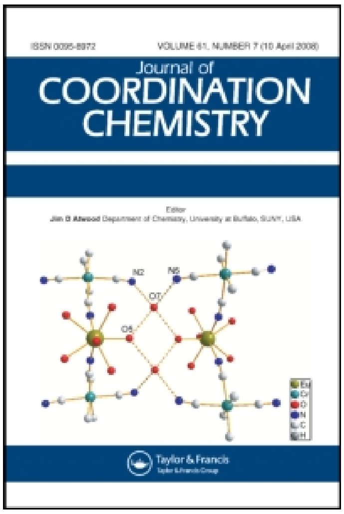

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SHORT COMMUNICATION

The EPR Spectrum of Copper (II) Doped Trans-bis (Clycino) Zinc (II) Monohydrate†

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The EPR spectrum of copper (II) doped trans-bis (glycino) zinc (II) hydrate has been studied previously on polycrystalline samples.[1] The information obtainable from polycrystalline samples is limited so in view of the biochemical importance of these compounds, a study of the EPR spectrum has been carried out on Cu(II) doped single crystals of the zinc(II) chelate. Information from the study of the chelate is compared to the results of a similar studies on a copper doped single crystal of glycine.[2,8]

Trans-bis (glycino) Zn(II) hydrate was prepared as previously described[3] and the chelate was identified through its infrared spectrum. Cu-doped crystals were prepared by adding small amounts of Cu^{+2} during the synthesis of the Zn chelate. Initial experiments indicated that there might be a difficulty in interpreting the spectrum because of the overlapping of the spectra arising from the two isotopes (^{63}Cu and Cu^{65}) present in naturally occurring copper, thus some of the samples upon which the spectrum was measured were doped with isotopically pure ^{63}Cu.

Single crystals of sufficient size were grown by the slow evaporation of an ethanol-water solution of the Cu-doped chelate. The crystals grow as plates elongated along [010] with the plate face being parallel to [001]. The crystal is triclinic with 16 molecules per unit cell. The crystal was mounted along each of the crystal axes and for each orientation spectra were recorded at 5° or 10° increments over a total rotation of at least 200°.

The spectra were recorded on a Varian E-9 EPR spectrometer operating at X-band frequency. The field was measured using a Magnion nmr-type gaussmeter by counting the frequency on a Hewlett Packard Model 5245 L frequency counter. The klystron frequency was measured with the same counter equipped with a model 5255A frequency converter. Since the spectrum was essentially identical at room temperature and liquid nitrogen temperature, measurements were carried out at room temperature.

When rotation was about the axis perpendicular to [001] planes and about the axis perpendicular to [100] planes absorption was observed from two magnetically non-equivalent sites whose principal axes are 120° apart. When the rotation was about an axis perpendicular to [010] planes the spectra from these two sites collapsed into a single spectrum. This situation is normal for mono-clinic systems. Each magnetic site gives rise to a series of four lines due to the coupling of the unpaired electron with the nuclear spin of copper ($I = 3/2$). Each of these lines is further split by interaction of the unpaired electron with the nuclear spin of the two nitrogen atoms ($I = 1$) of the ligands. Since 5 equally spaced lines were found in all orientations the two nitrogen atoms must be equivalent thus confirming the trans-configuration of the ligands about the copper.

The data could be fit to the normal spin-Hamiltonian for a doublet system: $\mathcal{H} = \beta(g_xH_xS_x + g_yH_yS_y + g_zH_zS_z + A_xS_xI_x + A_yS_yI_y$ + ligand terms. From the spacing of the Cu-hyperfine components it was apparent that there was some second order effects present. To minimize their effect on the parameters of the spin-Hamiltonian they were determined from the central pair of the Cu quartet.[2]

The principal values of the g-tensor were determined by the method of Geusic and Brown[5] as modified by Billings and Hathaway[6] to minimize the effect of small crystal misalignments. The principal values of the A-tensor were determined by the method outlined by Poole and Farach.[7] The g and A-tensors in the present study were found to have the same angular dependence indicating they have the same principal axes. The values for the parameters in the spin-Hamiltonian are given in Table I where they

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TABLE I
Spin-Hamiltonian parameters for Cu-glycine complexes

	Trans-bis (Glycino) Cu (II)	Cu-doped α-glycine Reference 2	Reference 8
g_z	2.276	2.2360	2.25
g_y	2.064	2.0554	2.05
g_x	2.057	2.0625	2.07
A_z	$174 \pm 1 \times 10^{-4}$ cm^{-1}	141×10^{-4} cm^{-1}	139
A_x	$32 \pm 2 \times 10^{-4}$	16×10^{-4}	44
A_y	$40 \pm 2 \times 10^{-4}$	14×10^{-4}	$\leqslant 6$

are compared with those obtained for copper (II) doped into a single crystal of glycine.[2,8]

The g-values in the plane of the molecule g_x and g_y are similar to those obtained for the Cu-doped glycine crystal. The g-values out of the molecular plane differ considerably indicating that the environments in this direction are probably different in the three cases.

Although the complete structure of the zinc chelate was not done, a partial analysis of their data led the authors[4] to feel that the structure is very similar to that of the cadmium chelate for which they could do a complete structure determination. The cadmium is in a distorted octahedral environment with approximately planar chelate groups with Cd-N and Cd-O bond lengths of about 2.3 A. At approximately right angles to the plane of these chelate rings, the free carboxyl oxygens of two neighboring glycine ligands approach the cadmium at a distance of about 2.5 Å completing the distorted octahedron. The present study tends to support this point of view. The EPR spectrum behaves as one would expect from a monoclinic crystal. Further, the principal values of the g and A tensors are in the range of those obtained from known distorted octahedral environments.[9] The g-values in the molecular plane are very similar to those found in the Cu-doped α-glycine crystals indicating that the distorted octahedral environment has little effect in this plane.

The fact that $g_{\parallel}-2 \approx 4(g_{\perp}-2)$ indicates that the ground state is that molecular orbital for which the main contribution from the central metal ion is $d_{x^2-y^2}$.

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