Electron Spin Resonance Study of Copper(II) Ions in Powder and Crystals of Aquatris(L-glutamato)cadmium(II) Monohydrate

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A single-crystal e.s.r. study has been carried out on copper(II) ions doped into aquatris(L-glutamato)cadmium monohydrate. The copper(II) site in this lattice was found to have approximate monoclinic symmetry with $g_z = 2.3545$, $g_y = 2.0920$, $g_x = 2.0678$, $A_Z = 0.0135$, $A_Y = 0.0020$, $A_X = 0.0027$, $A_Z^N = 0.0012$, $A_Y^N = 0.0009$, and $A_X^N = 0.0006$ cm^{-1}. The extent of non-coincidence of g and A principal directions was *ca.* 5° in the xy plane. It was concluded that a small admixture of $|3z^2 - r^2\rangle$ into the ground state formed by a linear combination of $|x^2 - y^2\rangle$ and $|xy\rangle$ could account for the experimentally determined anisotropy. The e.s.r. data taken at low temperatures have been related to molecular bond directions furnished by previously published room temperature X-ray data.

Amino-acids and dipeptides are small entities of biological importance because they can act as models for more complicated systems. It is well known that most of the non-protein-bound copper in the blood plasma is bound to amino-acid ligands.[1] Metal complexes with aspartic and glutamic acids have been the subject of a recent review [2] in which particular emphasis was devoted to the solution chemistry and the related structural problems connected with these molecules. Many studies have been previously reported [3–13] concerned with the binding properties of amino-acid molecules with copper(II) ions. In the case of bis(amino-acidato) complexes, where both *cis* and *trans* stereochemistries result, e.s.r. studies have proved to be essential for understanding their electronic properties. Unfortunately, many of these studies have suffered from inadequate magnetic dilution because single crystals of powders of the pure compounds were used. The structures do, however, suggest that at least rhombic g tensors should be expected although many examples were interpreted using axial symmetry.

Because of the biological relevance of these ligands it was decided to investigate the binding properties of amino-acids to metal ions. L-Glutamic acid was chosen since it gives rise to well defined complexes with zinc(II), copper(II), and cadmium(II) which are isostructural, but not isomorphous, as they involve the same distorted co-ordination polyhedron of donor atoms but with different bond parameters in the same crystal lattice.[14] In particular L-glutamic acid gives rise to two different stereochemistries with cadmium ions in the solid state. In the first the cadmium atom is six-co-ordinate, while in the second it is possible to find two chemically different seven-co-ordinate environments. Aquatris(L-glutamato)cadmium monohydrate was chosen as a host crystal for copper(II) ions in view of our interest in the e.s.r. features of low-symmetry compounds.[15,16] The co-ordination polyhedron around the cadmium atom is a highly distorted octahedron, and three molecules of the ligand are involved in the co-ordination to the metal. The metal site shows no element of symmetry although it was expected to approximate to C_s for the purposes of spectroscopic analysis.[17,18]

This paper reports an e.s.r. single crystal study due to copper(II) ions doped into aquatris(L-glutamato)cadmium monohydrate.

Theory

Electron Spin Resonance Data Analysis.—The e.s.r. data may be understood in terms of the various parameters which appear in the following spin Hamiltonian for copper(II) ($S = 1/2$, $I = 3/2$) and including hyperfine interaction with a single nitrogen nuclues ($I^N = 1$) [equation (1)]. The g, A,

$$\mathcal{H} = \beta \sum_{i=x,y,z} g_i B_i S_i + \sum_{j=X,Y,Z} A_j S_j I_j + P[I_{z^2} - \tfrac{1}{3}I(I+1)] + R[I_{x^2} - I_{y^2}] + \sum_{k=X_N,Y_N,Z_N} A_k^N S_k I_k^N \quad (1)$$

and A^N interaction matrices are all allowed to have different principal directions, as permitted by the absence of any point symmetry elements.[19] Although the quadrupole tensor, represented here in traceless form by parameters P and R, should strictly have principal axes differing from those for g, it turned out to be satisfactory to put $R = 0$ and to choose a common z axis.

Least-squares analysis of the angular variation of g^2, A^2g^2, and $(A^N)^2g^2$ in the crystalline planes was carried out using the first-order method of Waller and Rogers [20] for rotations about three orthogonal axes. The g values were estimated from the centre of each group of lines while copper A values were determined from mean hyperfine spacings. The A^N values were more difficult to measure since the nitrogen hyperfine splitting (h.f.s.) was not always well resolved. By this means g, A, and A^N principal values, as well as their direction cosines, were determined. Principal values of g were obtained as square roots of the diagonal elements of the g^2 tensor. The principal values of copper and nitrogen hyperfine interactions were treated separately and obtained by diagonalizing the tensor,[21] equation (2), where A refers respectively to A for copper and A^N for nitrogen.

$$A^2 = g^{-1}\, g\, A^2\, g\, g^{-1} \quad (2)$$

To correct for possible crystal misalignment, we used the particular strategy described by Waller and Rogers [20] in which starting angle shifts associated with each of the rotations about the three crystal principal axes were determined. These starting angle shifts were subsequently used to improve the accuracy in the determination of the g and A matrices.

It is to be stressed that the Waller–Rogers method is valid only to first order in perturbation theory under the conditions $g\beta B \gg A, A^N$ and assuming no quadrupole interaction. The data so obtained were then used to provide initial parameters for computer simulation of spectra in all orientations based on a program which diagonalizes the entire copper spin

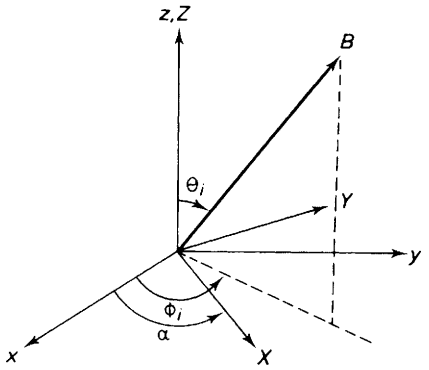

Figure 1. Co-ordinates for g and A for $^{63}Cu^{II}$ in aquatris(L-glutamato)cadmium monohydrate assuming monoclinic (C_s) symmetry. Non-coincidence angle is α; θ_i and φ_i are spherical polar co-ordinates of the d.c. magnetic field B, where $i = 1$ or 2 labels equivalent pairs of sites

Hamiltonian.[15,16,22,23] Effects of g anisotropy were allowed for in calculating the transition probabilities.[24,25] The nitrogen hyperfine interaction was taken into account by adding a first-order perturbation term to the energies obtained from the numerical diagonalization and using the approximation which puts A_Z^N along g_x. The polar angles θ and φ which the magnetic field makes with respect to the g reference frame, necessary for simulating each experimental spectrum, were calculated from the knowledge of the rotation matrices relative to the two sites (see Figure 1).

Results

Figure 2(*a*) shows a crystalline spectrum due to a single crystal when the magnetic field lies in the *ab* plane at 160° from the *a* axis. Spectra from the two sites can be clearly seen as well as the 1 : 1 : 1 pattern due to the presence of a single nitrogen nucleus. The computer simulation is also given. Figure 2(*b*) shows the spectrum when the magnetic field lies in the *bc* plane 60° from *b* and in Figure 2(*c*) the spectrum is shown for the magnetic field in the *ac* plane 35° from *c*. The spin Hamiltonian parameters are given in Table 1. The largest discrepancies between the first-order fits and the refinement resulting from computer simulation occur for g_y and A_Y. These are a consequence of ' second-order ' effects which were neglected in the Waller–Rogers analysis. The relatively large errors reported for the hyperfine coupling constants are a result of the small dimensions of the crystals. In Table 2 are reported the angles of non-coincidence between A and A^N with respect to the g reference system. The presumed errors on these angles are *ca.* ±2° for A and up to ±5° for A^N. Because of this relatively large error it is impossible to decide if the true point symmetry about the copper(II) ion is monoclinic or triclinic. Figure 3 shows a view of the co-ordination polyhedron together with the relative orientations of g, A, and A^N with respect to the framework of the complex.

A powder reflectance spectrum of the crystal under examination in the spectral region 7 000—20 000 cm^{-1} showed a broad peak centred at 13 000 cm^{-1}.

Discussion

To obtain the model depicted by Figure 3 it is necessary to consider all *four* possible combinations of g axes corresponding the four sites in the unit cell, in relation to *one* particular molecular framework (or alternatively *one* g axis set in relation to the *four* different molecules in the unit cell). While it would appear there are 24 ways of matching e.s.r. co-ordinates and sites in the crystal, it must be recognised that once a particular g-value set can be consistently identified with one of the four sets of unit-cell axes, the remaining three g-value sets and three sites can then be linked uniquely. Table 3 shows the comparison between the angles made by the correct g set and the matching molecular data for Cd–O(2″), Cd–O(3′), and Cd–O(5) bonds. The three oxygen bonds are those which form a nearly orthogonal set. As a result, it is realised that g_x lies close to the Cu–N bond as well as to Cu–O(3′). The remaining three possibilities do not make sense of possible bond formation by copper(II) in such a crystal. Thus each g orientation can be matched up with *one* particular molecular site. Figure 3 shows that the g_x and g_z directions lie in a plane which approximately contains the N, O(4), O(3″), and O(2′) atoms, while g_y is perpendicular to this plane, making an angle of *ca.* 8° with the Cu–O(5) bond. The orientation of A axes seems to be approximately collinear with the Cu–N and Cu–O(5) bonds and slightly away from the Cu–O(2″) bond. For the nitrogen h.f.s., however, the maximum component A_Z^N of 0.0012 cm^{-1} points towards the copper atom *ca.* 14° away from the Cu–N bond. The other two principal axes are not simply related to any particular crystallographic directions. Previously, it has been assumed that e.s.r. data at low temperatures may be compared with X-ray structural data obtained at room temperature. We found no evidence in support of a structural phase transition in the crystal used for e.s.r. measurements. Data for the bond directions were generated from the standard set reported with the crystal structure.[17]

These considerations give substance to the hypothesis that C_s monoclinic symmetry represents the local symmetry at the

Table 1. Spin-Hamiltonian parameters[a] for $^{63}Cu^{II}$ in aquatris(L-glutamato)cadmium monohydrate

	Waller–Rogers[b] method (first-order)	Crystal e.s.r. simulation refinement
(*a*) ^{63}Cu g values		
g_x	2.0678	2.0678 ± 0.0006
g_y	2.0884	2.0920 ± 0.0017
g_z	2.3534	2.3545 ± 0.0006
(*b*) ^{63}Cu Hyperfine		
10^4 A_X/cm^{-1}	25	27 ± 5
10^4 A_Y/cm^{-1}	12	20 ± 3
10^4 A_Z/cm^{-1}	137	135 ± 1
(*c*) ^{63}Cu Quadrupole		
10^4 P/cm^{-1}	—	4 ± 1
10^4 R/cm^{-1}	—	0
(*d*) N Hyperfine		
10^4 A_X^N/cm^{-1}	6	6 ± 2
10^4 A_Y^N/cm^{-1}	9	9 ± 2
10^4 A_Z^N/cm^{-1}	12	12 ± 1

[a] Absolute signs of hyperfine and quadrupole constants not determined. [b] Average from data for two equivalent sets of sites.

Table 2. Angles (°) of non-coincidence among A, A^N, and g principal axes

^{63}Cu	g_x	g_y	g_z	N	g_x	g_y	g_z
A_X	5	85	92	A_Z^N	26	81	66
A_Y	95	5	90	A_X^N	88	19	109
A_Z	88	90	2	A_Y^N	116	73	31
	Error ±2°				Error ≤ ±5°		

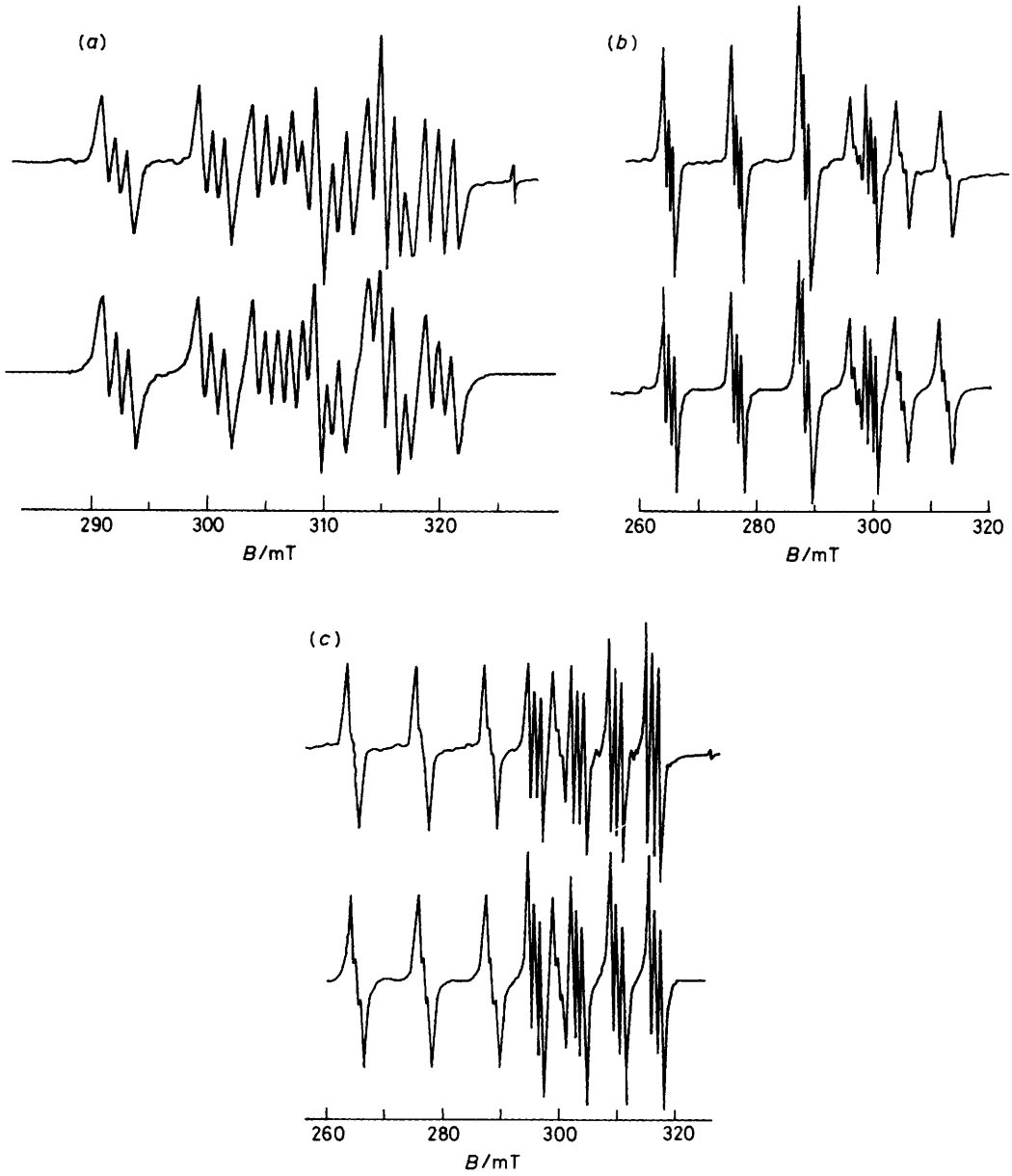

Figure 2. Experimental (upper) (120 K and ν = 9.145 GHz) and simulated (lower) e.s.r. spectra (using parameters in Table 2) (*a*) with the magnetic field vector in the *ab* plane at 160° from *a* (θ_1 = 103.0°, φ_1 = 164.8°, θ_2 = 60.0°, φ_2 = 160.8°); (*b*) with the magnetic field vector in the *bc* plane at 60° from *b* (θ_1 = 23.0°, φ_1 = 168.7°, θ_2 = 57.3°, φ_2 = 73.6°); and (*c*) with the magnetic field vector in the *ac* plane at 35° from *c* (θ_1 = 24.0°, φ_1 = −53.3°, θ_2 = 63.6°, φ_2 = −21.9°)

copper site since the g_z direction was found to be nearly perpendicular to the approximate plane of symmetry containing N, O(1), O(3′), and O(5).

In a recent study of copper L-glutamate in aqueous solution, an optical absorption peak was found at 13 500 cm^{-1} while the isotropic *g* and *A* values measured from e.s.r. measurements were 2.147 and 0.0059 cm^{-1} respectively.[26] In the present study, $g_{iso} = \frac{1}{3}(g_x + g_y + g_z) = 2.170$ while A_{iso} is the same as for the solution study. The difference in g_{iso} can probably be rationalized in terms of small differences in co-ordination in the solid.

The value of the axial quadrupole parameter $P = 0.0004 \pm 0.0001$ cm^{-1} seems small if the degree of distortion around the copper site compared with other systems is considered.[15,16,27] Probably it could be an indication of a small disturbance caused by atom O(4) to the co-ordination sphere of the metal ion, allowing it to move towards a relatively higher symmetry conformation. It is noted that Cd–O(4′) = 2.458(5) Å and Cu–O(4′) = 2.588(8) Å in the pure compounds.

A small number of papers have appeared concerning the interpretation of *g* matrices in low-symmetry copper complexes.[28–30] When the 'in-plane' *g* axes (g_x,g_y) lie close to ground state lobes, anisotropy and principal axis orientation is largely determined by $|3z^2 - r^2\rangle$ mixing into the ground state. Here, with approximately C_s (monoclinic) symmetry, the ground state orbital is given by equation (3). Since our

$$|\psi = a|x^2 - y^2\rangle + b|xy\rangle + c|3z^2 - r^2\rangle \qquad (3)$$

experimentally determined *g* orientations, g_x and g_y lie close to

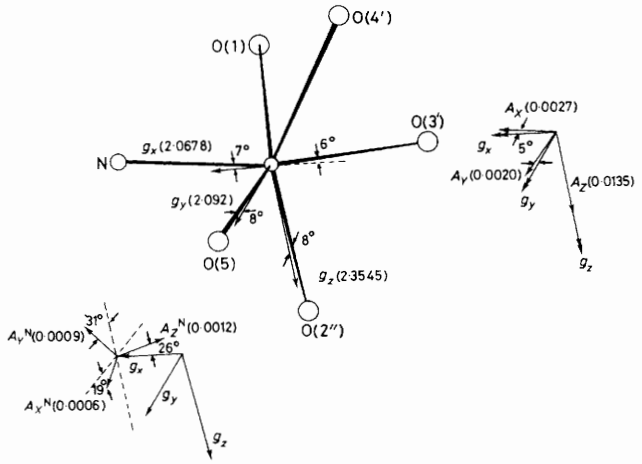

Figure 3. A view of the co-ordination polyhedron showing the principal directions of g, A (cm^{-1}), P, and A^N (cm^{-1}) with respect to the framework of the complex

Table 3. Angles [a] (°) between the g-axis set,[b] the corresponding Cu^{II} ligand bonds and crystal axes

	a	b	c
g_x	23	80	110
O(3')	27	82	115
g_y	88	25	65
O(5)	97	19	73
g_z	67	110	33
O(2'')	61	106	34

[a] To nearest degree. [b] Average from two sets of independent data.

metal–ligand bond directions [O(3'), O(5), N] then the ground state must be essentially $|x^2 - y^2\rangle$ with a little mixing of $|3z^2 - r^2\rangle$. The $|x^2 - y^2\rangle$ lobes should point towards O(5), O(3') and approximately towards N. A calculation based upon the results due to Hitchman *et al.*,[28] and assuming that N, O(1), O(3'), and O(5) and the copper atom lie in a plane, led to agreement with the measured values if $c = 0.04 \pm 0.05$. As has been explained both by Hitchman *et al.*[28] and Belford *et al.*,[30] the orientation of ' in-plane ' g values will be strongly influenced by the spatial orientation of ' out-of-plane ' $|xz\rangle$ and $|yz\rangle$ orbitals which mix into the ground state *via* spin–orbit coupling. On the other hand, we would expect the ' in-plane ' hyperfine constants A_X and A_Y to have their orientations fixed largely by the ' in-plane ' ground state lobes. In this case they should point along metal–ligand bonds, *e.g.* towards N, O(3'), and O(5).

Conclusions

We find that the symmetry properties of copper(II) ions in a low-symmetry aquatris(L-glutamato)cadmium monohydrate host crystal approximate to monoclinic C_s point symmetry, even though the strict crystal structure contains *no* elements of symmetry. It would be possible to establish the true lower symmetry (C_1) only if the spectral linewidths were considerably narrower than found here. In order to establish the appropriate spectral properties, data were collected in the three principal *crystal* planes and automatically reduced by the Waller–Rogers [20] methods. Careful comparison of magnetic and site symmetries must be made in order to obtain the correct matching sets, illustrated in Table 3. It has proved possible to account for the *ca.* 5° non-coincidence of g and A in the xy plane using the models proposed by Hitcham *et al.*[28] and Belford *et al.*[30]

Experimental

Crystals and Crystal Structure.—Aquatris(L-glutamato)-cadmium monohydrate is orthorhombic with space group $P2_12_12_1$ and unit-cell parameters $a = 11.61(1)$, $b = 10.79(1)$, and $c = 7.286(7)$ Å.[14,17] The cadmium atom co-ordination involves three molecules of L-glutamate and a water molecule, the first is co-ordinated through the amine nitrogen and the vicinal oxygen atom of the carboxylic group, the second *via* the other oxygen of the terminal carboxylic group, and the third by means of a carboxylic oxygen of the side-chain carboxylic group. A highly distorted octahedron of five oxygens and one nitrogen sets up the co-ordination geometry around the cadmium atom (the fifth oxygen is that of the water molecule).

Aqua (L-glutamato)copper(II) hydrate is six co-ordinate and isostructural with aquatris(L-glutamato)cadmium monohydrate but not isomorphous. The crystals belong to the same space group with unit-cell dimensions $a = 11.090$, $b = 10.321$, and $c = 7.240$ Å.[18] Crystals of the cadmium compound were prepared according to the procedure previously reported.[17] The ^{63}Cu as nitrate was added to the solution in a 0.5% ratio with respect to the cadmium ions. Very small crystals with well defined faces could be collected within a week. The orientation of the crystal axes was determined by measuring the most relevant angles among the crystalline faces using a reflection goniometer.

Spectroscopic Measurements.—A Varian E-12 spectrometer operating at 9.15 GHz and with 100 kHz magnetic field modulation was used to obtain the spectra. Low temperatures were achieved by means of a Varian nitrogen flow cryostat. The magnetic field was calibrated using an n.m.r. gaussometer, while the klystron frequency was accurately measured either by means of a Hewlett–Packard frequency meter type 540B or by means of a diphenylpicrylhydrazyl sample. In all experiments the d.c. magnetic field was horizontal and the microwave magnetic field vertical.

Due to the small dimensions of the crystals, two goniometers were employed to obtain crystal spectra. The first had only one degree of rotational freedom (about the vertical axis) while the second had rotational freedom about both vertical and horizontal axes.

Although there are four sites per unit cell, they become equivalent in pairs in the crystalline planes. The spectrum simplified to an eight-line pattern when the crystals were aligned correctly in crystal planes. Because some difficulty was experienced in aligning the crystals, all measurements were repeated at least twice on different crystals and the spectra were collected at intervals of at least 5° over a range of rotation of 0—180° in each case.

Optical powder reflectance spectra were obtained at room temperature by means of an Unicam SP 700 spectrophotometer equipped with a SP 735 powder reflectance apparatus. Magnesium oxide and the powder of the undoped salt were used alternatively as reference.

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