The Electron Spin Resonance of Copper(II) Schiff Base Complexes Containing Amino Acids as Part of the Ligand

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The electron spin resonance of frozen solutions of a range of copper complexes of Schiff bases with amino acids as a component of the base have been measured at 110 K. The complexes appear to be of distorted planar structure with two nitrogen and two oxygen coordinating groups. They are sufficiently flexible for the degree of planarity to be affected by the coordinated solvent. Sharp fine structure on one compound was analysed in terms of a hyperfine interaction from copper, the azomethine nitrogen and its associated proton.

Introduction

Schiff bases in which one of the coupling components of the base is an amino acid, readily form complexes with copper(II) [1]. When an additional complexing group such as an imidazole or thiol is present, it appears that the basic Schiff base arrangement remains unchanged and the additional group acts in various ways, such as a blocking group, or by coordination to the copper as an additional ligand, or by bridging two of the Schiff base entities by coordination through a second copper ion [2]. More complex Schiff base copper compounds are believed to be implicated in *in vivo* processes such as the non-oxidative transformation of pyridoxal-dependent enzymes [3]. In order to investigate the structure and bonding in this type of complex in more detail, we have measured the electron spin resonance of solids and frozen solutions of Schiff base complexes of either salicylaldehyde or naphthaldehyde with polyfunctional amino acids.

TABLE I. g and A Values for Each Complex. Abbreviations Used Are, sal = salicylaldehyde; gly = glycine; his = histadine; histam = histamine; ser = serine; cys = cysteine; pen = penicillamine.

		Solvent	$g_\parallel$	$g_\perp$			$A_{\parallel l}$ ($\times 10^4$ cm^{-1})	α_2
				g_1		g_2		
1.	SalglyCu·2H$_2$O	EtOH	2.257	2.063		2.024	174.9	0.80
2.		DMSO	2.269	2.064		2.024	177	0.82
3.		DMF	2.244	2.045		2.002	156.5	0.73
4.	SalhisCu·0.5H$_2$O	DMSO		2.103		2.003		
5.		DMF		2.073		2.002		
6.	SalhistamCu·3H$_2$O	DMSO	2.262	2.073		2.030	172	0.80
7.		DMF	2.258	2.058		2.017	186	0.83
8.	SaltryCu·2H$_2$O	DMSO	2.273	2.065		2.027	174	0.82
9.		DMF	2.267	2.047		2.002	183	0.83
10.	SalserCu·H$_2$O	DMSO	2.262	2.065		2.020	179	0.82
11.		DMF	2.220	2.057		2.004	197	0.82
12.	Salcys$_2$Cu$_2$·2H$_2$O	DMSO		2.076		2.003		
13.		DMF	2.270	2.067		2.019	169	0.80
14.	SalpenCu·1.5H$_2$O	DMF			2.057			
15.	SalpenCu$_2$0.5H$_2$O	DMF			2.057			
16.	NappenCu·H$_2$O	DMF	2.289	2.063		2.033	161	0.80

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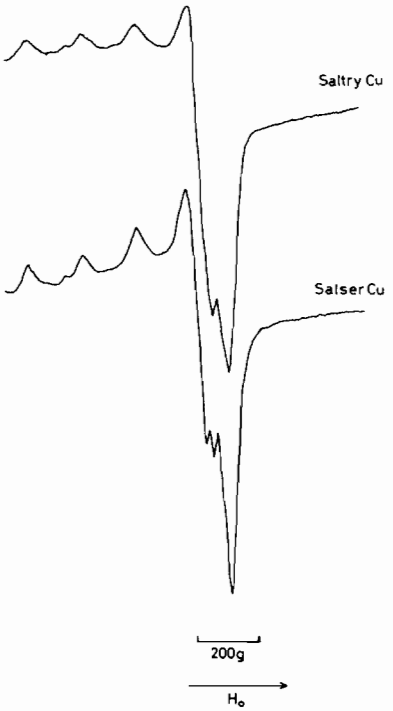


Fig. 1. The ESR spectrum of N-salicylidene tryptophan copper(II) and N-salicylididene serine copper(II) in frozen DMSO solution at 110 K.

Experimental

Materials and Methods

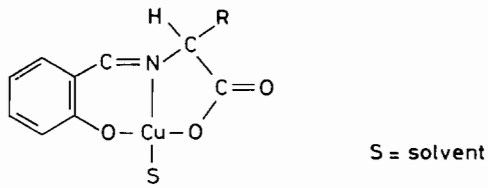
The complexes were prepared by published methods [1, 4]. Since the water required to dissolve the amino acids can cause hydrolysis of some of the Schiff base ligands and since copper(II) catalyses the oxidation of thiols to disulphide, not all possible compounds can be prepared and no one general method of preparation can be given [1]. The compounds prepared are listed in Table I, together with a key to the abbreviations used throughout. C, H and N analysis were within acceptable limits (0.4% on carbon) for each compound. Solutions were prepared in each case from the previously analysed solid.

The spectra of the solutions and solids were recorded by standard procedures using a Jeol JES FE 1-X X-band ESR spectrometer. For low-temperature measurements, a vacuum insulated jacket was placed round the sample in the cavity and the sample was cooled by passing a stream of cold nitrogen gas over the silica tube containing it. The temperature was measured by placing a gold/gold iron thermocouple in the cavity adjacent to the sample. All low-temperature measurements reported in this study were taken at 110 K.

Results and Discussion

The spectra of powdered solids as well as frozen solutions were measured but, although there was broad agreement between solid and solution spectra, the effect of spin interactions in the solid caused broadening and well-resolved spectra were obtained solely from the frozen solutions. Copper has a nuclear spin of 3/2 and two isotopes with similar magnetic moments. The copper hyperfine splitting is readily observed in the $g_{\parallel}$ spectrum (Fig. 1) and $g_{\parallel}$ and $A_{\parallel}$ can be evaluated. Since the compounds are of low symmetry, two components of $g_{\perp rp}$ are observed (g_1 and g_2) (Table I). However, except in a few cases there is insufficient structure to evaluate $A_{\perp rp}$ or A_1 and A_2.

$g_{\parallel}$ and $A_{\parallel}$ are both solvent-dependent, probably because DMSO and DMF replace water from the copper coordination sphere. These parameters have been investigated quite extensively for Schiff base copper complexes with different coordinating groups [5]. A plot of $A_{\parallel}$ against $g_{\parallel}$ shows that all the values lie in the same region as Schiffs base complexes with two nitrogen and two oxygen coordinating groups. However, the range of values for N_2O_2 Schiff bases in general is much larger [5]. The most planar complexes have the highest $A_{\parallel}$ to $g_{\parallel}$ ratios and decrease with increasing distortion through the area occupied by the amino acid compounds to lower ratios [5, 6]. Therefore, the structures of the amino acid Schiff base complexes appear to be quite closely related, irrespective of the nature of the side groups. Further, they appear to be monomeric, with the fourth coordination site occupied by a water or solvent molecule forming a distorted planar structure (A). In some cases further water or solvent molecules or potential complexing groups



(A)

in the amino acid side chain may also be coordinated to the copper.

With the exception of salgly Cu the $g_{\parallel}$ values were greater and the $A_{\parallel}$ values smaller for DMSO than for DMF. Therefore, it would appear that DMF adducts are more planar than those produced by DMSO. This is particularly true for salser Cu and, together with the unusual salgly Cu result, it indicates that although there is little evidence of strong coordina-

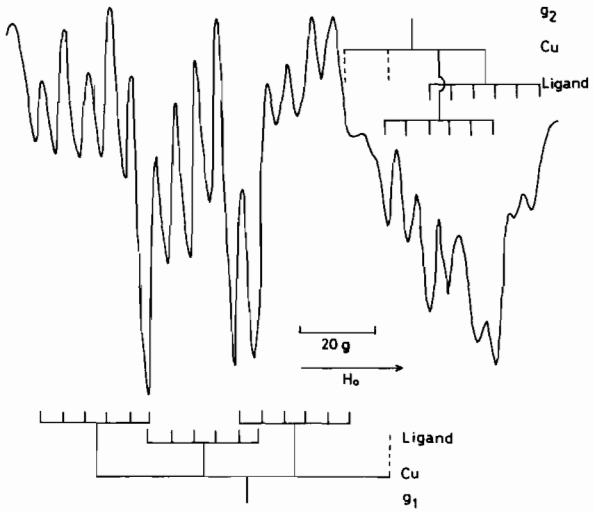


Fig. 2. The ESR of one component of the $g_{\parallel}$ spectrum of N-salicylidene serine copper(II) in frozen DMF solution at 110 K.

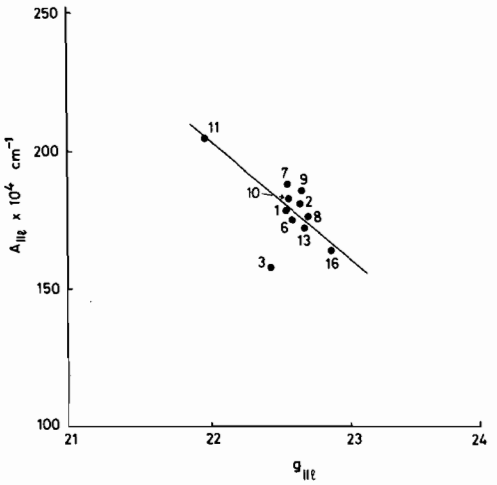


Fig. 3. A plot of $A_{\parallel}$ against $g_{\parallel}$ for copper Schiff base amino complexes as frozen solutions in DMF at 110 K. Numbers refer to the compound numbers of Table I.

tion from groups on the side chain, these side chains do have an influence on the final geometry of the complex.

The most planar compound investigated, salser Cu, is particularly well resolved. In the $g_{\parallel}$ spectrum of this complex, a set of six peaks appear on the side of each resonance. The separation between each peak is nearly equal but, if the separations are measured accurately, the system consists of a set of three peaks, each split into a doublet, as would be expected for a nitrogen hyperfine interaction with one proton. Since DMF is probably coordinated through the oxygen and should give rise to a more complex proton hyperfine spectrum, it seems clear that this structure is due to a hyperfine interaction with the azomethine group and its associated proton, confirming the coordination of the azomethine to the copper(II).

The ESR spectrum in the g_{1rh} region is also well resolved and can be fitted using eight six-line patterns similar to that used above. Thus, each of the copper hyperfine lines for g_1 and g_2 can be identified (Fig. 3).

The magnitude of the ligand hyperfine splitting is similar in both the parallel and perpendicular spectrum but the copper hyperfine splitting is much larger in the parallel spectrum. This suggests that there is a different mixture of isotropic and anisotropic terms in the two cases. The isotropic term is basically due to a Fermi contact interaction and is related mainly to the degree of covalency of the complex, whereas the anisotropic interaction arises from a dipolar interaction between the ligand and the metal ion. Since the ligand hyperfine interaction is mainly due to the isotropic term, this is confirmatory evidence that the azomethine group is bonded to the copper ion in this complex.

α^2, a term related to the degree of in plane σ bonding in the complex, was evaluated by the method of Kivelson and Neiman for each complex [7]. Values of α^2 can range from 1.0 for an ionic complex to 0.5 for a fully covalent one. Most of the complexes have a value of about 0.8 (Table I) and when the values for α^2 for the alanine and phenylalanine complexes which had been studied previously [8, 9] were re-evaluated according to the method used here, they also had values of about 0.8. This value places these compounds as more ionic than bis(salicylidene) 1,2-diaminoethane copper(II) [10] and related species and less ionic than EDTA or oxalate complexes [11]. They are similar to copper phthalocyanine and copper(II) imidazole [11] complexes.

There were some more specific differences between the compounds. Schiff base complexes containing the amino acids cysteine and penicillamine with thiol groups on the side chain were less well resolved and in some cases even the hyperfine splitting on $g_{\parallel}$ was only just observable. With sal(cys)$_2$-Cu$_2$, for which an additional copper site has been postulated [2], the $g_{\parallel}$ region had 6 rather than 3 poorly resolved bands suggesting that this postulate is probably correct. In the case of salhistCu and salhistamCu compounds there is also evidence of additional bands in both the the $g_{\parallel}$ and $g_{\perp rh}$ spectrum. These probably indicate an interaction of the imidazole group, but the spectra is insufficiently resolved to reach any firm conclusion.

Thus, in solution, copper Schiff base complexes containing amino acids as part of the ligand, all appear to have related structures consisting of a

monomeric, distorted Schiff base complex structure with at least one coordinated solvent molecule, and for which there is evidence of a direct copper azomethine bond. The structures are distorted from a planar configuration and are sufficiently flexible to be appreciably influenced by the addition of a solvent molecule.

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