An Electron Spin Resonance Study of Some Quadridentate Schiff Base Complexes of Copper(II)

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The X-band ESR spectra of a series of quadridentate Schiff base complexes of copper(II) have been examined in frozen xylene and chloroform solutions. Well resolved triplet state spectra were observed both at *g ca.* 2 and *g ca.* 4 due to dimeric forms of these complexes which exist in frozen solution. Magnetic and structural parameters have been determined by computer simulation of the triplet state spectra based on a lower than axial symmetry model for the copper(II) pair system.

The structural features of Schiff base compounds have been the subject of numerous investigations and more recently ESR spectroscopy has been used to study the dimeric forms of several copper(II) Schiff base complexes in frozen solution.[1–6] The application of a dipole-dipole coupled model to copper(II) dimers of low symmetry has enabled the ESR spectra to be analysed by computer simulation and has yielded values for the copper(II)-copper(II) separation, r, and the angle ξ (Fig. 1). In some cases it has been possible to compare structural data deduced from X-ray diffraction studies with similar information obtained from ESR spectra.[1,7]

Crystallographic studies on the dimeric forms of copper(II) Schiff bases indicate that the symmetry is monoclinic. However the host lattice relevant to the X-ray crystallographic studies is quite different from that involved in ESR measurements which are confined to isolated interacting pairs of copper(II) ions in solvent mixtures and it is possible that the stereochemistry of the dimers formed in solution may be dependent upon solvent effects.

Chikira and Isobe[2] concluded from computer simulations of the observed ESR lineshapes that the dimeric structure of bis(N-salicylidenemethylaminato)-copper(II), [Cu(MeSal)], in frozen toluene solution was similar to that found for the γ-form crystals as determined by X-ray methods. Furthermore it was found necessary to take into account the non-coincidence of the principal axes of the g tensor with those of the fine structure tensor in order to estimate such dimeric structures.[2]

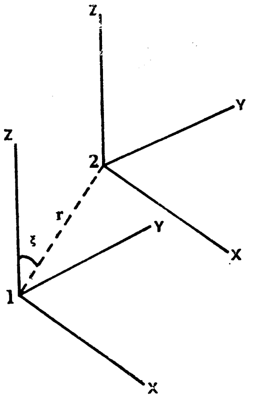
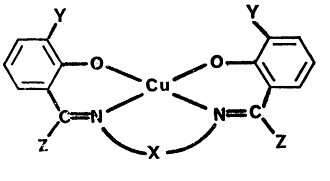


Fig. 1. Orientation of g tensor principal axes and internuclear axis for centrosymmetric metal ion dimers.

A more recent investigation by Chikira *et al.* involved a study of the triplet state ESR spectra due to the dimeric forms of the copper(II) complexes of some bidentate and quadridentate Schiff bases.[3] The spectra were analysed on the basis of the previously obtained results concerning the non-coincident g and fine structure tensors.[2] Their results indicated that the angles between the $g_{\parallel}$ axis and the copper-copper axis of the dimers of the quadridentate Schiff base complexes were considerably smaller than those of the bidentate ones. The lineshapes and the magnetic parameters of the bidentate Schiff base complexes were characterized by non-coaxial g and fine structure tensors whereas the quadridentate complexes were thought to show ESR spectra indicative of near coaxial g and fine structure tensors. It was concluded from this argument that the difference between the solid state and frozen solution dimeric structure of N,N'-ethylenebis-(salicylideneiminate)copper(II), [Cu(Salen)], was due to the fact that, in frozen solution the $g_{\parallel}$ axis almost coincides with the copper–copper axis.

These results are in direct conflict with the previously reported results of Toy *et al.*[1] who estimated the copper–copper distance and the angle between the $g_{\parallel}$ axis and the copper–copper axis for Cu(Salen) dimers in chloroform at 4.55±0.05 Å and 40±5° respectively. It was later claimed by Chikira *et al.* that the spectral patterns for the $\Delta Ms=\pm 1$ transition of Cu(Salen) could not be reproduced by the use of such non-coincident g and spin-dipole interactions.[3] The magnetic and structural parameters determined by Toy *et al*[1]. were obtained by computer simulation of the low field ($\Delta Ms=\pm 2$) components of the spectra only since, in all cases, the observation of the corresponding $\Delta Ms=\pm 1$ spectrum at *g ca.* 2 proved difficult due to masking in



X = $\underset{\mathrm{CH_3}}{\mathrm{CHCH_2}}$, $(CH_2)_3$
(pn) (tn)
Y = H, OCH_3
Z = H, CH_3

Fig. 2. Structural formulae of copper(II) Schiff base complexes.

that region by a strong signal due to the monomer species. On the other hand, the parameters determined by Chikira *et al.*[3] were based on computer simulation of the $\Delta Ms=\pm1$ spectra only and no data relevant to the $\Delta Ms=\pm2$ transitions was presented.

The present investigation involves the determination of structural and magnetic parameters of a number of copper(II) Schiff base complexes which include *N,N'*-isopropylenebis(salicylideneiminato)copper(II), Cu(Salpn); *N,N'*-propylenebis(salicylideneiminato)copper(II), Cu(Saltn); *N,N'*-isopropylenebis(3-methoxysalicylideneiminato)copper(II), Cu(3MeO-Salpn); *N,N'*-propylenebis(3-methoxysalicylideneiminato)copper(II), Cu(3MeO-Saltn); *N,N'*-isopropylenebis(7,7'-dimethylsalicylideneiminato)copper(II), Cu(7,7'Me_2Salpn) and *N,N'*-propylenebis(7,7'-dimethylsalicylideneiminato)-copper(II), Cu(7,7'Me_2Saltn). The structural formulae of these complexes are shown in Fig. 2.

The results obtained are based on computer simulation of both the $\Delta Ms=\pm1$ and $\Delta Ms=\pm2$ transitions in the ESR spectra due to the dimeric forms of the Schiff base complexes, and indicate that the g and fine structure tensors are in fact non-coincident.

Experimental

ESR spectra were recorded by means of a Varian E12 spectrometer. Cu(Salpn), Cu(Saltn), Cu(3MeO-Salpn) and Cu(3MeO-Saltn) were prepared by refluxing in ethanol the salicylaldehyde or 3MeO-salicylaldehyde complex of copper(II) with the appropriate diamine. Cu(7,7' Me_2Salpn) and Cu(7,7' Me_2Saltn) were prepared by refluxing in ethanol, copper(II) acetate, *o*-hydroxyacetophenone and the appropriate diamine.

In all cases the composition of the products was established by elemental analysis.

Results

Chikira *et al.*[3] calculated the magnetic parameters for a wide range of quadridentate Schiff base complexes, including Cu(Salpn), from the triplet state ESR spectra, at g *ca.* 2, arising from frozen toluene solutions of the complexes. However, even under these conditions, the ESR spectra included contributions from the doublet spectra due to monomeric forms of the Schiff bases.

Ideal conditions for computer simulation of triplet state ESR spectra arise when there is complete conversion to dimer and where the signals due to the $\Delta Ms=\pm1$ and $\Delta Ms=\pm2$ transitions are easily discerned and the resolution of their peaks is good enough to compare with computed lineshapes. A solvent which was found to provide these requirements was xylene. The ESR spectrum, at −140 °C, due to a xylene solution of Cu(Salpn) is shown in Fig. 3. Similar spectra were observed in the case of xylene solutions of Cu(Saltn), Cu(7,7' Me_2Salpn) and Cu(7,7' Me_2Saltn).

The ESR spectra of Cu(3MeO-Salpn) and 3MeO-Saltn) in xylene, at −140 °C, consisted of single broad lines, (approx. 150 gauss from peak to peak), indicative of the formation of aggregate forms of the Schiff bases under these conditions. The best circumstances for the observation of triplet state spectra were provided by chloroform, although monomer spectra of comparable intensity were also observed. The ESR spectrum, at −140 °C, due to a chloroform solution of Cu(3MeO-Salpn) is shown in Fig. 4. A chloroform solution of Cu(3MeO-Saltn) gave rise to a similar spectrum.

No triplet state spectra were obtained from chloroform solutions of the other Schiff bases although at sufficiently high concentrations (*ca.* 10^{-1} M), weak signals at g *ca.* 4 were observed due to small concentrations of dimer in solution. The ESR spectrum due to a solution of Cu(Saltn) in chloroform, at −140 °C, is shown in Fig. 5. The copper(II) Schiff base complexes are soluble in polar solvents such as ethanol and pyridine but under these circumstances triplet state ESR spectra are not observed.

It was found that Ni(Salpn) could readily be doped with Cu(Salpn) thus providing the conditions for diamagnetic dilution. The ESR spectrum at −140 °C due to Cu(Salpn) under these circumstances is shown in Fig. 6.

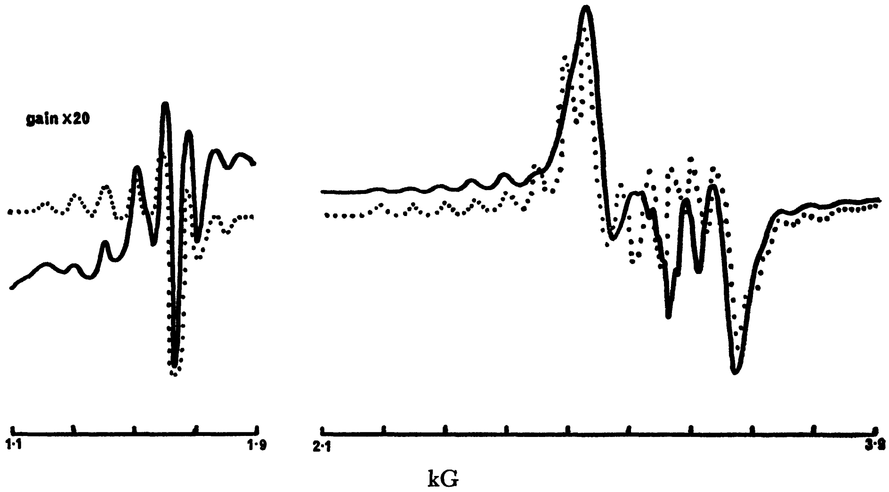


Fig. 3. X-Band ESR spectrum due to a xylene solution of Cu(Salpn) (1.0×10^{-2}M) at −140 °C; microwave frequency 9150 MHz. The dotted curves represent the computer simulation of the experimental spectrum using the parameters listed in Table 1. Baseline drift ignored in $\Delta Ms=\pm2$ spectrum.

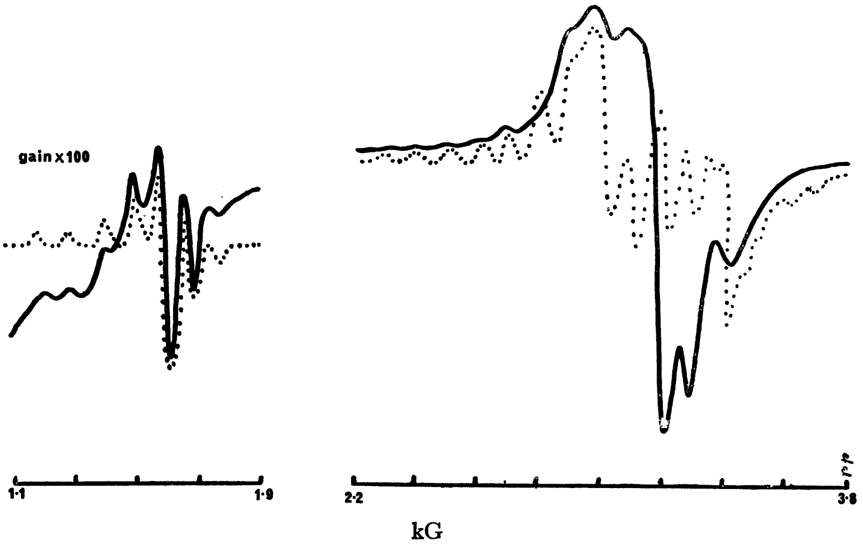


Fig. 4. X-Band ESR spectrum due to a chloroform solution of Cu(3MeO-Salpn) (3×10^{-3} M) at −140 °C; microwave frequency 9150 MHz. The dotted curves represent the computer simulation of the experimental spectrum using the parameters listed in Table 1. Baseline drift ignored in $\Delta Ms = \pm 2$ spectrum.

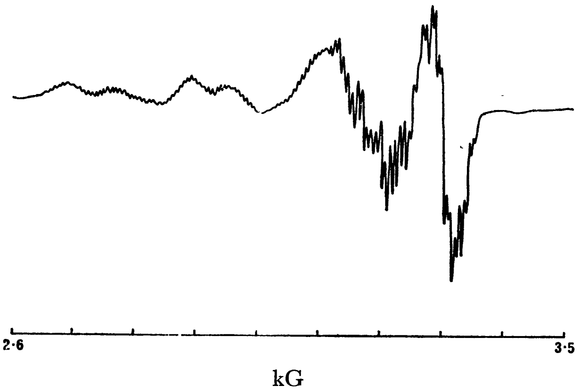


Fig. 5. X-Band ESR spectrum due to a chloroform solution of Cu(Saltn) (3×10^{-3} M) at −140 °C; microwave frequency 9150 MHz.

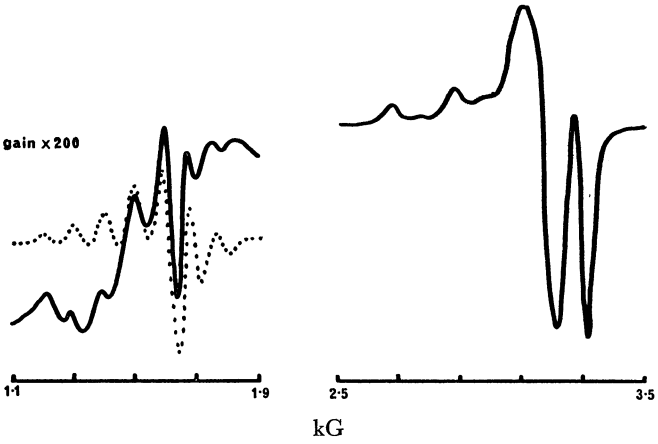


Fig. 6. X-Band ESR spectrum due to a powder sample of Cu(Salpn) doped into the corresponding nickel complex in a 1 : 9 ratio; microwave frequency 9150 MHz, temperature −140 °C. Baseline drift ignored in $\Delta Ms = \pm 2$ spectrum.

Quantitative Treatment of Results and Discussion

Observation of the ESR spectrum, shown in Fig. 3, for a frozen xylene solution of Cu(Salpn) indicates that negligible amounts of monomeric species are present under these conditions.

The low field (*g ca.* 4) component of the spectrum is attributed to $\Delta Ms = \pm 2$ transitions in the triplet state arising from magnetic dipole-dipole coupling of the copper(II) ions in a dimeric form of Cu(Salpn) while the signal at *g ca.* 2 is attributed to the corresponding $\Delta Ms = \pm 1$ transition.

The intensity pattern of peaks in the $\Delta Ms = \pm 2$ signal is indicative of a monoclinic arrangement of the copper(II) ions in the pair system[7] and the structural and magnetic parameters obtained by computer simulation of the experimental lineshape using this symmetry model are listed in Table 1.

Theoretical considerations involved in the computer simulation of an ESR spectrum using this model for the copper(II) pair system have been described previously.[7] The results of Chikira *et al.*[3] are in agreement with those of Lund and Hatfield.[6] who determined the magnetic parameters for a series of copper(II) dimers and concluded for Cu(Salen), that the principal axes of the *g* and fine structure tensors were coincident. However, as has been shown in a recent review,[8] Lund and Hatfield[6] omitted necessary terms in the Hamiltonian for lower than axial symmetry dimers and were therefore unable to reconcile their ESR results with known structural data. This has been discussed previously by two of the authors.[8] On the other hand Boyd *et al.*,[7] in examining many of the same systems in terms of a theoretical model which included all necessary terms for low symmetry dimers, did, in fact obtain very sensible agreement between X-ray and ESR structural parameters.

The effect of low symmetry on calculated spectra shows that the intensity pattern and field positions of

Table 1. Magnetic parameters for the dimeric forms of the copper(II) Schiff bases

Schiff base	Transition	r(Å)a)	$g_{\parallel}$b)	$g_{\perp}$b)	$10^4 A_{\parallel}$c) (cm^{-1})	$10^4 A_{\perp}$c) (cm^{-1})	ξd)
Cu(Salpn)	$\Delta Ms=\pm1$	3.95	2.18	2.03	225	10	35
	$\Delta Ms=\pm2$	4.10	2.17	2.03	200	10	35
Cu(Saltn)	$\Delta Ms=\pm1$	3.95	2.18	2.03	225	10	35
	$\Delta Ms=\pm2$	4.20	2.17	2.02	200	10	35
Cu(3MeO-Salpn)	$\Delta Ms=\pm1$	4.00	2.17	2.04	220	10	35
	$\Delta Ms=\pm2$	4.00	2.17	2.04	200	5	35
Cu(3MeO-Saltn)	$\Delta Ms=\pm1$	4.05	2.18	2.04	230	10	35
	$\Delta Ms=\pm2$	4.00	2.17	2.04	200	5	35
Cu(7,7′Me$_2$Salpn)	$\Delta Ms=\pm1$	4.00	2.18	2.03	230	15	35
	$\Delta Ms=\pm2$	4.20	2.17	2.02	205	10	35
Cu(7,7′Me$_2$Saltn)	$\Delta Ms=\pm1$	3.95	2.17	2.03	225	10	35
	$\Delta Ms=\pm2$	4.20	2.17	2.02	210	10	35
10% Cu(Salpn) in Ni(Salpn)	$\Delta Ms=\pm2$	4.20	2.16	2.02	200	10	35

a) ±0.05. b) ±0.005. c) ±5. d) ±2.

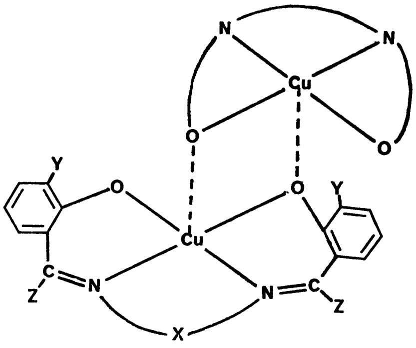


Fig. 7. Proposed structure for the dimeric forms of the copper(II) Schiff base complexes, present in frozen solution.

the lines in the low field ($\Delta Ms=\pm2$) region in particular, are affected considerably by variation in ξ.[7,8] This indicates the necessity of obtaining a well resolved low field spectrum before any conclusion about the symmetry of the copper(II) pair system can be made and unique set of structural and magnetic parameters determined.

The ESR spectrum due to a chloroform solution of Cu(3MeO-Salpn) at −140 °C is the result of the presence of a mixture of monomeric and dimeric species in solution. However the triplet state spectrum, due to the dimer, is still easily discerned at both *g ca.* 2 and *g ca.* 4 and the parameters obtained from computer simulation of this spectrum as well as that of Cu(3MeO-Saltn) in chloroform, are summarised in Table 1. A structure which meets the symmetry requirements as outlined in Table 1 is shown in Fig. 7 and involves a value of ξ of about 35°.

The ESR spectrum of Cu(Saltn) in CHCl$_3$ at −140 °C indicates the formation of a monomeric species only. The predominant feature of this spectrum, as well as those of Cu(Salpn), Cu(7,7′ Me$_2$Salpn) and Cu(7,7′-Me$_2$Saltn) in chloroform, is the appearance of extra hyperfine splitting in addition to that due to copper. Each line is split into approximately fourteen additional lines although the exact number is difficult to ascertain because of a certain degree of overlap. The separation of the lines is 7 G. Interaction of the unpaired electron on copper with two equivalent nitrogen nuclei each having a nuclear spin of 1, would be expected to result in the splitting of each copper hyperfine line into five lines with intensity ratios 1 : 2 : 3 : 2 : 1, and spacing between adjacent lines of 14—15 G. It is possible therefore that the lineshape may be the result of either the superposition of two or more monomer spectra or, that interactions with atoms other than nitrogen are occurring.

The signal observed at *g ca.* 4 in the ESR spectrum due to Cu(Salpn) doped into Ni(Salpn) indicates the formation of a dimeric species under these conditions, although only in small concentrations. The lineshape of the low field component of the spectrum again points to a monoclinic symmetry of the copper(II) pair system and the calculated magnetic and structural parameters from this spectrum are listed in Table 1. It can be seen from the similarity of these parameters to those obtained from frozen solution measurements, that the structural features of the copper(II) Schiff base are unchanged despite the gross change in host lattice.

Chikira *et al.* have studied the equilibrium between monomeric and dimeric forms of the copper(II) Schiff bases and have estimated equilibrium constants for the conversion of monomer to dimer by comparing the spectral intensities of the two species.[3] Their calculations concerning the quadridentate Schiff base complexes indicated that the K values (K is the equilibrium constant for the reaction $2\,M \rightleftharpoons M_2$, where M is the monomer) were not changed by branching methyl groups at the ethylene bridge. Contrary to their results however we have shown that when the iminoic nitrogens are bridged by a timethylene group, as in Cu(Saltn), the distribution of dimer in solution is unaltered and readily detectable triplet state ESR spectra are observed. A similar situation arises when there is a methyl group on the imine carbon in the Schiff bases derived from *o*-hydroxyacetophenone and, once again, increasing the size of the bridging group from two to three carbon atoms produced no noticeable effect on the ESR spectra of these complexes. No evidence for dimer formation involving the complex with a tetramethylene bridge could be detected due to the low solubility of this complex in common organic solvents.

The effect of substituents on the phenyl ring is more noticeable. The tendency to dimerise is greater in the substituted complexes as can be seen by comparing the ESR spectra of Cu(Saltn) and Cu(3MeO-Saltn) in frozen chloroform. In xylene or toluene the substituted complexes aggregate further whereas the unsubstituted complexes are essentially dimeric in these solvents. This result indicates that solvent effects also play an important part in the dimerization and polymerization of the copper(II) Schiff base complexes in frozen solution. In all cases association was more marked in xylene than in chloroform presumeably due to the greater solvating tendencies of the latter.

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