Structure and Stability of Carboxylate Complexes. Part XI.[1] The Molecular *g*-Values of Some Monomeric Copper Carboxylate Complexes

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The e.p.r. spectra of single crystals of copper(II) glycollate, lactate, hydrogen maleate, methoxyacetate, phenoxyacetate, and ethoxyacetate have been measured. A general method for obtaining molecular *g*-tensors from single-crystal measurements on pure compounds is described. Each complex has a distorted octahedral structure and the metal part of its ground-state wave-function (spin–orbit coupling being neglected) is composed of the linear combination $\psi = a|\mathbf{x}^2 - \mathbf{y}^2\rangle - b|3\mathbf{z}^2 - \mathbf{r}^2\rangle$ producing a wave-function $\psi \approx c\mathbf{x}^2 + e\mathbf{y}^2 + f\mathbf{z}^2$. The *g*-values of each complex have been used to estimate its wave-function parameters and the magnitudes of *c*, *e*, and *f* were apparently related to the ligand perturbation along *x*, *y*, and *z*, the greater the perturbation the larger the magnitude of the wave-function parameter. For donor atoms at comparable distances the wave-function parameters suggest a probable order of σ-perturbing power O(carboxylate) > O(water) > O(hydroxy). Although the methoxyacetate complex has a nearly regular compressed tetragonal structure, its ground-state wave-function lies approximately midway between what are usually called $|\mathbf{x}^2 - \mathbf{y}^2\rangle$ and $|3\mathbf{z}^2 - \mathbf{r}^2\rangle$. The axial symmetry of the bond lengths is not reflected in the ligand field and O(H_2O) produces a much stronger σ-perturbation than O(methoxy). An analysis of the energies of the electronic transitions $\psi' \longrightarrow \psi$ (where $\psi' = a|3\mathbf{z}^2 - \mathbf{r}^2\rangle + b|\mathbf{x}^2 - \mathbf{y}^2\rangle$) of the complexes with an angular overlap model suggests an order of σ-perturbing power O(carboxylate) > O(water) > O(hydroxyl) $\gg$ O(ether) in good agreement with the *g*-value interpretation, and values of *b* calculated from the electronic spectra are reasonably consistent with those estimated from the e.p.r. data.

THE fundamental equations relating the *g*-factors and hyperfine splitting constants of copper complexes to their ground-state wave-functions have long been established.[2] However, the vast majority of e.p.r. studies[3] have been concerned either with a detailed

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[1] Part X, M. Harrison, B. E. Moulds, and F. J. C. Rossotti, *Trans. Roy. Inst. of Technology*, in the press.

[2] B. Bleaney and K. W. H. Stevens, *Reports Progr. Phys.*, 1953, **16**, 108; B. Bleaney, K. D. Bowers, and M. H. L. Pryce, *Proc. Roy. Soc.*, 1955, *A*, **228**, and references therein.

[3] E. Konig, Magnetic Properties of Co-ordination and Organometallic Transition-metal Compounds,' vol. II/2 of Landolt–Bornstein, New Series, eds. K. H. Hellwege and A. M. Hellwege, Springer, Berlin, 1966.

analysis of the spectra of copper(II) ions present as slight impurities in diamagnetic host lattices, or with the rather limited data available from solution or powder measurements on pure copper compounds. An investigation of the former kind provides the maximum possible information on the unpaired electron density in a copper complex, particularly that between metal and ligand orbitals, as it allows the resolution of hyperfine interaction. However, it has the limitations that a suitable diamagnetic host must be available and that the precise molecular structure of the copper complex in the host lattice is unknown. Studies of the e.p.r. spectra of single crystals of pure copper complexes normally only give information on the molecular *g*-tensors, as hyperfine structure is obscured by the interactions between the paramagnetic ions. As the *g*-tensor is directly related to the distribution of the unpaired electron among the *d*-orbitals, however, much useful information can be gained from this quantity alone when it is combined with a knowledge of the molecular geometry and the crystal structure of the complex. Despite this, it is only recently that, largely through the work of Hathaway and his co-workers,[4] any systematic attempt has been made to measure the molecular *g*-tensors of copper complexes of various stereochemistries by this means.

It was recently suggested by Hitchman [5] that the interpretation of the rhombic *g*-tensors of copper complexes in terms of a ground-state wave-function of the form $\psi \approx |c\mathbf{x}^2 + e\mathbf{y}^2 + f\mathbf{z}^2\rangle$ should provide a particularly useful way of relating the electron density distribution of a copper ion to its ligand environment. As crystal structures had been determined by us for a number of closely related copper carboxylate complexes containing water, carboxylate, hydroxyl, and ether groups bonded to the copper ions at varying distances and in different combinations, it was felt that a study of their single-crystal e.p.r. spectra would provide a useful test of the feasibility of interpreting molecular *g*-values in this fashion. The compounds selected for this purpose were copper(II) glycollate, (±)-lactate, methoxyacetate, ethoxyacetate, phenoxyacetate, and hydrogen maleate.* The preparation of the crystals and the determination of their structures have been discussed.[6-8]

EXPERIMENTAL

The e.p.r. spectra were measured with a J.E.O.L. JES 3BX spectrometer operating at 9·4 GHz. A speck of powdered diphenylpicrylhydrazyl placed close to the crystal was used as an overall field calibrant, the *g*-value of the radical being taken as 2·0036. The microwave frequency was measured with a standard reference cavity and the linearity of the field sweep was calibrated from the distance (86·7 G) between the third and fourth lines of a sample of Mn^{2+} diluted into MgO. The crystals were mounted upon well-developed faces on the bottom or side of a quartz rod by use of a stereoscopic microscope and a drop of silicone grease. This rod was fixed into an ordinary quartz e.p.r. tube which was itself placed in a rotatable jacket having a calibrated scale attached to it. By this means, the orientation of the crystal relative to the waveguide could be measured with a vernier to ±1°. The *g*-values were measured for different orientations of the crystal relative to the magnetic field by rotating the crystal through 180° in 15° intervals. Alignment errors were checked by remounting the crystal.

RESULTS

Several methods of deriving molecular *g*-tensors from single-crystal e.p.r. studies have been described.[9] In effect, all of these use measured values of g^2 to calculate the *g*-tensor in terms of the crystal co-ordinate system, and then diagonalize this to obtain the principal molecular *g*-values g_1, g_2, and g_3. The orientation of the molecular *g*-axes with respect to the molecule is then estimated by comparing the eigenvectors of the crystal *g*-tensor with the direction cosines made by a chosen molecular co-ordinate system with the crystal axes. In the present study the *g*-ellipsoid was calculated directly in terms of the molecular co-ordinate system. This has the advantage that the position of the magnetic field in the molecule is known for every measurement. Moreover, diagonalization of the initial *g*-tensor gives the Euler angles relating the principal *g*-axes to the chosen molecular axes directly.[10]

Determination of the Molecular g-*Tensors*.—The projections made by the magnetic field vector H on the crystal axes of a monoclinic system having unit-cell dimensions a, b, c, $\alpha = \gamma = 90°$, $\beta \neq 90°$ ($\beta^* = 180° - \beta$) are determined in terms of three angles η, θ, and ϕ defined as in Figure 1. Here θ and ϕ define a crystal plane and η measures the position of H in this plane, relative to the *ac* crystal plane and the *a* axis. This is convenient because, for e.p.r. purposes, monoclinic space-groups exhibit mirror symmetry across the *ac* plane and this can be utilized to determine the precise position of H in the crystal co-ordinate system. The expressions giving H in crystal co-ordinates are (1a—c) [where the sign is decided by which quadrant of the *ac* plane (defined by the *ab* and *bc** planes) contains the projection of H], (1b), and (1c). These

$$H_a = H_c \cos\beta^* \pm (1 - H^2_c \sin^2\beta^* - \sin^2\eta \sin^2\theta)^{\frac{1}{2}} \quad (1a)$$

$$H_b = \sin\eta \sin\theta \quad (1b)$$

$$H_c = \cos\phi\,(\sin\eta\cos\theta - \cos\eta\tan\phi)/\sin\beta^* \quad (1c)$$

projections are converted into an orthogonal crystal co-ordinate system by use of the relationships (2). A

$$a' = a\sin\beta^*,\ b' = b,\ c' = c - a\cos\beta^* \quad (2)$$

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* Compounds are discussed by reference to the anion only.

[4] B. J. Hathaway, I. M. Procter, R. C. Slade, and A. A. G. Tomlinson, *J. Chem. Soc.* (*A*), 1969, 2219; B. J. Hathaway and D. E. Billing, *Co-ordination Chem. Rev.*, 1970, **5**, 143.

[5] M. A. Hitchman, *J. Chem. Soc.* (*A*), 1970, 4.

[6] C. K. Prout, R. A. Armstrong, J. R. Carruthers, J. G. Forrest, P. Murray-Rust, and F. J. C. Rossotti, *J. Chem. Soc.* (*A*), 1968, 2791.

[7] C. K. Prout, J. R. Carruthers, and F. J. C. Rossotti, *J. Chem. Soc.* (*A*), 1971, 554.

[8] C. K. Prout, J. R. Carruthers, and F. J. C. Rossotti, *J. Chem. Soc.* (*A*), 1971, 3342.

[9] D. S. Schonland, *Proc. Phys. Soc.*, 1959, **73**, 788; D. E. Billing and B. J. Hathaway, *J. Chem. Phys.*, 1969, **50**, 1476.

[10] M. A. Hitchman and R. Linn Belford, 'Electron Spin Resonance of Metal Chelates,' ed. T. F. Yen, Plenum Press, Inc., New York, 1969, ch. 7.

molecular co-ordinate system is chosen from the symmetry of the molecule in question and defined in the orthogonal crystal co-ordinates as an orthonormal set of vectors $x = a'_1b'_1c'_1$, $y = a'_2b'_2c'_2$, and $z = a'_3b'_3c'_3$. The magnetic vector H is converted into molecular co-ordinates by the matrix multiplication (3).

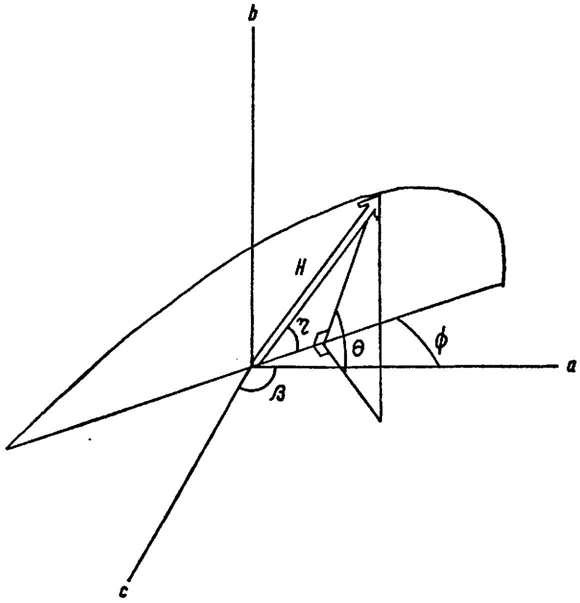

FIGURE 1 Diagram illustrating the angles used to specify the position of the magnetic field vector H in the crystal co-ordinates

$$\begin{bmatrix} H_x \\ H_y \\ H_z \end{bmatrix} = \begin{bmatrix} a'_1b'_1c'_1 \\ a'_2b'_2c'_2 \\ a'_3b'_3c'_3 \end{bmatrix} \begin{bmatrix} H_{a'} \\ H_{b'} \\ H_{c'} \end{bmatrix} \quad (3)$$

Pure copper complexes having one molecule in the asymmetric unit can be classified into three basic categories for the purposes of interpreting their e.p.r. data.

Category 1.—*Identical orientation of all the molecules in the unit cell.* The general expression for the measured g value of a molecule is (4). In order to solve this equation

$$g^2 = H^2_xg^2_{xx} + H^2_yg^2_{yy} + H^2_zg^2_{zz} + 2H_xHg^2_{xy} + 2H_xH_zg^2_{xz} + 2H_yH_zg^2_{yz} \quad (4)$$

for the g-tensor elements at least six linearly independent sets of data are required and these can be obtained by making measurements with rotations of H in at least three crystal planes.

Category 2.—*Different molecular orientations and slow electron exchange.* If the exchange of the unpaired electron between molecules is slow compared with the time-scale of the e.p.r. experiment (*i.e.*, compared with the inverse of the frequency of the microwave radiation used) then individual signals will be observed for molecules having different orientations in the unit cell. As far as e.p.r. is concerned, only two ' different ' molecules occur in a monoclinic system, the second being related to the first by reflection in the *ac* plane. If equation (3) gives the projections of H on one molecule, the projections on the second molecule are given by (5). Two e.p.r. signals are thus to be expected

$$\begin{bmatrix} H_x \\ H_y \\ H_z \end{bmatrix} = \begin{bmatrix} a'_1 & -b'_1 & c'_1 \\ a'_2 & -b'_2 & c'_2 \\ a'_3 & -b'_3 & c'_3 \end{bmatrix} \begin{bmatrix} H_{a'} \\ H_{b'} \\ H_{c'} \end{bmatrix} \quad (5)$$

from such a system except when H lies along b or is in the *ac* plane, whereupon the two molecules become equivalent. This coalescing of the e.p.r. signals provides a useful method of phasing plots of g^2 against angle, and so determining the position of H in the crystal very precisely for each measurement. Similar considerations apply to orthorhombic systems, though the symmetry operations (and corresponding matrix equations) will in general be different. The evaluation of the molecular g-tensor for a monoclinic crystal of this type is identical to that described for category 1 except that two values of g are usually obtained for each position of H.

Category 3.—*Different molecular orientations and rapid electron exchange.* (a) *Monoclinic systems.* If, as is usual for pure complexes, electron exchange occurs more rapidly than the time-scale of the e.p.r. experiment, then the unpaired electron ' sees ' an average of the environments of all the molecules in the unit cell, and only one e.p.r. signal is observed for all orientations of H. For a monoclinic crystal, if the different molecules are labelled **a** and **b**, the measured g-value is given by equation (6) where $g_{\mathbf{a}}$ and $g_{\mathbf{b}}$

$$g^2 = (g^2_{\mathbf{a}} + g^2_{\mathbf{b}})/2 \quad (6)$$

are obtained by using values of H_x, H_y, and H_z derived from equations (3) and (5), respectively, in equation (4). It is apparent that a plot of g^2 against angle will have a maximum or minimum along b for the rotation of H in any crystal plane containing the b axis *i.e.*, one principal direction of the crystal g-ellipsoid is restricted by symmetry to lie along b. This is again a useful means of determining accurately the position of H in the crystal for each measurement. However, because of the symmetry relationship between the two differently oriented molecules in the unit cell it is now impossible to obtain six linearly independent sets of values H^2_x *etc.* to solve equation (4). In essence, this is because the information which can be obtained about the crystal g-ellipsoid is restricted by symmetry to four quantities, the three crystal g-values and one direction, specifying the orientation of the two principal crystal g-directions lying in the *ac*-plane. Therefore only four of the elements of the molecular g-tensor can be determined, and one of the molecular g-directions must be specified by setting $g_{zz} = g_3$ and $g_{xz} = g_{yz} = 0$ in the expressions for $g_{\mathbf{a}}$ and $g_{\mathbf{b}}$ in equation (6). To solve the resulting equation rotations of H must be made in at least two crystal planes (or at least three, if each of these contains b).

(b) *Orthorhombic systems.* In this case, the crystal g-ellipsoid contains only three variables, three g-values, as symmetry restricts the principal crystal g-directions to lie along the crystal axes. All of the principal directions of the molecular g-tensor must therefore be specified, so that in equation (4) g_{xx}, g_{yy}, and g_{zz} become the principal molecular g values g_1, g_2, and g_3, with the off-diagonal elements g_{xz}, g_{yz}, and g_{xy} all being set equal to zero. The resulting equation (6) can be solved by rotations of H being made in at least two crystal planes.

Computation of the Molecular g-*Tensors*.—The first step in the determination of a molecular g-tensor is the choice of a molecular co-ordinate system. The molecular structures of the six complexes studied are illustrated in Figure 2. In the case of the phenoxyacetate there are two molecules in the asymmetric unit; however, their geometry is very similar [6] and only one of them is shown in the Figure. The symmetry of every complex approximates closely to C_{2h}

except for that of the lactate, which is C_2. In these point-groups the z-axis is defined, while x and y are not. The following general co-ordinate system was therefore used for the complexes containing chelate ligands: the z-axis is along the Cu–O bond perpendicular to the chelate rings, the x-axis is in the plane containing z, and the Cu–O (carboxylate) bond and is orthogonal to z [*i.e.*, almost exactly along the Cu–O(carboxylate) bond], and y is orthogonal to x and z [*i.e.*, approximately along the Cu–O (hydroxyl or ether) bond]. For the hydrogen maleate complex, z is along the shortest Cu–O(water) bond direction, x is almost exactly along the intermediate bond direction and is orthogonal to z, and y is orthogonal to these. The Cu–O(ether and hydroxyl) bonds and, in the case of the hydrogen maleate, the longest Cu–O(water) bonds were always in the (+ +) and (— —) quadrants of the xy-plane. The matrix which transforms a unit vector expressed in orthogonal crystal co-ordinates into molecular co-ordinates for each complex is given in Table 1.

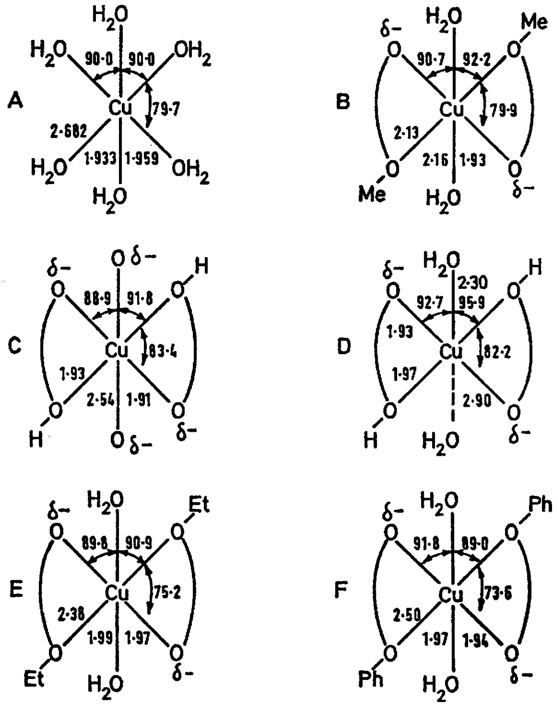

FIGURE 2 Molecular structures of the complexes

For every compound, measurements of g^2 were made for *ca.* 20 positions of H in each of two or more crystal planes. The angles θ and ϕ used to define each crystal plane were obtained from the crystal morphology (as deduced from X-ray diffraction or optical goniometry). The angle η was usually obtained from plots of g^2 against angle, phased, as described previously, by use of the symmetry properties of the space-group. Where this could not be done in a straightforward manner the method used is described below with the individual results of each complex. For every measurement, H was transformed into molecular co-ordinates by use of equations (1), (2), and (3) or (5). The resulting set of molecular projections and the measured g-value were fitted to the form of equation (4) appropriate to the category of the complex (averaged, where necessary, over the different molecules in the unit cell) and solved for the molecular g-tensor elements by a least-squares method. Where the complete form of equation (4) could be used the g-tensor was diagonalized to give the principal g values g_1, g_2, and g_3 and the three Euler angles A, B, and C by which the molecular axes must be rotated to convert them into the principal g-axes. These angles are defined according to Goldstein:[11] first rotate by A about z to give $x'y'z$, then by B about x' to give x', y'', z', then by C about z' to give x'', y''', z', with each rotation being anticlockwise. When the direction of g_3 had to be specified (Category 3a) B and C were necessarily zero, but when all of the directions of the molecular g-axes were specified each of the Euler angles was zero. For each compound the molecular projections of H and the residual error [g^2(measured) — g^2(calculated)] were calculated for every measurement, as well as a total root-mean-square error. The whole procedure was carried out with a FORTRAN (IV) computer programme. The final precision of the results was estimated not from the r.m.s. error (which can be misleading if the equations are ill-defined) but by calculating each g-tensor by use of different combinations of the sets of data obtained from different mountings of the crystal. For the lactate and hydrogen maleate complexes data from rotations in different crystal planes could be used in various combinations to estimate the precision of the g-tensors. Individual details of the measurements made on each complex are given below, together with the category of the compound. The measured values of g^2, with the angles η, θ, and ϕ defining the direction of H in the crystal, are given in Table 2 and the calculated parameters defining each molecular g-tensor are listed in Table 3.

TABLE 1

Transformation matrices of the complexes

Complex	Transformation matrix [a]			Ref.
Glycollate	0·6096	0·7283	0·3130	6
	−0·3070	0·5809	−0·7538	
	0·7309	−0·3634	−0·5777	
Lactate	0·5106	−0·8597	0·0141	6
	−0·8528	−0·5084	−0·1192	
	0·1096	0·0488	−0·9928	
Hydrogen maleate	0·6361	0·0000	−0·7716	8
	−0·7716	0·0000	−0·6361	
	0·0000	1·0000	0·0000	
Phenoxyacetate	−0·5072	0·0475	0·8605	6
	0·4251	0·8824	0·2018	
	−0·7497	0·4681	0·4678	
Ethoxyacetate	0·5418	0·1299	−0·8304	7
	0·2818	0·9027	0·3251	
	0·7919	−0·4102	0·4525	
Methoxyacetate	−0·6651	−0·5385	0·5173	6
	−0·5927	−0·0407	−0·8044	
	0·4543	−0·8416	−0·2921	

[a] See text for method of calculation.

Ethoxyacetate (Triclinic, Category 1).—The complex formed as large plates with the *ac*-face well developed. As two of the triclinic angles are very close to 90° ($\alpha = \gamma = 91{\cdot}6°$)[7] the equations (1a)—(c) and (2) relating H to the crystal co-ordinates were used without modification. Measurements were made with rotations of H in the *ab*, *bc*, and *ac* crystal planes. However, because of the triclinic crystal symmetry there was no direct relationship between the g-ellipsoid and the crystal axes. To estimate the

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[11] H. Goldstein, 'Classical Mechanics,' Addison-Wesley, Reading, Massachusetts, 1950, p. 107.

TABLE 2

Experimental results for the complexes

Ethoxyacetate

ab plane

$\theta = 90°$	$\phi = 0°$
g^2	η
4·369	−15·0
4·289	0·0
4·363	15·0
4·561	30·0
4·840	45·0
5·124	60·0
5·322	75·0
5·396	89·9
5·317	−75·0

bc plane

$\theta = 90°$	$\phi = 62°$
4·576	49·1
4·361	34·1
4·292	19·1
4·387	4·1
4·621	−10·9
4·936	−25·9
5·238	−40·9
5·449	−55·9
5·523	−70·9
5·428	−85·9
5·201	−73·1
4·441	40·25
4·298	25·25
4·326	10·25
4·512	−4·75
4·809	−19·75
5·134	−34·75
5·398	−49·75
5·531	−64·75
5·498	−79·75
5·324	85·25

ac plane

$\theta = 0°$	$\phi = 0°$
4·257	−14·2
4·284	−31·2
4·343	−47·2
4·421	−61·2
4·489	−76·2
4·529	88·8
4·535	74·8
4·519	58·8
4·449	43·8
4·380	28·8
4·311	13·8
4·268	−1·2
4·257	−14·2
4·283	−31·2
4·273	5·0
4·256	−10·0
4·267	−25·0
4·314	−40·0
4·374	−55·0
4·442	−70·0
4·492	−85·0
4·516	80·0
4·508	65·0

Phenoxyacetate

bc plane

$\theta = 90°$	$\phi = 69·6°$
g^2	η
4·300	1·5
4·283	1·5
4·788	−37·3
4·474	−37·3
4·544	−22·3
4·307	−22·3
4·342	−7·3
4·263	−7·3
4·354	7·7
4·266	7·7
4·564	22·7
4·319	22·7
4·822	37·7
4·498	37·7
5·059	52·7
4·753	52·7
5·266	−67·3
4·965	−67·3

ab plane

$\theta = 90,°$	$\phi = 0°$
4·297	−19·2
4·263	−19·2
4·503	−4·2
4·377	−4·2
4·601	10·8
4·315	10·8
4·889	25·8
4·267	25·8
5·171	40·8
4·376	40·8
5·361	55·8
4·616	55·8
5·369	−79·2
5·070	−79·2
4·861	−22·7
4·269	−22·7
4·869	−7·7
4·355	−7·7
5·443	−67·7
4·834	−67·7

ac plane

$\theta = 0°,$	$\phi = 0°$
4·403	−3·5
4·474	11·5
4·531	26·5
4·549	41·5
4·528	56·5
4·466	71·5
4·386	86·5
4·309	−78·5
4·264	−63·5
4·245	−48·5
4·285	−33·5
4·482	11·0
4·541	26·0
4·559	41·0
4·534	56·0
4·477	71·0
4·394	86·0
4·314	−79·0
4·258	−64·0
4·238	−49·0
4·264	−34·0

Lactate

ab plane

$\theta = 90°,$	$\phi = 0°$
g^2	η
4·356	72·0
4·297	87·0
4·325	−78·0
4·389	−63·0
4·515	−48·0
4·644	−33·0
4·741	−18·0
4·783	−3·0
4·761	12·0
4·676	27·0

*bc** plane

$\theta = 90°,$	$\phi = 90°$
4·328	73·2
4·275	88·2
4·318	−76·8
4·453	−61·8
4·636	−46·8
4·824	−31·8
4·992	−16·8
5·049	−1·8
5·012	13·2
4·545	55·0
4·383	70·0
4·295	85·0
4·317	−80·0
4·432	−65·0
4·607	−50·0
4·793	−35·0
4·943	−20·0
5·035	−5·0
5·017	10·0
4·907	25·0
4·734	40·0
4·531	55·0
4·406	70·0
4·309	85·0
4·309	−80·0

ac plane

$\theta = 0°$	$\phi = 0°$
4·499	55·0
4·391	40·0
4·429	25·0
4·582	10·0
4·816	−5·0
5·076	−20·0
5·311	−35·0
5·424	−65·0
5·238	−80·0
5·211	−84·5
4·952	80·5
4·689	65·5
4·485	50·5
4·403	35·5
4·463	20·5
4·654	5·5
4·911	−9·5
5·178	−24·5
5·380	−39·5
5·459	−54·5
5·392	−69·5
5·211	−84·5
4·955	80·5
4·689	65·5
4·488	50·5

Hydrogen maleate

*bc** plane

$\theta = 90°$	$\phi = 90°$
g^2	η
4·391	76·3
4·356	−88·7
4·403	−73·7
4·489	−58·7
4·614	−43·7
4·754	−28·7
4·880	1·3
4·334	−87·9
4·394	−72·9
4·501	−57·9
4·622	−42·9
4·773	−27·9
4·884	2·1
4·741	32·1
4·344	85·5
4·355	−79·5
4·426	−64·5
4·553	−49·5
4·683	−34·5
4·803	−19·5

ab plane

$\theta = 90°,$	$\phi = 0°$
5·026	−10·4
4·626	49·6
4·482	64·6
4·357	79·6
4·351	−85·4
4·462	−70·4
4·590	52·0
4·437	67·0
4·372	82·0
4·363	−83·0
4·445	−68·0
4·586	−53·0
5·007	−8·9
5·026	6·1
4·949	21·1
4·800	36·1
4·460	66·1
4·372	−83·9
4·453	−68·9

ac plane

$\theta = 0°,$	$\phi = 0°$
5·276	12·0
4·970	−3·0
4·689	−18·0
4·450	−33·0
4·380	−48·0
4·420	−63·0
4·645	−78·0
5·456	57·0
4·496	−69·5
4·760	−84·5
5·063	80·5
5·331	65·6
5·496	50·5
5·519	35·5
5·408	20·5
5·134	5·5
4·840	−9·5
4·554	−24·5
4·374	−39·5
4·377	−54·5
4·497	−69·5
5·490	31·0
5·341	16·0
5·038	1·0
4·769	−14·0
4·490	−29·0
4·360	−44·0
5·393	61·0
5·515	46·0
5·500	31·0
5·344	16·0

Glycollate

ab plane

$\theta = 90°,$	$\phi = 0°$
g^2	η
4·531	67·0
4·439	82·0
4·435	−83·0
4·519	−68·0
4·674	−53·0
4·850	−38·0
5·006	−23·0
5·104	−8·0
5·104	7·0
5·012	22·0

ac plane

$\theta = 0°,$	$\phi = 0°$
5·129	1·4
5·212	−13·6
5·182	−28·6
5·048	−43·6
4·833	−58·6
4·597	−73·6
4·427	−88·6
4·338	76·4
4·366	61·4
5·136	−2·0
5·226	−17·0
5·173	−32·0
5·012	−47·0
4·784	−62·0
4·565	−77·0
4·407	88·0
4·338	73·0
4·397	58·0

Methoxyacetate

*bc** plane

$\theta = 90°,$	$\phi = 90°$
4·995	41·6
4·897	51·6
4·743	71·6
4·715	−88·5
4·771	−68·5
4·951	−48·5
5·142	−28·5
5·277	−8·5
5·273	11·6
5·148	31·6
4·949	51·6
5·238	−17·6
5·300	−2·6
5·273	12·4
5·175	27·4
5·031	42·4
4·883	57·4
4·765	72·4
4·712	87·4
4·738	−77·6
4·842	−62·6
4·991	−47·6
5·140	−32·6

(011) plane

$\theta = 54·5°,$	$\phi = 0°$
4·768	9·0
4·597	−6·0
4·480	−21·0
4·440	−36·0
4·495	−51·0
4·632	−66·0
4·791	−81·0
4·967	−84·0
5·078	69·0
5·111	54·0
5·060	39·0
4·459	−36·5
4·507	−51·5
4·635	−66·5
4·808	−81·5
4·967	83·5
5·081	68·5
5·118	53·5
5·060	38·5
4·936	23·5
4·768	8·5

angles η used in equations (1a)—(c) the crystals were therefore mounted for each rotation with H as nearly as possible along one axis. The measured angles were then adjusted so that the plots of g^2 against angle for the rotations of H in different planes were consistent (the *ab* and *bc* rotations having to give the same value of g^2 along *b* and values of g^2 along *a* and *c* consistent with the *ac* rotation).

Phenoxyacetate * (Monoclinic, Category 2).—The crystals were large plates with the *ac*-face well developed. Two e.p.r. signals were usually obtained for each position of H, and in solving equation (4) it was assumed that the larger value of g^2 was always associated with the greater value of H_z. Rotations of H were made in the *ab*, *ac*, and *bc* crystal planes. Although there are two molecules in the asymmetric unit of this compound, their orientation is virtually identical.[6] The g-tensor was calculated by use of a molecular co-ordinate system defined for each of the molecules in turn, and the Euler angles were found to differ by less than 1° (Table 3).

TABLE 3

The principal molecular g-values and directions of the complexes

	Principal molecular g-values [a]			R.m.s. of	Euler angles in degrees [ab]		
Complex	g_1	g_2	g_3	g^2	A	B	C
Ethoxyacetate	2·061(3)	2·364(2)	2·087(6)	0·011	1·6(30·0) [c]	3·7(0·5)	1·6(27·0) [c]
Phenoxyacetate [d]	2·061(3)	2·353(1)	2·068(1)	0·010	80·8(2·5)	2·1(0·8)	−77·6(2·2)
Phenoxyacetate [e]	2·061(3)	2·353(1)	2·068(1)	0·010	80·8(2·5)	1·8(0·8)	−77·9(2·2)
Methoxyacetate	2·028(4)	2·368(1)	2·223(1)	0·013	−0·60(0·05)	—	—
Glycollate	2·064(6)	2·086(6)	2·313(1)	0·010	10·1(7·0)	—	—
Hydrogen maleate	2·089(0·5)	2·353(0·4)	2·085(0·3)	0·012	−1·8(0·1)	—	—
Lactate	2·057(6)	2·114(4)	2·330(6)	0·027	—	—	—

[a] The numbers in parentheses represent the possible errors (×10^3 for the g-values). [b] See text for a precise definition of these; in each case (A − C) is approximately equal to the angle through which the molecular x- and y-axes must be rotated to align them with the directions of g_1 and g_2. [c] Although these angles are subject to a large possible error (A − C) never exceeds ±3°. [d] Calculated by use of a co-ordinate system defined from the centrosymmetric molecule in the asymmetric unit. [e] Calculated by use of a co-ordinate system defined from the non-centrosymmetric molecule in the asymmetric unit.

Methoxyacetate (Monoclinic, Category 3a).—This complex crystallized as large rods with the (011) *etc.* faces well developed. Spectra were measured with rotations of H in the (011) and *bc** crystal planes. The molecular g-values of $g_1 = 2{\cdot}028$, $g_2 = 2{\cdot}368$, $g_3 = 2{\cdot}223$ agree fairly well with the values $g_1 = 2{\cdot}0266$, $g_2 = 2{\cdot}3447$, $g_3 = 2{\cdot}2241$ found for this complex by Bew *et al.*[12]

Glycollate (Monoclinic, Category 3a).—The small, diamond-shaped crystals of this compound had the *ab*-face well developed and rotations of H were made in the *ab* and *ac* crystal planes. Attempts were also made to obtain measurements in the *bc*-plane but it was not possible to mount the small crystal accurately enough to get consistent results so these were not used in the final estimation of the g-tensor.

Hydrogen Maleate (Monoclinic, Category 3a).—This compound formed as large rods with the *ab*, *ac*, and (011) *etc.* crystal faces well developed. Rotations of H were made in the *ab*, *ac*, and *bc** crystal planes.

Lactate (Monoclinic, Category 3b).—The large, plate-like crystals of this complex had the *ab*-face well developed, and rotations of H were made in the *ab*, *ac*, and *bc** planes. Unfortunately, the z-axis defined for this complex lies almost exactly in the *ac* crystal plane. This effectively removes one of the pieces of information which can be gained from the crystal g-ellipsoid (its orientation in the *ac*-plane), and means that this complex had to be considered under the above category of 3b in determining its molecular g-values.

DISCUSSION

Interpretation of the Molecular g-*Tensors*.—The ligand-field symmetry in each of the complexes can be considered as being derived from the octahedron. Two types of perturbation lower the symmetry from O_h; a perturbation along the axes due to the inequivalence of the ligand donor atoms and differences in the metal–ligand bond lengths, and a perturbation between the axes caused by the presence of the chelate rings and distortions of the bond angles from 90° (Figure 2). The rigorous interpretation of the g-tensors of complexes of such low symmetry would be very complicated. However, the behaviour of the in-plane g-ellipse of approximately square planar complexes of C_{2h} symmetry in which the four strong bonds lie in the xy-plane has been investigated[13] for various possible bonding situations. It was found that for complexes of this kind there should be a pronounced tendency for the perturbation along the axes to dominate the g-anisotropy producing principal g-axes lying close to the metal–ligand bond directions, and that the g-values could then be interpreted to a good approximation by use of the relatively simple expressions appropriate to complexes of D_{2h} or C_{2v} symmetry. These considerations apply directly to the lactate and glycollate complexes in which the angular distortion occurs between the metal–ligand bonds of comparable length, and also to a less extent to the methoxyacetate complex, though here the large difference between the Cu–O(carboxylate) and Cu–O(methoxy) bond lengths (1·93 and 2·13 Å, respectively) makes any significant rotation of the principal g-axes away from the bond directions unlikely. Unfortunately, as has been mentioned, the principal g-directions could not be determined for the lactate complex, and could not be found very accurately for the glycollate, though for the latter complex they were approximately 10 and 17° away from the Cu–O(carboxylate) and

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* Diaquobisphenoxyacetatocopper(II) described in ref. 6.

[12] M. J. Bew, D. E. Billing, R. J. Dudley, and B. J. Hathaway, personal communication.

[13] M. A. Hitchman, C. D. Olson, and R. L. Bedford, *J. Chem. Phys.*, 1969, **50**, 1195.

Cu–O(hydroxyl) bond directions, respectively. In copper methoxyacetate, g_1 was *ca.* 0·6° away from the Cu–O(carboxylate) bond direction, with g_2 being *ca.* 9·5° away from the Cu–O(methoxy) bond direction, in good agreement with the perturbation from the carboxylate oxygen atom being much stronger than that from the ether oxygen atom. For each of the other complexes the angular distortion to the ligand field occurred between bonds of very different lengths (Figure 2). Any significant rotation of g_1 away from the shorter bond direction would therefore be extremely unlikely and none was observed (Table 3).

Estimation of the Ground-state Wave-function Parameters.—The near-coincidence of the principal g-axes with the bond directions thus suggests that, to a good approximation, the g-values of the complexes can be interpreted by use of the expressions appropriate to the point-group D_{2h} (or, in the case of the lactate, C_{2v}). In these point groups $|\mathbf{x}^2 - \mathbf{y}^2\rangle$ and $|3\mathbf{z}^2 - \mathbf{r}^2\rangle$ belong to the same representation, and the metal part of the ground-state can therefore be written[14] as $\psi = a|\mathbf{x}^2 - \mathbf{y}^2\rangle - b|3\mathbf{z}^2 - \mathbf{r}^2\rangle$, with the normality condition $a^2 + b^2 = 1$. The expressions for the g-shifts are[5] (7),

$$\Delta g_{\mathbf{x}} = -2\lambda k_1^2(a - \sqrt{3}b)^2/E_{\mathbf{yz}} \qquad (7a)$$

$$\Delta g_{\mathbf{y}} = -2\lambda k_2^2(a + \sqrt{3}b)^2/E_{\mathbf{xz}} \qquad (7b)$$

$$\Delta g_{\mathbf{z}} = -8\lambda k_3^2 a^2/E_{\mathbf{xy}} \qquad (7c)$$

where $k^1 = k_{\mathbf{yz}}k_{\psi}$, $k_2 = k_{\mathbf{xz}}k_{\psi}$, and $k_3 = k_{\mathbf{xy}}k_{\psi}$, k being in each case the orbital reduction parameter[15] of the orbital denoted by the subscript; the other symbols have their usual significance. It has been suggested[5] that a useful way of representing the ground-state wave-functions of complexes of this kind is as in (8), where C

$$\psi = C|c\mathbf{x}^2 + e\mathbf{y}^2 + f\mathbf{z}^2\rangle \qquad (8)$$

is a constant. The relationships between the parameters in equations (7) and (8) are[5] $c = (b + \sqrt{3}a)$, $e = (b - \sqrt{3}a)$, and $f = -2b$, with the normality condition $c^2 + e^2 + f^2 = 6$.

In equations (7) and (8), $\mathbf{x}$, $\mathbf{y}$, and $\mathbf{z}$ represent the directions of the principal g-axes. In order to compare the wave-functions of the complexes most easily it is convenient to define a general co-ordinate system with $\mathbf{x}$, $\mathbf{y}$, and $\mathbf{z}$ along the directions of the lowest, middle, and largest molecular g-values (these axes generally differ from the axes x, y, and z of the C_{2h} point-group used in discussing the structures of the molecules). The nature of the bond along which each molecular g-value (now labelled $g_{\mathbf{x}}$, $g_{\mathbf{y}}$, and $g_{\mathbf{z}}$) is approximately directed is given in Table 4.

TABLE 4

The nature of the bonds along the molecular g-directions and the excited state energies of the complexes

	Molecular g-values			Nature of donor group and bond length[a] along direction of:			Excited-state energies kK[b]		
Complex	$g_{\mathbf{x}}$	$g_{\mathbf{y}}$	$g_{\mathbf{z}}$	$g_{\mathbf{x}}$	$g_{\mathbf{y}}$	$g_{\mathbf{z}}$	$E_{\mathbf{xz}}$	$E_{\mathbf{yz}}$	$E_{\mathbf{xy}}$
Hydrogen maleate	2·085	2·089	2·353	Water 1·933(0·2)	Water 1·959(0·2)	Water 2·682(0·2)	13·6	13·7	16·3
Phenoxyacetate	2·061	2·068	2·353	Carboxylate 1·94(1)[c] 1·94(1)[d]	Water 1·97(1)[c] 1·98(1), 1·99(1)[d]	Ether 2·50(1)[c] 2·44(1), 2·50(1)[d]	15·55	15·23	~14·8[e]
Ethoxyacetate	2·061	2·087	2·364	Carboxylate 1·97(1)	Water 1·99(1)	Ether 2·39(1)	14·5	13·6	11·6
Glycollate	2·064	2·086	2·313	Carboxylate 1·91(1)	Hydroxyl 1·93(1)	Carboxylate 2·54(1)	13·7[f]	13·7[f]	~12·5[e]
Lactate	2·057	2·114	2·330	Carboxylate 1·93(2)	Hydroxyl 1·97(2)	Water 2·30(2) 2·90(2)[g]	13·1[f]	13·1[f]	11·6
Methoxyacetate	2·028	2·223	2·368	Carboxylate 1·93(1)	Water 2·16(1)	Ether 2·13(1)	12·1	16·1	~12·1[e]

[a] Measured in Å; the estimated standard deviations are given in parentheses × 10^2. Unless shown otherwise the bond lengths along the positive and negative axis directions are equal. [b] Estimated from the single crystal polarized electronic spectra (refs. 16, 24). [c] Centrosymmetric molecule. [d] Non-centrosymmetric molecule. [e] The energy of this orbital could only be estimated approximately. [f] Since the electronic transitions to these levels are apparently polarized between, rather than along the bond directions (ref. 24), average values have been used (the observed transitions occur at 13·5 and 13·85 kK for the glycollate and 12·55 and 13·6 kK for the lactate). [g] Long contact to carboxylate.

The ground-state wave-function of each complex was calculated in terms of the parameters in equation (8) and the results are listed in Table 5 together with the orbital reduction parameters. The method of calculation assumed that $k_1 = k_2 = k_{\perp}$; in fact small differences between $k_{\perp}$ and k_2 would not alter the calculated wave-function parameters appreciably.[5] In these cases approximate values were used for this quantity and although this does not affect the wave-function parameters it means that k_3^2 could not be calculated accurately. The possible errors were estimated by calculating the wave-function parameters for each compound by use of the most extreme values of g commensurate with the experimental results. An iterative procedure was used in the calculations. The first approximation set $b^2 = 0$. Then equations (7a) + (7b) give $k_{\perp}^2$ which can be substituted into equations (7a)—(7b) to give b. The orthonormality condition then gives a, and equation (7c) k_3^2. The process was

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[14] B. R. McGarvey, 'Electron Spin Resonance of Transition Metal Complexes,' in 'Transition Metal Chemistry,' ed. R. L. Carlin, Marcel Dekker, Inc., New York, 1966, vol. 3, p. 160.

[15] M. Gerloch and J. R. Miller, *Progr. Inorg. Chem.*, 1968, **10**, 1.

repeated to the required accuracy. The value used for λ was -828 cm^{-1}.

*Assignment of the Electronic Spectra.**—The single-crystal polarized electronic spectra cannot be used in the interpretation of the g-values. The wave-function parameters were therefore calculated by setting E_{xz} and E_{yz} equal to the mean of the observed energies. They were also estimated by use of both possible assignments for each pair of bands, *i.e.*, $E_{xz} = 12{\cdot}55$, $E_{yz} = 13{\cdot}6$ and $E_{xz} = 13{\cdot}6$, $E_{yz} = 12{\cdot}55$ kK for the lactate. The spread of wave-function parameters found was considerably less than that expected from the uncertainty in the g-values. The hydrogen maleate, lactate, and ethoxyacetate also showed a weak band which was absent from z-polarization, and this was assigned as $|\mathbf{xy}\rangle \longrightarrow |\mathbf{x}^2 - \mathbf{y}^2\rangle$. In the phenoxyacetate and glycollate this transition was unresolved and E_{xy} was therefore arbitrarily assigned to about the midpoint of the spectrum. The uncertainty in E_{xy}, ± 2 kK, in these two complexes, and in the methoxyacetate, causes a large possible error in k^2 (Table 5) but does not significantly affect the estimation of the wave-function parameters as it only occurs in the expression for g_z.

TABLE 5

The wave-function parameters and orbital reduction coefficients of the complexes

	Wave-function parameters [a]			Orbital reduction parameters [a]	
Complex	c	e	f	$k_\perp^2$	k_3^2
Hydrogen maleate	1·738(1)	−1·726(1)	−0·012(2)	0·696(1)	0·864(1)
Phenoxyacetate	1·751(6)	−1·712(6)	−0·039(13)	0·578(5)	0·780(100)
Glycollate	1·774(20)	−1·686(25)	−0·088(40)	0·599(5)	0·590(100)
Ethoxyacetate	1·791(15)	−1·667(20)	−0·124(35)	0·604(10)	0·635(3)
Lactate	1·825(15)	−1·622(22)	−0·203(40)	0·645(30)	0·577(9)
Methoxyacetate	1·924(10)	−1·437(30)	−0·487(30)	0·833(27)	0·690(100)

[a] See text for a definition of these parameters; the possible errors are given in parentheses $\times 10^3$.

Correlation of the Wave-function Parameters with the Molecular Structures.—The dependence of the parameters in a ground-state wave-function of the form $\psi = C|c\mathbf{x}^2 + e\mathbf{y}^2 + f\mathbf{z}^2\rangle$ upon the ligand field perturbations along the $\mathbf{x}$, $\mathbf{y}$, and $\mathbf{z}$ axes has been discussed in detail.[5] In the limiting case of D_{4h} symmetry where the ligand perturbations along $\mathbf{x}$ and $\mathbf{y}$ are equal, and greater than that along $\mathbf{z}$, $\Delta g_x = \Delta g_y$ and the wave-function parameters are $c = \sqrt{3}$, $e = -\sqrt{3}$, $f = 0$, *i.e.*, the ground-state is pure $|\mathbf{x}^2 - \mathbf{y}^2\rangle$. If the ligand perturbation along $\mathbf{z}$ is increased while that along $\mathbf{y}$ is decreased, then mixing of $|\mathbf{x}^2 - \mathbf{y}^2\rangle$ and $|3\mathbf{z}^2 - \mathbf{r}^2\rangle$ occurs and $c \neq e \neq f \neq 0$. When the ligand perturbation along $\mathbf{y}$ equals that along $\mathbf{z}$, these being less than that along $\mathbf{x}$, the complex again has axial symmetry (though with $\mathbf{x}$ now the unique axis) and $\Delta g_y = \Delta g_z$, $\Delta g_x = 0$ with wave-function parameters $c = 2$, $e = f = -1$, *i.e.*, the ground-state is $|2\mathbf{x}^2 - \mathbf{y}^2 - \mathbf{z}^2\rangle$. Thus, a ground-state wave-function of this form can very conveniently represent the transition between the two limiting Jahn–Teller distorted structures expected for Cu^{II}, namely elongated tetragonal and compressed tetragonal. Simple theory suggests that there should be a relationship between the wave-function parameter and the ligand-field perturbation along each axis, with the greater absolute magnitude of the wave-function parameter being associated with the greater ligand perturbation. On electrostatic grounds this is because the electron ' hole ' should tend to concentrate along the direction of greatest ligand-field potential, while a naïve molecular orbital approach suggests that the most strongly antibonding orbital should tend to have the lowest electron occupancy.

Dependence of the Wave-function Parameters on Bond Lengths.—The above considerations suggest that in a complex in which the same donor is bonded to the copper ion along all three axes, there should be an inverse correlation between the absolute value of the wave-function parameters and the bond lengths. The only complex of this type studied here is the hydrogen maleate, for which this is indeed found to be the case (Tables 4 and 5). Moreover, if one compares complexes in which the same sets of donor atoms are bonded at various distances along two axes, then for each complex the difference in the magnitudes of the wave-function parameters along these axes should parallel the difference in the bond lengths. This indeed appears to be the case for the lactate and glycollate complexes. The difference between the Cu–O(hydroxyl) and Cu–O(carboxylate) bond lengths is 0·02 for the glycollate and 0·04 Å for the lactate, while the difference in magnitude of the wave-function parameters along these bond directions is 0·088 and 0·203, respectively. However, this trend does not seem to be followed for the phenoxyacetate and ethoxyacetate complexes. Although the greater disparity between the Cu–O(carboxylate) and Cu–O(water) bond lengths occurs for the former complex (*ca.* 0·04 as opposed to 0·02 Å), the greater difference between the magnitudes of the wave-function parameters occurs for the latter (0·124 as opposed to 0·039). This seems to be due to the anomalously long Cu–O(carboxylate) bond in the ethoxyacetate complex (1·97 Å); this bond length lies between 1·91 and 1·94 Å in all of the other compounds studied here (Table 4).

It might be expected that some approximate, general correlation would exist between the equilibrium distance taken up by a particular donor atom and the magnitude of the wave-function parameter along that bond direction. The bond lengths for the various donor groups are plotted against the magnitudes of the wave-function

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* To be reported in detail in a later Part of this series.

parameters in Figure 3. For the six Cu–O(water) bond lengths in the four aquo-complexes studied here there does indeed seem to be an inverse correlation between bond length and wave-function parameter [the lactate Cu–O(water) bond length was not included, as this complex is effectively five-co-ordinate]. This is illustrated by the dotted line in Figure 3). It is of interest to consider how data on other systems compare with those presented here. The molecular g-values $g_x = 2{\cdot}04$, $g_y = 2{\cdot}14$, and $g_z = 2{\cdot}36$ of the distorted octahedral group $Cu(H_2O)_6^{2+}$ in $K_2Cu(SO_4)_2,6H_2O$ have been measured by Bleaney *et al.*[16] The polarized crystal spectrum of this complex has not been reported, but the reflectance spectrum consists of a broad peak centred at *ca.* 12,500 cm^{-1}.[17] Using this as the value of E_{xz}, E_{yz}, and E_{xy}, and assuming a possible error of 0·01 in each g-value, we can calculate approximate values of the ground-state wave-function parameters as $c = 1{\cdot}88(3)$, $e = -1{\cdot}63(6)$, and $f = -0{\cdot}36(9)$ (where the number in parentheses represents the possible error $\times 10^2$). The three Cu–O(water) bond lengths in $K_2Cu(SO_4)_2,6H_2O$ are 1·94, 2·07, and 2·28 Å [17,18] and it can be seen from the inclusion of the wave-function parameters of this complex in Figure 3 that their correlation with the Cu–O distances agrees reasonably well with that in the present study.

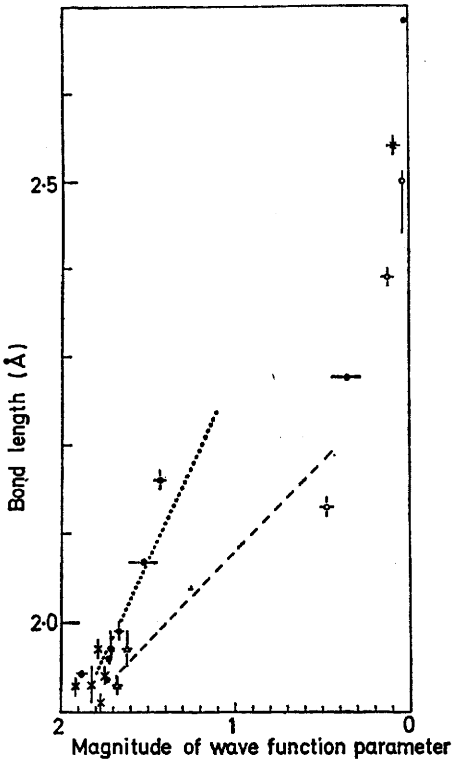

FIGURE 3 Diagram showing the relationship between bond length and the magnitude of the wave-function parameter along that bond direction for various donor atoms; ●, O(water); ○, O(ether); △, O(hydroxyl); ×, O(carboxylate)

An inverse correlation is also observed for the two Cu–O(hydroxyl) groups and three Cu–O(ether) groups and this is illustrated by the broken line in Figure 3. There seems to be no coherent variation in the Cu–O(carboxylate) bond length with wave-function parameter, though, as expected, the bond lengths are generally smaller than those in approximately square planar copper complexes with four Cu–O(carboxylate) bonds [*e.g.*, in copper maleate the mean of the four Cu–O(carboxylate) bond lengths is 1·985 Å[8]]. The anomalously long Cu–O(carboxylate) bond in the ethoxyacetate complex has already been mentioned. It should be emphasized that correlations of the above kind are only expected to be obeyed very approximately, as they neglect the influence of such factors as changes in interligand repulsions when different ligands are involved, crystal packing forces, and hydrogen bonding. These correlations can therefore only really be applied meaningfully on a statistical basis, and it will be interesting to see how future e.p.r. results on copper complexes of accurately known crystal structures fit into the pattern suggested by the present work.

Dependence of the Wave-function Parameters on the Donor Atom Ligand-field Strengths.—As the mixing of $|3\mathbf{z}^2 - \mathbf{r}^2\rangle$ and $|\mathbf{x}^2 - \mathbf{y}^2\rangle$ to form the ground-state is related to the difference in ligand perturbation along **x** and **y**, the g-values of the complexes can be used to provide a comparison of the ligand-field strengths of the various donor groups involved. The Cu–O(carboxylate) bond direction is invariably associated with the largest wave-function parameter suggesting that this group produces the greatest ligand perturbation. This does not seem to be merely a question of distance, as the difference in magnitude between the wave-function parameters along **x** and **y** in the phenoxyacetate (0·039) is considerably larger than that in the hydrogen maleate (0·012), although the bond lengths along these directions in the two compounds are comparable (Table 4); in the phenoxyacetate the shorter bond is to a carboxylate oxygen, while in the hydrogen maleate it is to a water molecule, the longer bond being in each case to a water molecule. Similarly, comparison of the wave-function parameters along **x** and **y** in the phenoxyacetate and lactate complexes suggests that a water molecule produces a stronger ligand field than a hydroxyl group.

The methoxyacetate seems, from the bond-length data, to be a fairly regular example of the unusual tetragonally compressed form of a Jahn–Teller distorted copper complex (Figure 2), but the values of $c = 1{\cdot}92$, $e = -1{\cdot}44$, and $f = -0{\cdot}49$ of the wave-function parameters fall almost exactly between the two extremes of the elongated and compressed octahedra, showing that the ground-state is an almost equal admixture of $|\mathbf{x}^2 - \mathbf{y}^2\rangle$ and $|3\mathbf{z}^2 - \mathbf{r}^2\rangle$. Thus, although the *structure* suggests near-axial symmetry the *ligand field* must

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[16] B. Bleaney, R. P. Penrose, and B. I. Plumpton, *Proc. Roy. Soc.*, 1949, *A*, **198**, 406.

[17] R. C. Marshall and D. W. James, *J. Inorg. Nuclear Chem.*, 1970, **32**, 2543.

[18] D. J. Robinson and C. H. L. Kennard, submitted for publication, quoted in ref. 17.

depart drastically from this symmetry. Moreover, the fact that $|e| \gg |f|$ shows that although the water oxygen atom is slightly further from the copper ion it produces a much stronger ligand field than the methoxy-oxygen atom. This means that in order to produce the same ligand perturbation as the water molecule, the methoxy-oxygen atom would have to be considerably closer to the copper ion, and a comparison of the dotted and broken lines in Figure 3 suggests that for equivalent wave-function parameters the Cu–O(ether and hydroxyl) distance is indeed considerably shorter than that to a water molecule. Moreover, in the nickel methoxyacetate complex, which is isomorphous with its copper analogue, and in which the electron density distribution of the *d*-electrons must be close to spherically symmetrical, the Ni–O(methoxy) bond length (1·99 Å) is considerably shorter than those to the carboxylate (2·05 Å) and water (2·07 Å) oxygen atoms.[19]

The above results thus suggest that, for donor atoms at comparable distances, the order of ligand-field strengths is O(carboxylate) > O(water) > O(hydroxyl) and O(water) ≫ O(methoxy).

Correlation of the Information Obtained from the g-Values with that Derived from the Electronic Spectra.—It is clearly of interest to see whether the information derived from the e.p.r. data can be estimated by other means, and the analysis of the electronic spectra of the complexes provides one way of doing this.

The angular overlap model (or a slight modification of it) as developed by Schaffer and Jørgensen[20,21] has been used with considerable success by several workers[22,23] to interpret the electronic spectra of copper complexes, and it seems ideally suited to the present study. This theory relates the antibonding energies of the *d*-orbitals to the square of overlap between the metal and donor atom orbitals. The destabilization of an antibonding *d*-orbital relative to a non-bonding one is proportional to $H_L{}^2S^2/(H_M - H_L)$ where H_L and H_M are the diagonal matrix elements for the ligand and metal orbitals respectively and S is the metal–ligand orbital overlap.[20,23] If it is assumed that each complex has a distorted octahedral structure, the ligand field can be taken to consist of the sum of six perturbations directed along the positive and negative axes of the octahedron.[21] The orbitals $|\mathbf{3z^2 - r^2}\rangle$ and $|\mathbf{x^2 - y^2}\rangle$ are affected only by perturbations of σ symmetry. The only donor atom involved is oxygen, though this is present in carboxylate, hydroxyl, water, and ether groups. We are primarily interested in comparing the ligand-field strengths produced by these four groups and the simplest way to do this seems to be to assume the same relationship between overlap and metal–ligand distance r for each group. This is necessarily a simplification, as it ascribes the differences in ligand perturbation of the four groups solely to the differences in energy of the oxygen *p*-orbitals (H_L in the above expression). In fact, at any particular Cu–O distance differences in overlap might also occur, but as long as the variation of the overlap as a function of distance is essentially the same for the four donor groups, as seems likely, this should not greatly affect comparisons between their donor power. The antibonding energies of the *d*-orbitals are therefore expressed in terms of four constants related to the σ-antibonding powers of the four donor groups at a particular distance, chosen arbitrarily as 1·93 Å. The antibonding contribution from group i at distance r along axis $\mathbf{j}$ is then given by equation (9) where S represents the appropriate diatomic

$$e_a(\mathbf{j}) = (S_r)^2 \times \sigma_i{}^*(S_{1\cdot 93})^2 \qquad (9)$$

overlap. Following Schaffer and Jørgensen[21] the matrix elements involving $|\mathbf{x^2 - y^2}\rangle$ and $|\mathbf{3z^2 - r^2}\rangle$ under a rhombic ligand field V are given by equation (10).

$$\langle \mathbf{x^2 - y^2}|V|\mathbf{x^2 - y^2}\rangle = \tfrac{3}{4}[e_a(+\mathbf{x}) + e_a(-\mathbf{x}) + e_a(+\mathbf{y}) + e_a(-\mathbf{y})] \qquad (10a)$$

$$\langle \mathbf{3z^2 - r^2}|V|\mathbf{3z^2 - r^2}\rangle = \tfrac{1}{3}\langle \mathbf{x^2 - y^2}|V|\mathbf{x^2 - y^2}\rangle + e_a(+\mathbf{z}) + e_a(-\mathbf{z}) \qquad (10b)$$

$$\langle \mathbf{3z^2 - r^2}|V|\mathbf{x^2 - y^2}\rangle = \sqrt{\tfrac{3}{4}}[e_a(+\mathbf{y}) + e_a(-\mathbf{y}) - e_a(+\mathbf{x}) - e_a(-\mathbf{x})] \qquad (10c)$$

The eigenvalues of this 2×2 matrix give the energy of the electronic transition $\Psi' \longrightarrow \Psi$ where $\Psi = a|\mathbf{x^2 - y^2}\rangle - b|\mathbf{3z^2 - r^2}\rangle$ and $\Psi' = a|\mathbf{3z^2 - r^2}\rangle + b|\mathbf{x^2 - y^2}\rangle$, and the eigenvectors yield the mixing coefficient b. The energy of this transition has been fairly unambiguously assigned for each complex from their polarized crystal spectra,[12,24] and the diatomic overlap between a copper 3*d*-orbital and an oxygen 2*p*-orbital has been estimated as a function of distance by Smith.[25] The set of four $\sigma_i{}^*$ parameters most consistent with the six observed transition energies was calculated by a minimum-seeking, least-squares technique and the values obtained were 6·78 kK for carboxylate, 6·56 for water, 6·35 for hydroxyl, and 2·10 for ether. The observed and calculated transition energies, and the calculated mixing coefficients b as well as their values estimated from the e.p.r. data, are in Table 6. The method of estimating the $\sigma_i{}^*$, which was done with a specially written FORTRAN (IV) computer programme, involved making an initial guess of these parameters. The final values obtained were, however, quite insensitive to this initial choice [and also relatively insensitive to small changes in $E_{\Psi' \longrightarrow \Psi}$(observed)].

It can be seen that the best fit to the electronic spectra is obtained with an order of σ-perturbing power O(carboxylate) > O(water) > O(hydroxyl) ≫ O(ether).

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Although the actual values of the σ_i^* parameters should probably not be taken as more than a qualitative guide to the σ-perturbing power of the groups involved, the agreement between the analyses of the g-values and electronic transition energies is very gratifying, as the two approaches are quite unrelated. In particular, the electronic spectra provide a fairly unambiguous confirmation that the σ-perturbing power of the ether groups in the methoxyacetate complex is very low. It can be noted that the series of ligand-field strengths estimated here provides a direct comparison of the σ-bonding ability of the donor groups involved, and in this respect it differs from the spectrochemical and nephelauxetic series, which in their usual forms are unable to separate the effects on the σ- and π-orbitals individually.

TABLE 6

The observed and calculated energies of the transition $\Psi' \longrightarrow \Psi^{\bullet}$ (where $\Psi^{\bullet} = a|\mathbf{x}^2 - \mathbf{y}^2\rangle - b|3\mathbf{z}^2 - \mathbf{r}^2\rangle$ and $\Psi' = a|3\mathbf{z}^2 - \mathbf{r}^2\rangle + b|\mathbf{x}^2 - \mathbf{y}^2\rangle$), and the values estimated for the mixing coefficient b from the electronic spectral and e.p.r. data

	Transition energy/ kK		Mixing coefficient b estimated from:	
Complex	Calculated	Observed [a]	Electronic spectra	E.p.r.[a]
Hydrogen maleate	11·41	11·50(0·1)	0·029	0·006(0·001)
Phenoxyacetate	11·74	12·10(0·2)	0·056	0·020(0·007)
Glycollate	11·31	11·50(0·2)	0·057	0·044(0·020)
Ethoxyacetate	10·76	10·10(0·2)	0·039	0·062(0·018)
Lactate	10·00	9·75(0·1)	0·088	0·102(0·020)
Methoxyacetate	9·58	9·80(0·2)	0·298	0·244(0·015)

[a] The estimated possible error is given in parentheses.

If the complexes are placed in the order of increasing participation of $|3\mathbf{z}^2 - \mathbf{r}^2\rangle$ in the ground-state it can be seen that with the exception of the ethoxyacetate complex (the anomalous behaviour of which has already been discussed) the order suggested by the electronic spectral analysis is the same as that found from the g-values. The agreement between the absolute values of the coefficients b estimated by the two methods is probably about as good as can be expected in every case except the hydrogen maleate, when it is remembered that the off-diagonal element [equation (10c)] from which b is calculated is very sensitive to the difference in the Cu–O bond lengths along $\mathbf{x}$ and $\mathbf{y}$, and the sum of the standard deviations is generally comparable with this difference (Table 4). The discrepancy in the case of the hydrogen maleate is rather disturbing, as this is the complex with the best-defined structure. However, it is also the complex with the smallest admixture of $|3\mathbf{z}^2 - \mathbf{r}^2\rangle$ in the ground-state, and it is possible that in this case the assumption of an axial orbital reduction parameter may be affecting the result adversely; this would almost certainly tend to make the value of b calculated from the g values too small.[5]

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