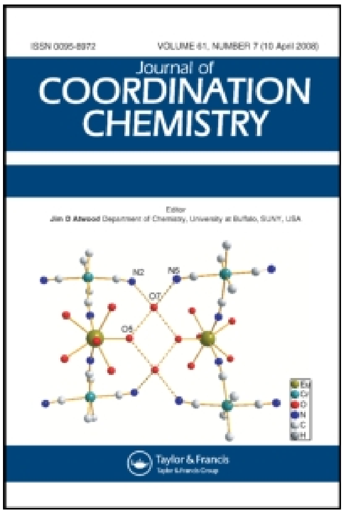

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THE EPR SPECTRUM OF COPPER-DOPED SINGLE CRYSTALS OF GLYCYLGLYCINE†

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The EPR Spectrum of Cu(II)-doped into a single crystal of α-glycylglycine is reported. The results show that there are several magnetically non-equivalent sites, only two of which were strong enough to be analysed. The values parameters in the spin Hamiltonian deduced from the data are: $g_z = 2.242 \pm 0.003$, $g_x = 2.062 \pm 0.005$, $g_y = 2.044 \pm 0.005$, $A_z = 162.8 \pm 1$ G, $A_x = 32.6 \pm 2.0$ G, $A_y = 21.6 \pm 2.0$ G. The Cu(II) environment seems to be square planar and involving four ligand molecules, each molecule forming one bond with the copper. The nitrogens are located in the trans position. The bonding is chiefly in-plane σ-bonding.

INTRODUCTION

The biochemical importance of the bonding of metals to amino acids and polypeptides has led to the investigation of several chelates of copper II by use of electron spin resonance and optical spectroscopy. Windsch and Welter[1] have studied copper-doped single crystals of glycine and triglycine sulfate. Copper(II) complexes in deuterated crystals of α-glycine, L-alanine and dimethylalanine have been studied by Fujimoto and co-workers[2,3] while Hirasawa and Kon[4] have studied a copper-doped crystal of L-histadine hydrochloride monohydrate. The electron spin resonance spectrum of the complexes of copper with glycine, L-alanine and L-leucine doped into the diamagnetic zinc complexes have been studied in polycrystalline samples.[5] In this paper we report the results of a study of the electron spin resonance spectrum of copper(II) doped into a single crystal of glycylglycine. Attempts to grow single crystals of the cadmium and zinc salts doped with the copper complex were unsuccessful but copper doped crystals of α-glycylglycine were readily grown and of sufficient size to be conveniently studied.

EXPERIMENTAL

Glycylglycine was obtained from the Mann Research Laboratories and used without further purification except in single crystal preparations. Single crystals were grown by slow evaporation of an aqueous solution of glycylglycine to which was added small amounts of copper nitrate.

Spectra recorded originally were too complicated to interpret. The complexity arose from the transitions arising from both of the naturally occurring copper isotopes, the presence of several magnetically non-equivalent sites in the crystal and the coupling of the unpaired electron to the nuclear spins of nitrogen and hydrogen atoms of the ligand. Some of the complexity was removed by using isotopically pure ^{63}Cu for the doping. The complexity was further reduced by growing the single crystal by slow evaporation of a D_2O solution. Such a procedure presumably replaces the labile protons on the ligand nitrogen atoms with deuterium and eliminates the proton super-hyperfine structure. These substitutions reduced the complexity of the spectrum so that it was possible to identify and analyse the spectrum of two magnetically non-equivalent sites. Crystals were grown with several levels of ^{63}Cu doping but all levels of doping showed the presence of several magnetically non-equivalent sites.

The spectra were recorded by a Varian E-9 EPR Spectrometer operating at X-band frequency. All spectra were recorded at room temperature. The field strength was monitored by a nmr type gaussmeter (Magnion), the frequency being counted by a Hewlett-Packard Model 5245*l* counter. The klystron frequency was measured with the same counter equipped with a Model 5255A frequency converter. In order to separate the spectra arising from

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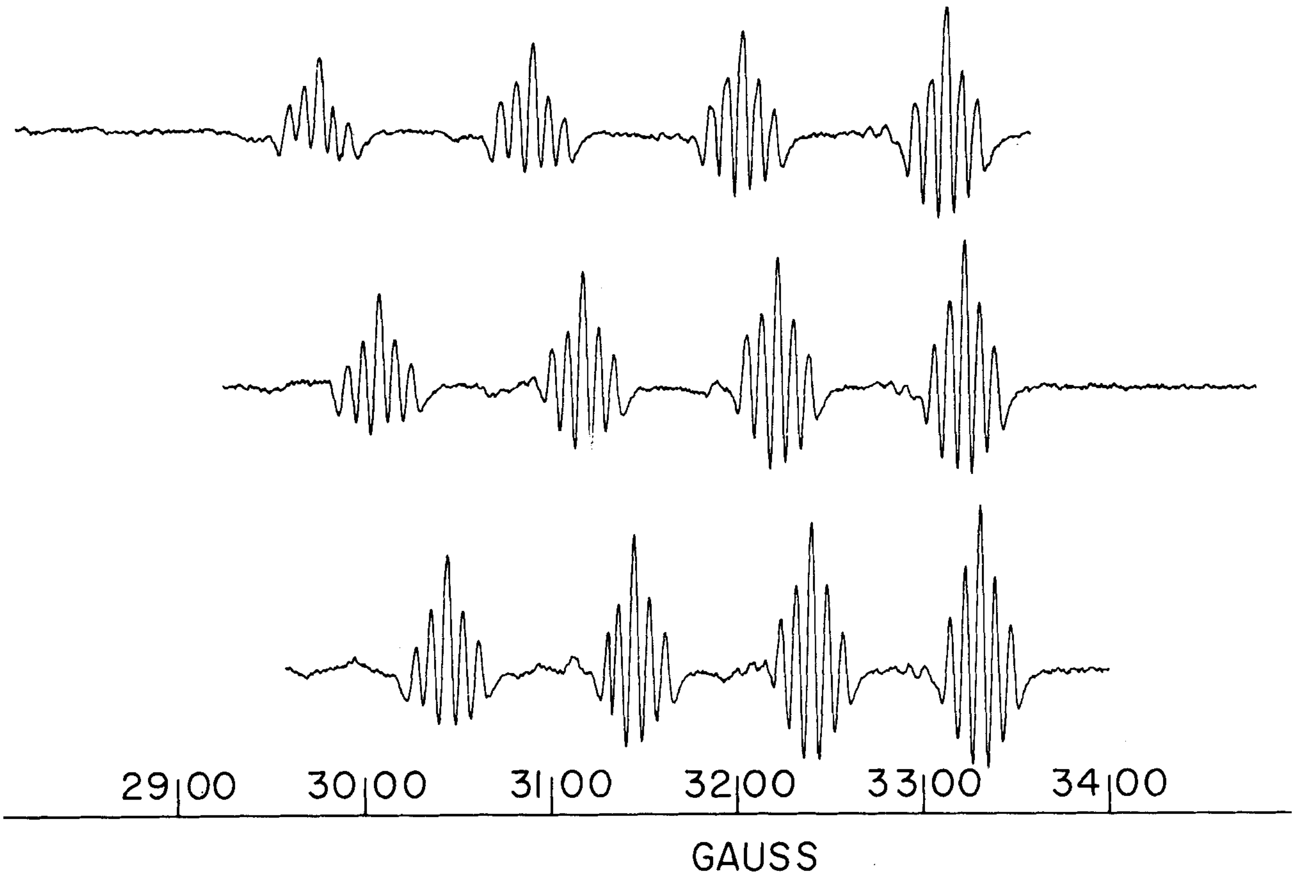

FIGURE 1 Sample EPR spectra from a copper-doped single crystal of α glycylglycine. The spectra were taken at X-band and the spectra shown were taken at 10° intervals. The static magnetic field is in the ac′ plane. The presentation is second derivative. Smaller lines between major signals arise from other magnetic sites.

magnetically non-equivalent sites some measurements were made at K-band frequencies.

The unit cell[6] of pure α-glycylglycine is monoclinic, with a = 7.81, b = 9.57, c = 9.41 Å and β = 124° 35′, contains four molecules and belongs to the space group P 21/a. Spectra were recorded at 5° or 10° intervals around the a and b crystal axes and around a c′ axis which was chosen perpendicular to the ab plane. Four non-equivalent sites were observed when the magnetic field was parallel to either the ab or the bc′ plane. In the ac′ plane the four sites merged into two, one set of the collapsed sites assuming extreme values for both g and A_{Cu}. It was not possible to identify the spectrum from each site in all orientations. Attention was focused on the prominent spectra from two sites in the ab and bc′ planes which collapsed to a single spectrum in the ac′ plane. Sample spectra are shown in Figure 1. This pattern of hyperfine splitting and superhyperfine splitting due to the nitrogen nuclei of the ligands is present in all crystal orientations, indicating that the two ligand nitrogens are in a trans configuration.

The EPR-spectrum could be fit to the usual spin-Hamiltonian for a doublet state:

$$\begin{aligned}\mathcal{H} &= \beta(g_xH_xS_x + g_yH_yS_y + g_zH_zS_z) + A_x^{\mathrm{Cu}} \cdot S_x \cdot I_x^{\mathrm{Cu}} \\ &\quad + A_y^{\mathrm{Cu}}S_y \cdot I_y^{\mathrm{Cu}} + A_z^{\mathrm{Cu}}S_z \cdot I_z^{\mathrm{Cu}} + A_\perp^N S_z \cdot I_z^N \\ &\quad + A_\perp^N(S_x \cdot I_x^N + S_y \cdot I_y^N) \quad \text{and higher terms.}\end{aligned}$$

Since the axes of rotation chosen are not necessarily the principal axes of the g-tensor the data were reduced by the method of Geusic and Brown[7] for rotations about any three mutually orthogonal axes. The modification of this method suggested by Billings and Hathaway[8] to reduce the effect of small crystal misalignments was also used. The A-values were determined in a similar manner as described by Poole and Farach.[9] A second order effect could be

TABLE I
The magnetic parameters for several Cu-doped amino-acid crystals

	α-Glycylglycine[a]	α-Glycine[b]	L-Alanine[b]
g_z	2.242 ± 0.003	2.2360 ± 0.0003	2.2261 ± 0.0003
g_x	2.062 ± 0.005	2.0554 ± 0.0005	2.0547 ± 0.0005
g_y	2.044 ± 0.005	2.0625 ± 0.0005	2.0567 ± 0.0005
A_z	162.8 ± 1 G	135 ± 1 G	187 ± 1 G
A_x	32.6 ± 2.0	17 ± 2	32.5 ± 2
A_y	21.6 ± 2.0	14 ± 2	32.5 ± 2
A_{N_z}	~ 11.0 G		

[a]This work
[b]Reference 2

observed for the coupling of the unpaired electrons to the copper nucleus. To minimize the effect of higher order effects, the central pair of the Cu-quartet was used in the data reduction as suggested by Fujimoto and Janecha.[2]

The g - tensor and the copper hyperfine splitting tensor were found to have the same angular dependence. The g - tensor and the A - tensors therefore, have the same principal directions. The results of the data analysis are presented in Table I where they are compared to those obtained from Cu-doped crystals of glycine and alanine.[2] The nitrogen hyperfine splitting constant A was found to be essentially identical to previous studies.[1,2]

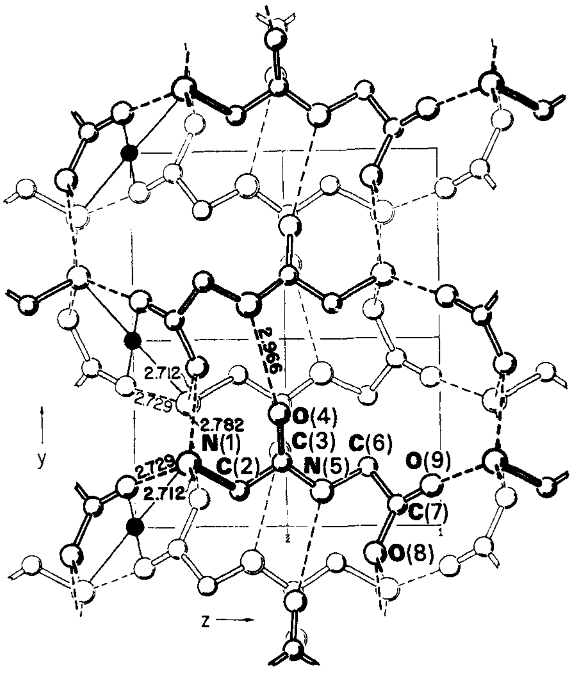

FIGURE 2 A sketch of the unit cell of α-glycylglycine looking along the a-axis. The probable sites for the Cu(II) ions are indicated in black. Sketch reproduced from reference 6 with permission.

The direction cosines for the principal magnetic axes together with the x-ray analysis of the host crystal[6] allows location of the Cu^{2+} ions (see Figure 2). It should be noted that in these sites each Cu^{2+} ion is bonded to the terminal atoms of four glycylglycine molecules. This is unique in this series of compounds, however in Cu-doped crystals of L-alanine, three alanine molecules contribute to the complex.[2] Two magnetically non-equivalent locations are shown in the Figure 2, although they are structurely the same. They are related by a mirror reflection in the ac plane. The sites have N–N and O–O distances[14] of 4.25 and 3.98 Å respectively which is comparable with the distances found in other copper complexes,[3,11,12] Spectra from other sites were observed at some orientations. The spectra arising from the location shown is consistently much stronger, in fact, due to this difference in intensity and the overlapping of the spectra from the several non-equivalent sites only data due to these sites could be reduced and analysed successfully.

BONDING

The molecular orbitals for copper in a pseudo-square planar environment have been described by many authors.[10,11] The ground state is given by a copper $d_{x^2-y^2}$ orbital in a linear combination with a ligand orbital of the same B_{1g} irreducible representation. Anisotropy in the g-values arises from spin-orbit coupling with mixes the ground state with the various excited states belonging to the irreducible representations B_{2g} and E_g. The B_{1g} state accounts for σ bonding to the copper. The B_{2g} and E_g states represent in-plane and out-of-plane π bonds respectively.

From the resonance results one can calculate values of the ground state coefficient a_1 and the Fermi parameter κ by solving the equations for the principal A^{Cu} values. The *b* coefficients could not be determined as accurately due to a lack of reliable optical data. The calculated values are listed in Table II. The results give the same picture that prevails in this series of compounds. The bonding is primarily in plane σ-bonding. In plane π-bonding is not as strong as in the related compounds and $b_2 \approx b_3 \approx 1$ which indicates very little out of plane π bonding.

The *g*-values exhibited by copper in the several environments observed so far do not seem to vary significantly. The glycine complex seems to be a

TABLE II
Bonding parameters for copper-doped single crystals of amino-acids

	α-Glyclyglycine	α-Glycine	L-Alanine
a_1^2	0.726	0.629	0.730
κ	0.440	0.425	0.468
b_1^2	0.7851		
b_2^2	1		

trans-complex involving two glycine molecules. Only one nitrogen seems to be bonded to the copper for the alanine complex. The complex involves three alanine molecules and the g-values are not too different from those observed in glycine or from those determined in the present work.

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