An Electron Spin Resonance Study of Some Copper(II) Complexes of Unsaturated Carboxylic Acids

By **William J. Newton** and **Brian J. Tabner**,* Chemistry Department, University of Lancaster, Lancaster LA1 4YA

The electron spin resonance spectra of copper(II) complexes with acrylic, allylacetic, and vinylacetic acids are reported together with some of their adducts of the type $Cu(O_2CR)_2L$. The e.s.r. spectra can be interpreted in terms of a dimeric species in which the two copper atoms are exchange-coupled. Computer simulations of the e.s.r. spectra have been used to interpret the experimental spectra and to establish values of $g_{\parallel}$, $g_{\perp}$, and D.

MANY copper(II) complexes are known to exist as dimers in which there exists a magnetic exchange interaction between the two paramagnetic copper ions.[1-6] These interactions arise from coupling of the spins of the two ions, and lead to magnetic properties different to those observed for monomeric copper(II) complexes.[1,2] The magnetic susceptibility of these dimeric complexes shows a characteristic deviation from the Curie–Weiss law resulting in a subnormal magnetic moment. Perhaps the best known example of this behaviour is copper(II) acetate monohydrate[7] which is typical of a large range of copper(II)–carboxylic acid derivatives.

Over ten years ago Edmondson and Lever[8] reported the magnetic properties of a group of copper(II) complexes of unsaturated aliphatic (*i.e.* acrylic, allylacetic, and vinylacetic) acids, together with some of their adducts with nitrogen and phosphorus donor ligands. They were able to obtain evidence to support the view that these complexes were dimeric, which suggested that it would be of interest to examine the e.s.r. spectra of these compounds.

Exchange coupling of two copper(II) ions leads to a singlet state and a paramagnetic triplet state. Triplet state e.s.r. spectra are, of course, commonly found in organic radicals but in the case of copper(II) complexes the singlet–triplet separation is often substantially greater and the zero-field splitting within the triplet can often be similar to $h\nu$. At the usual X-band e.s.r. frequency of *ca.* 9 GHz the absorptions are therefore spread over many hundreds of mT. In such a complex the polycrystalline or frozen solution spectrum is a sum over all possible orientations. Discrete absorptions will occur at those magnetic fields where the external field lies along one of the principal magnetic axes of the triplet. E.s.r. spectra of copper(II) dimers have been successfully interpreted using the positions of these absorptions and following the same approach as used for organic triplets.[9] However, a complication in copper(II) complexes arises not only from the large zero-field splitting but also from the anisotropic nature of g and of the hyperfine interaction. In view of these differences between organic triplets and copper(II) dimers, Smith and Pilbrow[6] have attempted to produce computer simulations of the experimental spectra of the latter. This approach, based on the successful computer simulation of the experimental e.s.r. spectra, has been used for the copper(II) complexes of the unsaturated carboxylic acids reported here.

RESULTS AND DISCUSSION

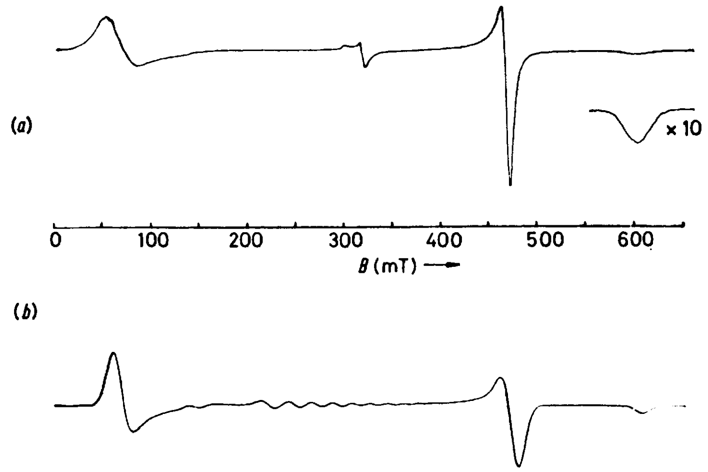
General Observations.—The spin Hamiltonian for triplets may be written[9] as in equation (1), where D

$$\hat{\mathscr{H}} = \mu_B\mathbf{B}.\mathbf{g}.\hat{S} + D\hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2) - \frac{2D}{3} \quad (1)$$

and E are the zero-field splitting parameters. The computational procedures involved in the solution of the spin Hamiltonian for polycrystalline and frozen solution samples are given in the review by Smith and Pilbrow.[6] However, a few points are worth noting. The computer program does not allow for hyperfine structure from interaction with the copper nuclei. This characteristic seven-line pattern is sometimes observed, particularly on the $\Delta M_S = \pm 2$ absorption. However, of the various spectra reported here only two, those of the polycrystalline and frozen solution spectra of tetrakis(allylacetato)bis(pyridine)dicopper(II), showed evidence for this hyperfine structure (and then only on the high- and low-field absorptions).

In understanding the computer simulations, it is helpful to consider the angular dependence of the position of the absorption and the probability for each transition. This information can be obtained directly from the computer program and reveals an added complication in that $\delta H/\delta\theta$ is not always zero at the axes. However, the field position corresponding to $\delta H/\delta\theta = 0$ does not differ greatly from that when $\theta = 0°$ (or $90°$), and with the linewidths used in these simulations it results only in a broadening of the appropriate absorption. However this problem, which depends on the value of D, does not appear to arise with the values of D required in the present simulations.

Interpretation of the E.S.R. Spectra.—The e.s.r. spectra of eight copper(II) unsaturated carboxylic acid complexes were recorded as polycrystalline samples and in frozen solution. The spectra all reveal the same general features, consisting of a moderately strong absorption at *ca.* 40—70 mT, an absorption of varying intensity at g *ca.* 2, a strong absorption at *ca.* 460 mT, and a weak absorption at 590—600 mT. The intensities of the three main absorptions decrease with a decrease in temperature, while the intensity of the absorption at g *ca.* 2



(*a*) Experimental polycrystalline e.s.r. spectrum obtained for tetrakis(vinylacetato)bis(pyridine)dicopper(II) at −120 °C; (*b*) computer-simulated spectrum using the parameters given in Table 1 (for ease of presentation the same linewidth parameter has been selected for each absorption)

remains virtually unchanged. The g *ca.* 2 absorption has therefore been assigned to a small percentage of monomeric impurity present to a different extent in each of the samples. It was noticeable that the linewidth of the three triplet absorptions differed. The linewidth of the high- and low-field absorptions was *ca.* three times that of the absorption at *ca.* 460 mT. This effect is clearly seen when the computer simulated spectra are compared with the experimental spectra. In addition there appears to be little evidence in most of the experimental spectra for a splitting of the absorption at *ca.* 460 mT, indicating that in most of the complexes studied E was very close to zero. [There was a possible indication of a small non-zero value of E in the polycrystalline spectra of three complexes of the type $Cu(O_2CR)_2$.]

A typical experimental spectrum together with its computer simulation is shown in the Figure. From the full range of computer simulations obtained in the present work it is possible to make a number of general observations. The position of the low-field absorption appears to be principally dependent upon the value of D selected for the simulation. Small variations in $g_{\parallel}$ and $g_{\perp}$ do not introduce a shift in the position of this absorption, whereas a change in 0.02 cm^{-1} in the value of D produces a shift of *ca.* 19 mT. The value of D has a similar influence on the position of the high-field absorption. Again the value of $g_{\perp}$ has little effect but the position of this absorption is influenced by $g_{\parallel}$. (A change in $g_{\parallel}$ from 2.36 to 2.44 shifts the position of this absorption to lower fields by *ca.* 21 mT.) The value of D has less influence on the position of the absorption at *ca.* 460 mT. An increase of 0.02 cm^{-1} in the value of D shifts this absorption to higher fields by *ca.* 6.5 mT. The value of $g_{\parallel}$ has little effect, but a change in $g_{\perp}$ from 2.06 to 2.09 produces a shift to lower fields of *ca.* 7 mT.

Hyperfine structure was only clearly observed in the experimental spectrum of polycrystalline tetrakis(allylacetato)bis(pyridine)dicopper(II). In this spectrum the expected 1 : 2 : 3 : 4 : 3 : 2 : 1 septet for two equivalent copper(II) nuclei was observed with a splitting constant of 6.1 mT. This value is just slightly lower than the 6.7 mT splitting observed by Wasson *et al.*[10] in the polycrystalline spectrum of copper(II) cyanoacetate but agrees closely with the value observed in some other dimeric copper(II) carboxylates.[11-13] It was also possible to observe very

TABLE 1

Data obtained from computer simulations of e.s.r. spectra of copper(II)–unsaturated carboxylic acid complexes at −120 °C

Complex		$g_{\parallel}$	$g_{\perp}$	D (cm^{-1})	$\sigma_{\parallel}$(mT) [a]	$\sigma_{\perp}$(mT) [a]
Vinylacetate	Powder	2.44	2.09	0.36	12	7
	Frozen $CHCl_3$	2.41	2.06	0.35	12	5
Vinylacetate–pyridine	Powder	2.44	2.09	0.38	12	4
	Frozen $CHCl_3$	2.44	2.08	0.37	13	4
Vinylacetate–pyrazine	Powder	2.40	2.08	0.36	13	7
	Frozen $CHCl_3$ [b]					
Vinylacetate–triphenylphosphine	Powder	2.44	2.08	0.36	12	4
	Frozen $CHCl_3$	2.42	2.06	0.35	14	4
Acrylate	Powder	2.40	2.06	0.35	10	7
	Frozen $CHCl_3$	2.38	2.06	0.35	15	4
Acrylate–pyridine	Powder	2.44	2.09	0.38	13	5
	Frozen $CHCl_3$	2.38	2.06	0.36	14	4
Allylacetate	Powder	2.40	2.12	0.35	10	10
	Frozen $CHCl_3$	2.40	2.06	0.35	12	4
Allylacetate–pyridine	Powder	2.46	2.09	0.38	11	4
	Frozen $CHCl_3$	2.44	2.07	0.36	12	4

[a] Linewidth parameter. [b] Solubility too low.

poorly resolved splitting in the frozen-solution spectrum of the same complex. In this case the hyperfine splitting on the low-field absorption was *ca.* 8.0 mT. The failure to observe hyperfine splitting on the absorption at *ca.* 460 mT in any of the samples is presumably a consequence of a much smaller value of $A_{\perp}$, in accord with values found in similar complexes.[5,11,13]

Computer simulations were obtained for each of the copper(II) complexes studied and the parameters used to produce these simulations are summarised in Table 1. The accuracy to which it has been possible to obtain the values of $g_{\|}$, $g_{\perp}$, and D varies from one spectrum to another but the main problem here arises from the characteristically broad low- and high-field absorptions in the experimental spectra, and in particular from the low intensity of the high-field absorption. The position of the much sharper absorption at *ca.* 460 mT was more accurately determined but unfortunately its position in the computer-simulated spectra is a function of the value of D selected to fit the positions of the high- and low-field absorptions. The g values required in the computer simulations of the experimental spectra are fairly typical of those usually observed in copper carboxylate complexes.[5,7,10–15]

The values of D obtained for the copper(II) complexes in this study lie in the typical range of values found for several other copper(II) carboxylates (see Tables 1 and 2). It is noticeable that the value of D is higher for the three complexes of the type $Cu(O_2CR)_2L$, where L is pyridine, than it is for the corresponding $Cu(O_2CR)_2$ complex. This is true for both the polycrystalline and the frozen-solution measurements. It is interesting to note that the same trend can be observed in the values of D obtained for a series of benzoic acid derivatives[15] (see Table 2). Typically the values of D in the pyridine adduct appear to be 0.02—0.03 cm^{-1} greater than in the corresponding $Cu(O_2CR)_2$ complex. There is often a significant difference in magnetic properties between a $Cu(O_2CR)_2$ complex and the corresponding $Cu(O_2CR)_2L$ complex. For example, the value of the exchange integral, J, is often greater in complexes of the latter type.[10,15,16] This increase in J has been interpreted in terms of a decrease in the positive charge on the copper ions.[1] Differences in structure between the two types of complex are also sometimes observed.[1] Clearly an increase in D cannot be interpreted as being due to an increase in J alone. In this respect the determination of the value of J for the above complexes would be of interest.

TABLE 2

A comparison of the values of D for complexes of the types $Cu(O_2CR)_2$ and $Cu(O_2CR)_2L$ (L = pyridine) obtained from the polycrystalline e.s.r. spectra

Carboxylate ligand	D for $Cu(O_2CR)_2$ complex	D for $Cu(O_2CR)_2L$ complex
Vinylacetate	0.36	0.38
Allylacetate	0.35	0.38
Acrylate	0.35	0.38
α-Naphthoate [a]	0.34	0.37
Benzoate [b]	0.33	0.36
o-Methylbenzoate [b]	0.34	0.37
m-Methylbenzoate [b]	0.33	0.36

[a] Taken from ref. 11. [b] Taken from ref. 15.

EXPERIMENTAL

Preparations.—The copper complexes reported in this study were all prepared as previously described.[8] The C, H, and N analyses of the complexes were performed by the Microanalytical Laboratory, Manchester. These agreed well with those calculated for the appropriate complex.

E.S.R. Measurements.—E.s.r. spectra were recorded at −120 °C on a Varian E3 spectrometer employing a Varian E4557 variable temperature unit.

Calculations.—All computer simulations of e.s.r. spectra were performed using a ICL 1905F computer in conjunction with a Calcomp 925/1039 Graph Plotter. The program used in the calculations was a slightly modified version of the program EXCHANGE described in detail by Smith and Pilbrow[6] and kindly made available to the authors.

[8/2124 *Received, 11th December*, 1978]

REFERENCES

[1] M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, 1964, **64**, 99.

[2] P. W. Ball, *Co-ordination Chem. Rev.*, 1969, **4**, 361.

[3] G. F. Kokoszka and R. W. Duerst, *Co-ordination Chem. Rev.*, 1970, **5**, 209.

[4] G. F. Kokoszka and G. Gordon, *Transition Metal Chem.*, 1969, **5**, 181.

[5] J. H. Price, J. R. Pilbrow, K. S. Murray, and T. D. Smith, *J. Chem. Soc.* (*A*), 1970, 968.

[6] T. D. Smith and J. R. Pilbrow, *Co-ordination Chem. Rev.*, 1974, **13**, 173.

[7] B. Bleaney and K. D. Bowers, *Proc. Roy. Soc.*, 1952, **A214**, 451.

[8] B. J. Edmondson and A. B. P. Lever, *Inorg. Chem.*, 1965, **4**, 1608.

[9] E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, 1964, **41**, 1763.

[10] J. R. Wasson, C. Shyr, and C. Trapp, *Inorg. Chem.*, 1968, **7**, 469.

[11] J. Lewis, F. E. Mabbs, L. K. Royston, and W. R. Smail, *J. Chem. Soc.* (*A*), 1969, 291.

[12] Y. V. Yablokov, V. V. Gavrilov, A. V. Ablov, and L. N. Milkova, *Doklady Akad. Nauk S.S.S.R.*, 1970, **191**, 1102.

[13] S. J. Baum and G. F. Kokoszka, *Nature*, 1969, **222**, 665.

[14] L. N. Romanenko, Y. V. Yablokov, V. V. Gavrilov, L. N. Milkova, and A. V. Ablov, *Doklady Akad. Nauk S.S.S.R.*, 1969, **188**, 1332.

[15] F. G. Herring, B. Landa, R. C. Thompson, and C. F. Schwerdtfeger, *J. Chem. Soc.* (*A*), 1971, 528.

[16] R. W. Jotham, S. F. A. Kettle, and J. A. Marks, *J.C.S. Dalton*, 1972, 428.