An Electron Spin Resonance Study of the Dimeric Form of Some Copper(II) Schiff-base Complexes

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The X-band e.s.r. spectra due to the copper(II) Schiff-base complexes, namely bis(N-methylsalicylaldiminato)-copper(II), NN'-ethylenebis(salicylideneiminato)copper(II), NN'-phenylenebis(salicylideneiminato)copper(II), NN'-ethylenebis(o-aminobenzylideneiminato)copper(II), and NN'-phenylenebis(o-aminobenzylideneiminato)-copper(II) in chloroform solution at 77 K exhibit low-field lines, which are attributed to $\Delta M_s = \pm 2$ transitions within the triplet state due to dimeric forms of these complexes which exist in frozen solution. The salient features of the low-field lines have been satisfactorily accounted for by means of computer simulated spectra based on dipole–dipole coupled pairs of copper(II) ions in dimers with lower than axial symmetry. The results obtained for the internuclear separations of the copper(II) ions are compared with those obtained from crystallographic data.

A NUMBER of investigations of the structural features of copper(II) Schiff-base complexes point to the fact that the copper(II) possesses essentially planar stereochemistry capable of accommodating tetrahedral, pyramidal, or octahedral distortions. The close packing of these chelates in the solid phase results in relatively short metal ion–metal ion separations but occasionally packing may be described in terms of the formation of discrete dimer units where the dimer symmetry is lower than axial. Recently the application of a dipole–dipole coupled model to copper(II) dimers of low symmetry, such as indicated in Figure 1, has enabled e.s.r. spectra to be analysed by computer simulation, allowing comparisons of X-ray and e.s.r. data to be made,[1] the e.s.r. simulation yielding the copper(II)–copper(II) separation, r, and the angle ξ.

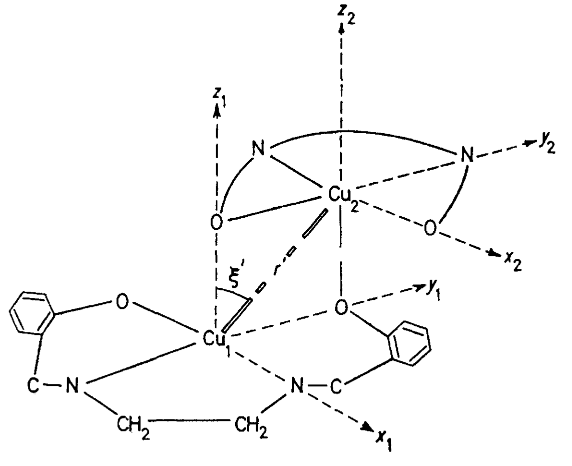

FIGURE 1 Bridging arrangement of Cu(salen) units in the crystalline state showing alignment of magnetic axes. r' Represents the internuclear copper–copper vector while ξ' represents the distortion from axial symmetry

In this case, the copper(II) Schiff-base complexes provide a further opportunity to compare structural data deduced from X-ray diffraction studies with similar information obtained from e.s.r. spectra by taking account of the symmetry properties of the dimer. The Schiff-base complexes studied include NN'-ethylenebis-(salicylideneiminato)copper(II) [Cu(salen)], NN'-phenylenebis(salicylideneiminato)copper(II) [Cu(saloph)], and bis(N-methylsalicylaldiminato)copper(II) [Cu(mesal)] whose structures have been determined by X-ray methods.[2-4] Structural studies point to the importance of out-of-plane interactions of the metal ion in being responsible for dimer formation. In order to investigate the effect of out-of-plane bonding to an imine group instead of phenolic oxygen, the study was extended to include the copper(II) Schiff-base complexes formed from o-aminobenzaldehyde and ethylenediamine [Cu(amben)], and o-aminobenzaldehyde and phenylenediamine [Cu(amphen)]. In those latter two cases, no information was available about whether the copper(II) ions occur in dimeric units.

RESULTS

Previous investigations of the e.s.r. spectra of copper(II) chelates have shown that solvent composition can be of critical importance in obtaining well resolved spectra at sample temperatures of 77 K where the solvent provides the host lattice.[5] Thus it was found that addition of toluene to chloroform solutions of the copper(II) Schiff-base complexes improved the resolution of their e.s.r. spectra, and the solvent composition commonly used here consisted of chloroform containing 20% by volume of toluene.

The X-band e.s.r. spectrum of a chloroform–toluene solution of Cu(salen) at 77 K consisted of a signal at g *ca.* 2 typical of that expected from a monomeric copper(II) species, while at low field, *ca.* 1500 G, a very weak signal was detected. However similar solutions containing Cu(saloph), Cu(mesal), Cu(amben), or Cu(amphen) at 77 K and similar instrument gain gave the well resolved low field lines shown by Figure 2. These low field components of the spectra are attributed to $\Delta M_s = \pm 2$ transitions arising from the magnetic dipolar coupling between the copper(II) ions in dimeric species which exist in frozen solutions containing the copper(II) Schiff-base complexes. The very low intensity of the signal observed in the case of the Cu(salen) chelate clearly indicates that only a very minor proportion of the copper(II) present exists in dimer form. In all cases observation of the $\Delta M_s = \pm 1$ transitions at g

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[1] P. D. W. Boyd, A. D. Toy, T. D. Smith, and J. R. Pilbrow, preceding paper.

[2] D. Hall and T. N. Waters, *J. Chem. Soc.*, 1960, 2644.

[3] H. Montgomery and B. Morosin, *Acta Cryst.*, 1961, **14**, 551.

[4] E. C. Lingafelter, G. L. Simmons, B. Morosin, C. Scheringer, and C. Freiburg, *Acta Cryst.*, 1961, **14**, 1222.

[5] J. R. Pilbrow, A. D. Toy, and T. D. Smith, *J. Chem. Soc.* (*A*), 1969, 1029.

ca. 2 proved difficult due to the dominant signal in this region of the monomer species. Some $\Delta M_s = \pm 2$ spectra were also obtained from powders of the pure compounds or for zinc(II) or nickel(II) compounds containing a small proportion of copper(II). These results differed from the frozen solution cases but have not yet been completely analysed.

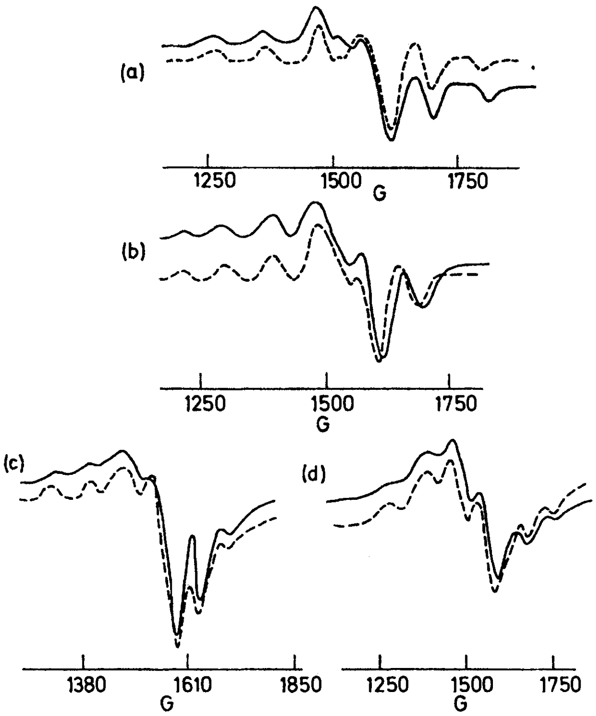

FIGURE 2 Comparison of experimental (solid line) and computed (dashed line) e.s.r. spectra for copper(II) Schiff-base chelates in chloroform containing 20% by volume of toluene at 77 K and 9140 MHz; (a) Cu(saloph); (b) Cu(amben); (c) Cu(mesal); (d) Cu(amphen); the relevant structural and magnetic parameters are listed in Table 1

TABLE 1

Calculated parameters for dimeric species

Complex	r/Å	$g_{\parallel}$	$g_{\perp}$	$10^{-4}A$/cm^{-1}	$10^{-4}B$/cm^{-1}	ξ/deg.	σ/G
Cu(saloph)	4·5 ± 0·05	2·175 ± 0·005	2·030 ± 0·005	210 ± 5	10 ± 5	40 ± 5	15
Cu(amben)	4·5 ± 0·05	2·150 ± 0·005	2·050 ± 0·005	205 ± 5	10 ± 5	40 ± 5	20
Cu(mesal)	4·5 ± 0·05	2·22 ± 0·01	2·040 ± 0·005	170 ± 10	10 ± 10	40 ± 5	20
Cu(amphen)	4·5 ± 0·05	2·130 ± 0·005	2·035 ± 0·005	195 ± 5	10 ± 5	40 ± 5	20
Cu(salen) *	4·55 ± 0·05	2·150 ± 9·005	2·055 ± 0·005	205 ± 5	20 ± 5	40 ± 5	20

* Computed lineshape compared with published spectrum (ref. 8) to obtain parameters listed. Errors listed give range of parameters over which theoretical curves compatible with the observed e.s.r. lineshape are obtained.

Interpretation of the Results.—Crystallographic studies of the dimeric forms of the copper(II) complexes of Schiff-bases indicate that the symmetry of the copper(II)–copper(II) pair is closely monoclinic. The host lattice relevant to the X-ray crystallographic studies is quite different from that involved in the e.s.r. measurements, which are confined to isolated interacting pairs of copper(II) ions in solvent mixtures. The stereochemistry of the dimers formed in solvent mixtures may involve solvent effects also.

To attempt to account in some detail for the observed e.s.r. spectra, we begin by assuming that the overall symmetry features will be similar to those in the solid compounds. This is represented in Figure 1, which anticipates the structures proposed for the copper(II) Schiff-base dimers in frozen solution.

The spin-Hamiltonian for the pair of ions (labelled 1 and 2) requires two g-values and copper(II) hyperfine constants and dipolar and isotropic exchange interactions. Thus equation (1), where the g-values and hyperfine constants,

$$\mathscr{H} = \Sigma\{\beta[g_{\parallel}H_zS_{iz} + g_{\perp}(H_xS_{ix} + H_yS_{iy})] + AS_{iz}I_{iz} + B(S_{ix}I_{ix} + S_{iy}I_{iy})\} + \mathscr{H}_{\text{dip}} - JS_1 \cdot S_2 \quad (1)$$

etc., all have the usual meanings. For monoclinic dimer symmetry as represented by Figure 1, the form of $\mathscr{H}_{\text{dip}}$ has been discussed in detail previously.[1] If $|J| \lesssim 30$ cm^{-1} the perturbation methods used before are appropriate. We note that susceptibility studies on similar Schiff-base compounds show no evidence of strong exchange coupling.[6,7] We therefore assume that $|J| \lesssim 30$ cm^{-1} and thus use the perturbation theory results for line positions and transition intensities as a function of orientation, which are incorporated in a FORTRAN 32 computer simulation program.[1] It turns out that $\Delta M_s = \pm 2$ transitions are not strongly influenced by the precise value of J.[1]

Table 1 summarises the structural and magnetic parameters obtained from a comparison of computer simulated $\Delta M_s = \pm 2$ e.s.r. spectra and the experimental results. The computed spectra in each case are shown as dashed curves in Figure 2, where it is evident visually that agreement with experiment is very satisfactory. Since the experimental results for Cu(salen) of Carlisle and Hatfield[8] were better resolved than our own, we based the computer simulation in that case on their results. Structural data thus obtained is compared with the available crystallographic information in Table 2.

When comparing these two sets of structural data, it must be borne in mind that the e.s.r. data is pertinent to dimeric molecules isolated from one another by molecules of the host lattice (*i.e.* solvent). We conclude from the lack of agreement that relationships between molecules under these circumstances might well be different to those

TABLE 2

Comparison of e.s.r. and X-ray structural data

Complex	r/Å	ξ/deg.	r'/Å	ξ'/deg.	Ref.
Cu(saloph)	4·5	40			3
Cu(amben)	4·5	40			
Cu(mesal)	4·5	40	3·33		4
Cu(amphen)	4·5	40			
Cu(salen)	4·55	40	3·18	39	2

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[6] J. Lewis and R. A. Walton, *J. Chem. Soc.* (*A*), 1966, 1559.

[7] M. D. Hobday and T. D. Smith, *J. Chem. Soc.* (*A*), 1970, 1085.

[8] G. O. Carlisle and W. E. Hatfield, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 633.

in the pure compound where packing considerations arising from the stacking of dimeric units could become important.

DISCUSSION

A crystal structure study of the chloroform adduct of Cu(salen) indicates an increase in the out-of-plane Cu–O bond to 2·79 from 2·41 Å observed in Cu(salen).[9] In the *p*-nitrophenol adduct, the *p*-nitrophenol makes a similar, but much stronger, bond with the ligand oxygen atoms, and the dimer bond is further weakened to the point where it is no longer considered to exist. Under these circumstances the chelate molecules are stacked plane to plane to form chains, successive molecules being separated by *ca.* 3·5 Å.[10]

The major structural effect brought about by the isolation of the dimer unit in the host lattice formed by the organic solvent is an increase in the copper(II)–copper(II) distance, though the overall symmetry of the pair system is unchanged. This increase in r must entail a substantial increase in the distance over which the out-of-plane copper(II)–oxygen interaction occurs. In fact, this increase in the out-of-plane copper(II)–oxygen distance is such as to make this bond no longer important in bringing about dimer formation. On the other hand, it is difficult to conceive alternative conformations of the Schiff-base ligand, such as sharing the ligand between two copper(II) sites which could certainly account for the copper(II)–copper(II) separation.

It is proposed that in each case, the dimeric unit of the Schiff-base chelates is formed by an alignment of parallel planes similar to that observed in the pure complex, but that the planes of the chelates are now further apart. The forces holding the components of the dimer together are suggested as arising from π–π interactions of the multiple bond system which comprise the chelates. Such a proposal explains the following: (i) in each case the dimer occurs only to a minor extent; (ii) the proportion of dimer formed in the Cu(saloph) chelate is greater than for Cu(salen), the former possessing an extra π system in the bridging portion of the ligand; (iii) the distance between the copper(II) ions is insensitive to the change from phenolic oxygen to imine nitrogen.

EXPERIMENTAL

The e.s.r. spectra of the compounds investigated were recorded at room temperature and at 77 K with a Varian 100 kHz multipurpose cavity in conjunction with a 3 cm spectrometer of conventional design. Magnetic susceptibility measurements were made at various temperatures by the Gouy method.[7] All solvents used were freshly distilled and dried over Linde 4 Å molecular sieves.

Analysed samples of bis(*N*-methylsalicylaldiminato)-copper(II), *NN'*-ethylenebis(salicylindeneiminato)copper(II), *NN'*-phenylenebis(salicylideneiminato)copper(II), *NN'*-ethylenebis(*o*-aminobenzylideneiminato)copper(II), and *NN'*-phenylenebis(*o*-aminobenzylideneiminato)copper(II) were prepared by methods described in the literature.

[2/099 *Received, 17th January*, 1972]

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[9] E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc.* (*A*), 1970, 406.

[10] E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc.* (*A*), 1970, 450.