \tag{5}$$

Table 2 *Molecular orbital and magnetic parameters*

Complex (solvents)	α^2	β^2	$\chi_M \times 10^6$ (CGS)	μ_{eff} (BM)	K
1 (Cf)	0.588	0.724	1364	1.81	0.253
1 (DMSO)	0.590	0.746	1385	1.82	0.254
1 (DMF)	0.591	0.745	1398	1.83	0.254
1 (Py)	0.601	0.814	1414	1.84	0.258
2 (Cf)	0.582	0.732	1363	1.81	0.250
2 (DMSO)	0.588	0.786	1387	1.82	0.253
2 (DMF)	0.589	0.798	1398	1.83	0.253
2 (Py)	0.595	0.830	1408	1.84	0.256
3 (Cf)	0.578	0.746	1368	1.81	0.249
3 (DMSO)	0.583	0.786	1392	1.83	0.251
3 (DMF)	0.584	0.788	1404	1.83	0.251
3 (Py)	0.593	0.854	1411	1.84	0.257

$$K = (A_0/P) + (g_0 - 2.0023). \quad (6)$$

The magnetic moment of the complexes (table 2) clearly indicate the absence of any anti-ferromagnetic coupling. The values further support that the complexes are mononuclear.

Conclusions:

1. The complexes under consideration are found to possess square planar Cu[2N, 2O] moiety in chloroform.

2. In the solution of DMSO, DMF and pyridine, the coordination positions are found to be occupied by the solvent molecules.

3. The axial interaction of the solvent molecules is hindered if the size of the methylene bridge increases.

4. The bonding solvents pull the electron from copper.

5. The complexes are mononuclear in these solvents and the anti-ferromagnetic coupling is absent.

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COORDINATION-POLYMERS OF Mn(II), Co(II), Ni(II), Cu(II) AND Zn(II) WITH SOME NOVEL SCHIFF BASES

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THE demand for new polymeric materials with high thermal and chemical stability has stimulated research in polymer chemistry[1–8]. The present study is concerned with the preparation and characterization of coordination polymers of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with the Schiff bases derived from 2-hydroxy-1-naphthaldehyde with *o*-dianisidine (DNDA), *p*-phenylenediamine (DNPPA), and benzidine (DNBN). The complexes were characterized by analytical, magnetic, thermogravimetric and spectral data.

Preparation of the Schiff-bases

The diamine (dianisidine or paraphenylenediamine or benzidine) solution in acetone (50 c.c. of 0.01 M) was added dropwise to 0.02 mol solution of 2-hydroxy-1-naphthaldehyde in 50 c.c. acetone with continuous stirring. The mixture was heated for about 30 min on a water bath and allowed to cool overnight. The resulting coloured precipitates were filtered, repeatedly washed with hot acetone and dried under suction. The purity of the compounds was checked by TLC, yield 60–70%.

The schiff bases are insoluble in water, ethanol, chloroform and acetone but soluble in DMF. The composition is given in table 1.

The schiff bases of 2-hydroxy-1-naphthaldehyde with *o*-dianisidine, paraphenylene diamine and benzidine are abbreviated as DNDA(L), DNPPA-(L') and DNBN(L") respectively.

A mixture of 0.002 mol solution of schiff base (DDNA/DNPPA/DNBN) in hot DMF and 0.002 mol solution of the metal salt in DMF-H_2O, was refluxed over sand bath for 3 to 6 h. The coloured precipitates were filtered, washed with hot DMF and dried. All the complexes were coloured, stable, insoluble in common organic solvents (ethanol, acetone, carbon tetrachloride, methanol, benzene, *n*-hexane, DMF and DMSO).

The analytical data of the complexes (table 1) agree with the general formula $(ML\ 2H_2O)_n$ where M = Mn(II), Co(II), Ni(II), Cu(II) or Zn(II) and L = L or L' or L". However in the case of Cu(II)-DNPPA and Cu(II) DNBN, there are two additional molecules of associated H_2O. Zn(II) complexes with L' and L" could not be isolated. The analytical values of the ligand and the metal complexes for C, H and N agreed with the calculated values within 1.4%. The colour and composition of the complexes are given in table 1.

The spectra of the compounds show characteristic band near 3400 in DNDA, DNBN and at 3300 in DNPPA; 1315 DNDA, DNBN and DNPPA are attributed to O–H stretching and deformation respectively. The absorptions near 1555–1530 and 1290–1265 may be assigned to C–O stretching and