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ESR Studies of the Cu(II) Complexes with the ONS Chelating Schiff Bases

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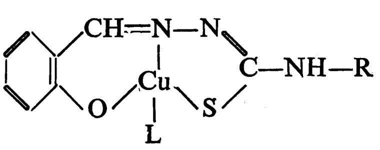
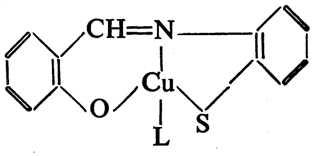
The interactions between Cu(II) complexes of tridentate Schiff bases containingthe ONS donor atoms (condensation products of 2-hydroxyaryl aldehydes and thiosemicarbazides or *o*-aminothiophenol) and molecules of polar solvents have been ESR studied both in liquid and in frozen solutions. On the basis of the ESR copper hyperfine structure parameters and the nitrogen superhyperfine splittings the presence of two different adducts with nitrogen coordinating solvents has been established and the structure of the adducts depending on the ligand nature has been discussed.

INTRODUCTION

The thiosemicarbazones derived from thiosemicarbazides and 2-hydroxyaryl aldehydes as well as the Schiff bases derived from *o*-aminothiophenol and 2-hydroxyaryl aldehydes can coordinate as the dianionic tridentate ligands via the hydroxyl oxygen, the imino nitrogen and the sulphur to form the Cu(ONS) complexes represented by (1) and (2), respectively.



(1)



(2)

The vacant coordination position around Cu(II) ion can be occupied in the solid state by the bridging atom of the adjacent molecule; planar tri-covalent oxygen atom in the binuclear Cu(II) complexes of thiosemicarbazones and pyramidal tri-covalent alternate oxygen and sulphur atoms in the polymeric chain structure postulated for Cu(II) complexes with Schiff bases of *o*-aminothiophenol[2]. As shown in the present work and earlier data the bridge bonds can be readily cleaved by polar solvent molecule L to give monomeric Cu(ONS)L complexes[1,3,4]. The tridentate character of the thiosemicarbazones and the *o*-aminothiophenol derivatives have encouraged us to undertake ESR investigations on their Cu(II) complexes on formation of the different adducts in solutions. Our previous studies[5–7], which considered the Cu(II) complexes of tridentate Schiff bases with ONO donor set, revealed that the solvent molecules L (coordinating via oxygen or nitrogen atom) occupy a non-equatorial position. In the present work the effect of substitution of oxygen atom for sulphur one in the chelate ring (leading to the ONS donor set) on adduct formation and the effect of the different ligands on the ESR parameters of the Cu(II) complexes in relation to the structure of the adducts are investigated. It has been suggested that a number of thiosemicarbazones acting as tridentate chelating agents sequester metal ions which are involved in carcinogenesis[9]. These ligands have also been extensively studied because of their antitubercular, antibacterial and antifungal activities and have been used as analytical complexing agents[3].

EXPERIMENTAL

The thiosemicarbazones and their Cu(II) complexes were prepared according to literature methods[3]. The elemental analyses for copper, carbon, nitrogen and hydrogen confirm the formation of Cu(II) complexes with tricoordinate thiosemicarbazones formulae Cu(tsc-al) in general, and in particular Cu(tsc-sal), Cu(tsc-naphthal), Cu(4phtsc-sal), Cu(4phtsc-naphthal) where ths-al is the condensation product of the following thiosemicarbazones and 2-hydroxyaryl aldehydes: thiosemicarbazide (R=H) and salicylaldehyde, thiosemicarbazide (R=H) and 2-hydroxy-1-naphthaldehyde, thiosemicarbazide (R=4-phenyl) and salicylaldehyde, thiosemicarbazide (R=4-phenyl) and 2-hydroxy-1-naphthaldehyde, respectively.

The Schiff bases of *o*-aminothiophenol and *o*-aminophenol and their Cu(II) complexes were prepared according to Muto[4]. The elemental analyses for copper, carbon, nitrogen and hydrogen confirmed the formation of Cu(II) complexes with tridentate Schiff bases formulae Cu(*o*-aminothiophenol-sal), Cu(*o*-aminothiophenol-naphthal) and Cu(*o*-aminophenol-sal). The solvents were purified by the standard method[8]. The ESR spectra were recorded on JEOL JES-ME X-band spectrometer using a nuclear magnetometer MJ 110 and microwave frequency meter JES-SH-30X.

RESULTS AND DISCUSSION

Properties of Complexes in the Solid State

The investigated complexes in the temperature range 77–295 K are ESR silent. In some cases only very weak signals of the monomeric impurities were observed, the strongest one in the case of Cu(tsc-naphthal).

The absence of the ESR spectra may be related to the significant broadening of the ESR signals as a result of an interaction between Cu(II) ions in dimeric or polymeric compounds which is in agreement with the magnetic data obtained on those compounds earlier[1,2]. Strong antiferromagnetism has been implicated for Cu(tsc-sal)[1] complexes through dimeric associations whereas infinite spiral chain interactions have been suggested for Cu(*o*-aminothiothiophenol-naphthal). On the other hand, a weak antiferromagnetism involving infinite linear chains of copper ions has been proposed for Cu(*o*-aminothiophenol-sal)[2].

Properties of Complexes in Solutions

As shown in Figures 1 and 2 solution ESR spectra of all studied

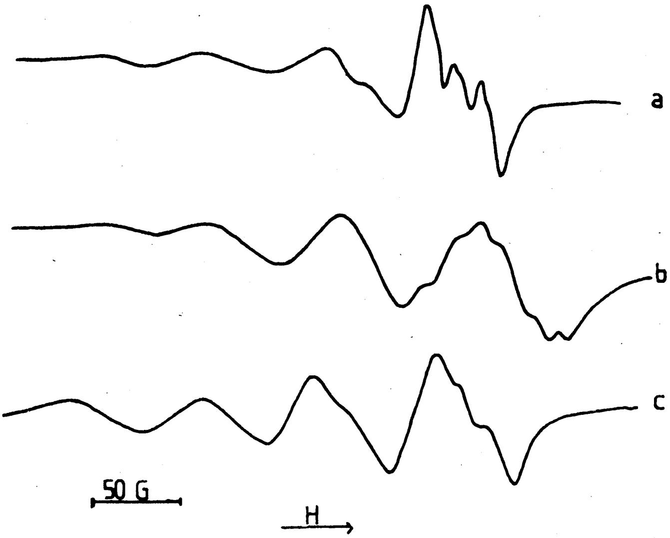


Fig. 1 ESR spectra of Cu(4phtsc-naphtal) at 295 K : (a) in DMF (L), (b) after addition of L_1 = pyridine to the DMF (L) solution, (c) in pyridine (L)

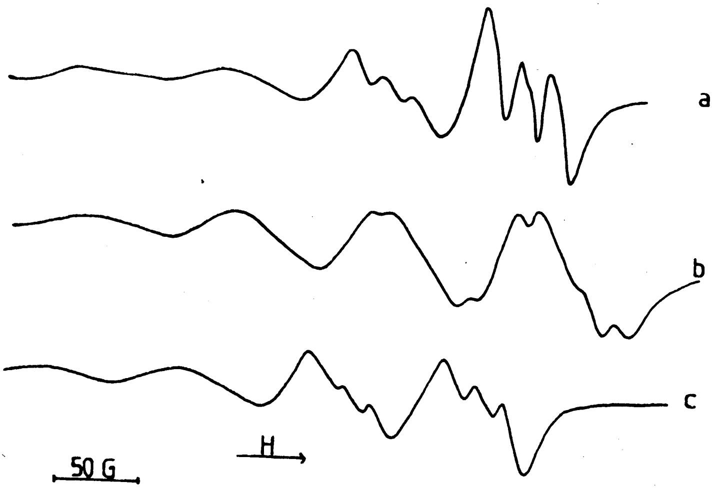


Fig. 2 ESR spectra of Cu(*o*-aminothiophenol-sal) at 295 K ; (a) in DMSO (L), (b) after addition of L_1 = pyridine to the DMSO (L) solution, (c) in pyridine (L)

Cu(ONS) complexes consists of the well resolved signal due to hyperfine interaction and are typical of a monomeric copper(II) complex[5]. In oxygen-coordinating solvents such as DMSO, DMF and NMF the spectra (Figures 1a and 2a) exhibit three lines of superhyperfine splitting (SHFS) corresponding to interaction of the unpaired electron of Cu(II) ion with a single ^{14}N nucleus.

TABLE 1

ESR SPECTRAL PARAMETERS OF Cu(II) THIOSEMICARBAZONE COMPLEXES AT ROOM TEMPERATURE IN PURE SOLVENTS (L) AND AFTER ADDITION OF PYRIDINE (L_1) TO THE SOLUTION

Compound	Solvent (L)	g_{iso}	A_{iso}	Pyridine (L_1) added	
				g_{iso}	A_{iso}
Cu(tsc-sal)	DEF	2.094	73	2.089	85
	DMF	2.093	74	2.087	85
	DMSO	2.095	72	2.097	85
	Pyridine	2.096	73		
Cu(tsc-naphthal)	DEF	2.091	80	2.089	89
	DMF	2.092	77	2.088	88
	DMSO	2.094	72	2.088	87
	Pyridine	2.093	73		
Cu(4phtsc-sal)	DEF	2.091	74	2.089	87
	DMF	2.091	71	2.088	82
	DMSO	2.097	72	2.094	85
	Pyridine	2.097	73		
Cu(4phtsc-naphthal)	DEF	2.098	75	2.087	88
	DMF	2.091	76	2.090	85
	DMSO	2.097	74	2.091	87
	Pyridine	2.098	73		
Cu(*o*-aminothiophenol-sal)	DEF	2.094	63	2.091	80
	DMF	2.095	64	2.087	83
	DMSO	2.098	62	2.096	84
	Pyridine	2.096	68		
Cu(*o*-aminothiophenol-naphthal)	DEF	2.093	73	2.090	86
	DMSO	2.094	67	2.097	87
	Pyridine	2.096	75		
Cu(*o*-aminophenol-sal)	DEF	2.113	76	2.108	85
	DMF	2.117	74	2.110	86
	DMSO	2.121	73	2.118	83
	Pyridine	2.120	71		

Parameters A are given in 10^{-4} cm^{-1} units.

DEF = N,N-Diethylformamide, DMF = N,N-Dimethylformamide.

DMSO = Dimethyl sulphoxide.

Similar pattern of SHFS is observed for the spectra of complexes in nitrogen-coordinating solvent such as pyridine (Figure 1c and 2c). The results implicate that only imine nitrogen atom as coordinating Cu(II) ion in XY plane can give rise to ^{14}N SHFS of the order of the magnitude (18 G) observed here. Apparently, the bound solvent molecule L (completing the coordinating number four) is not coplanar with ONS ligand in the formed Cu(ONS)L complex.

TABLE 2

ESR SPECTRAL PARAMETERS OF Cu(II) THIOSEMICARBAZONES COMPLEXES AT 77 K IN PURE SOLVENTS (L) AND AFTER ADDITION OF PYRIDINE (L_1) TO THE SOLUTION

Compound	Solvent(L)	$g_{\parallel}$	$A_{\parallel}$	Pyridine (L_1) added	
				$g_{\parallel}$	$A_{\parallel}$
Cu(tsc-sal)	DEF	2.196	192	2.194	187
	DMF	2.200	192	2.193	186
	Pyridine	2.195	185		
Cu(tsc-naphthal)	DEF	2.186	198	2.189	187
	DMF	2.188	200	2.192	190
	Pyridine	2.193	184		
Cu(4phtsc-sal)	DEF	2.193	185	2.192	186
	DMF	2.195	185	2.191	188
	Pyridine	2.194	185		
Cu(4phtsc-naphthal)	DEF	2.191	186	2.187	188
	DMF	2.183	179	2.193	189
	Pyridine	2.191	114		
Cu(*o*-aminothiophenol-sal)	DEF	2.189	190	2.200	180
	DMF	2.183	179	2.195	182
	Pyridine	2.197	180		
Cu(*o*-aminothiophenol-naphthal)	DMF	2.183	187	2.196	185
	Pyridine	2.197	185		
Cu(*o*-aminophenol-sal)	DEF	2.254	189	2.239	187
	DMF	2.251	188	2.240	186
	Pyridine	2.240	187		

Parameters A are given in 10^{-4} cm^{-1} units.

The inspection of the Tables 1 and 2 reveals that A_{iso} and $A_{\parallel}$ parameters for Cu(ONS)L complexes derived from *sal* are smaller in comparison with those stated for the *naphthal* derivatives. The reduction of hyperfine structure parameters usually suggests the greater degree of tetrahedral distortion[10]. Significantly smaller A_{iso} parameters observed for Cu(*o*-aminothiophenol-sal)L compounds provide additional support to the conclusion that stereochemical factors influence the observed ESR parameters. Addition of the nitrogen coordination ligands such as pyridine (py) to the solution of the complexes in oxygen coordinating solvent (DMSO, DMF, DEF) yields quite different ESR spectra indicative of new adducts (Figures 1b and 2b). The ESR spectra of these adducts show five lines of SHFS due to two ^{14}N atoms coordinated in the same plane. The results reveal that under these conditions, pyridine (L_1) probably occupies the fourth equatorial position forcing the earlier solvent (L) ligand occupy an axial coordination site giving rise to new Cu(ONS)L_1L adducts.

Increasing of Cu : L_1 ratio progressively the ESR spectrum undergoes changes corresponding to the intermediate species Cu(ONS) (py) (DMF) and is reversed back to original spectra but corresponding to Cu(ONS) (py) species (Fig. 3). It is noteworthy that the five-line spectra assigned to Cu(ONS)L_1L adducts can be observed in apparently wider range of

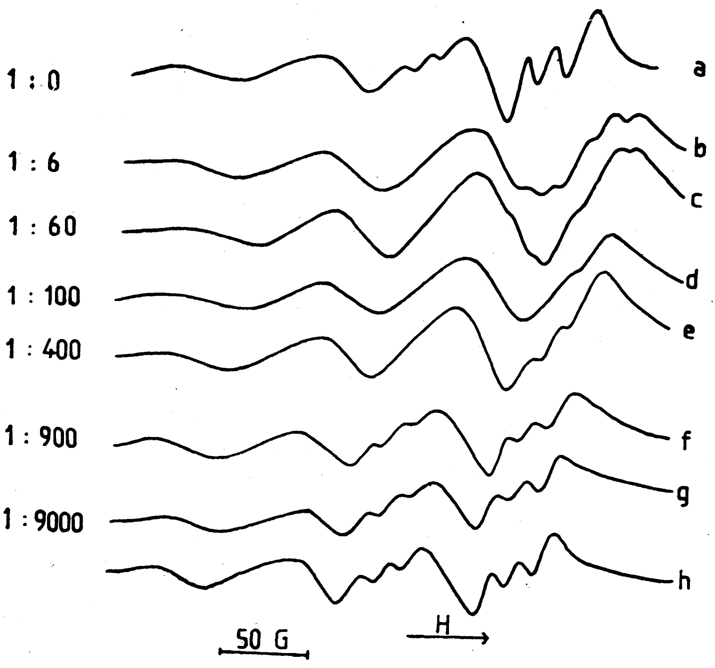


Fig. 3 ESR spectra of Cu(tsc-naphthal) at 295 K : (a) in DEF (b-g) after a gradual addition of pyridine (py) to the DEF solution, (h) in pyridine

Cu : L_1 ratio in the liquid than in the frozen solutions. Thus, at room temperature the five-line spectra are seen when the ratio Cu : L_1 is within the limits 6–60 whereas at liquid nitrogen temperature (Fig. 4) when this ratio exceeds 6, the spectra resembles to the spectrum of final Cu(ONS) (py) adduct. This fact suggests that during the freezing the equilibrium: Cu(ONS) (py) (DMF $\rightleftharpoons$ Cu(ONS) (py) + DMF is significantly shifted to Cu(ONS) (py) complex even for the relatively low Cu : L_1 ratio. Hence, the liquid solutions are much useful for study of Cu(ONS)L_1L adducts. The characteristic increase of A_{iso} parameters and in general, decrease of g_{iso} parameters for the new Cu(ONS)L_1L complexes can be interpreted as due to changes in the symmetry from pseudotetrahedral for the tetracoordinate adducts to the square-pyramid for the pentacoordinate adducts[6,7].

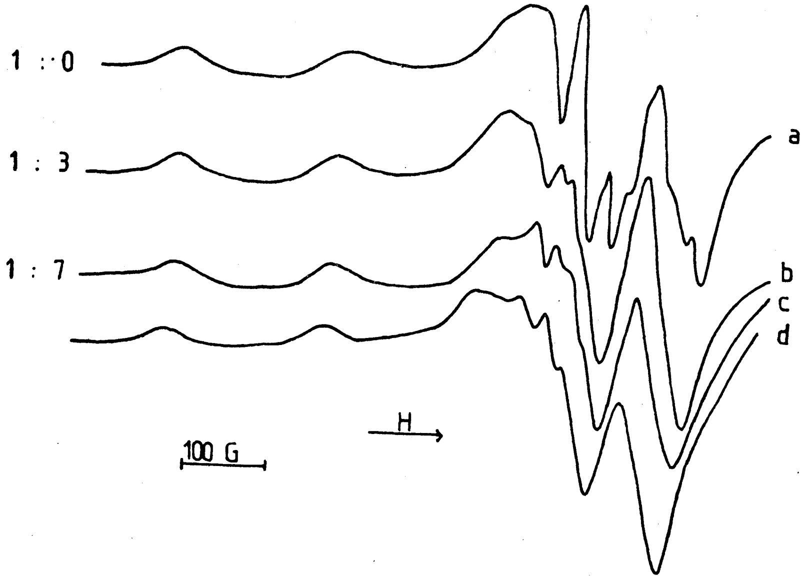


Fig. 4 ESR spectra of Cu(tsc-naphthal) at 77 K : (a) in DEF (b-c) after a gradual addition of pyridine (py) to the DEF solution, (d) in pyridine

Finally, inspection of the data (Tables 1 and 2) for comparable complexes with slightly different donor sets *viz.* CuONS and CuONO (Cu-*o*-aminophenol-sal) reveals that more electron donating sulphur is responsible for the decrease of parameters. This is consistent with Peisach ond Blumberg[11] observations and has been recently supported for other Cu(II) complexes with sulphur containing ligands[12].

The results presented here for Cu(ONS) complexes when compared with those reported previously for Cu(ONO)[6,7] and Cu(ONN)[13] complexes prove that formation of two type adducts in the solutions appears to be general phenomenon for Cu(II) complexes of tridentate Schiff bases. The characteristic transition from three line ^{14}N SHFS to five line ^{14}N SHFS observed in solution ESR spectrum relevant to particular adducts may be used as diagnostic of tridentate character of Schiff bases. On the other hand, the formation of the adduct with five line ^{14}N SHFS spectrum may be applied to analyses of very small contents of nitrogen coordinating ligand present in the solutions as the admixture in the oxygen coordinating solvents.

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