Crystal structure and EPR spectra of glycilglycilglycinocopper(II)bromide sesquihydrate

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The title compound, Cu(glyglygly)Br·1·5H$_2$O, crystallizes in the space group C2/c, with a = 21.468(7), b = 6.716(5), c = 16.166(6) Å, β = 98.39°, and Z = 8. The tripeptide is bonded to one Cu(II) ion through the nitrogen [Cu—N = 1.97(1) Å] and oxygen [Cu—O = 2.019(8) Å] atoms of the amino end glycine residue and to another Cu(II) through one oxygen atom [Cu—O = 1.931(9) Å] of the terminal carboxyl group. This give rise to covalently bonded and infinite ···—Cu—tripeptide—Cu—··· chains. These chains are linked to one another by a network of H-bonds involving the water molecules and bromide ions. The Cu(II) ion is in a distorted tetragonal pyramidal coordination polyhedron. At the corner of the base of the pyramid are the terminal glycine nitrogen and oxygen atoms of one tripeptide, a carboxylic oxygen of another tripeptide and a bromide ion. The fivefold coordination is completed with a water molecule at the top of the pyramid [Cu—Ow = 2.286(9) Å]. For all orientations of the applied magnetic field the single crystal EPR spectra display a single anisotropic exchange collapsed resonance without hyperfine structure. Its position was measured in three perpendicular planes and the crystal g-tensor evaluated from the data. This tensor is interpreted in terms of the contributing Cu(II) complexes in the unit cell to deduce the principal values g$_1$ = 2.273, g$_2$ = 2.050 and g$_3$ = 2.131 for the molecular gyromagnetic tensor. We also discuss the magnitude of the exchange interaction between neighboring copper ions in the lattice on the basis of the features in the EPR spectra and the structural information.

KEY WORDS: Cu(II) complex; crystal structure; EPR spectra.

Introduction

Metal—amino acid complexes are simple compounds useful to study the bonding of metal ions to biological molecules.[1-3] Metal ions with open electronic shells can be used as probes for the electronic

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structure and magnetic interactions using EPR and other spectroscopic techniques.[4,5] A detailed view of the chemical bonding may be obtained if this information is used together with structural data.

We report here a structural study by X-ray diffraction methods and a spectroscopic EPR study on the copper complex of the tripeptide gly—gly—gly with bromine, Cu(glyglygly)Br·1·5H$_2$O. EPR data were obtained in single crystal Cu(glyglygly)Br·1·5H$_2$O and in powdered samples of Cu(glyglygly)Br·1·5H$_2$O and of the isomorphous compound Cu(glyglygly)Cl·1·5H$_2$O.[6] Information on the electronic structure of the copper ions and about the exchange interaction between them in the Cu(glyglygly)Br·1·5H$_2$O lattice is obtained and discussed in terms of the structural data. The structural and EPR results for Cu(glygly-

gly)Br·1·5H$_2$O and Cu(glyglygly)Cl·1·5H$_2$O are then compared and discussed.

Experimental

Sample preparation

Single crystals of Cu(glyglygly)Br·1·5H$_2$O were grown by slow evaporation of a saturated equimolar water solution of glycilglycilglycine and CuBr$_2$. Blue-green crystals of about 1 × 1 × 0.5 mm^3 suitable for EPR measurements were obtained at room temperature in a few days. A similar method was followed to obtain single crystals of Cu(glyglygly)Cl·1·5H$_2$O from a saturated equimolar solution of glycilglycilglycine and CuCl$_2$·2H$_2$O. These crystals were, however, much smaller than those of the isomorphous bromide compound.

Diffraction data and structure determination and refinement

Crystal data, data collection procedure, structure determination methods, and refinement results for Cu(glyglygly)Br·1·5H$_2$O are summarized in Table 1. The two hydrogens of the terminal amino group were located from a difference Fourier map and incorporated in the molecular model. The map also showed the two hydrogen atoms attached to the α carbon of the terminal amide peptide and one of the hydrogen atoms bonded to the other two α carbons. However, these and the rest of the hydrogen atoms in the tripeptide molecule were positioned on stereochemical grounds and included with the amino hydrogens in the structure factor calculation with a common fixed temperature parameter B = 3.96 A^2.

EPR measurements

Room-temperature single crystal EPR spectra of Cu(glyglygly)Br·1·5H$_2$O at 9.8 GHz were obtained on a Bruker ER-200 spectrometer equipped with a 12″ rotating magnet and a Bruker cylindrical cavity working in the TE011 mode with 100 KHz magnetic field modulation. To orient the single crystal sample, a natural (100) face was glued to a cleaved KCl cubic sample holder, which define a set xyz of orthogonal axes. The b and c crystal axes of the sample were aligned along

Table 1. Crystal data, data collection details and structure refinement results for Cu(glyglygly)Br·1·5H$_2$O

Formula	C$_6$H$_{10}$N$_3$O$_4$CuBr·1·5H$_2$O
Color/shape	Blue-green/fragment
Formula weight	358.6
Space group	$C2/c$
Temp. C°	20
Cell constants[a]	
a, Å	21.468(7)
b, Å	6.716(5)
c, Å	16.166(6)
β, deg	98.39(3)
Cell volume, Å^3	2306(3)
Formula units/unit cell	8
D_{calc}, g cm^{-3}	2.066
μ_{calc}, cm^{-1}	53.41
Diffractometer/scan	Enraf-Nonius CAD-4/ω-2θ
Radiation, graphite monochromator	Mo $K\alpha$(λ = 0.71069 Å)
Max. crystal dimens., mm	0.2755 × 0.25 × 0.075
Scan width	0.8 + 0.35 tan θ
Standard reflection	7 3 3
Decay of standard	±2%
Reflections measured	1865
2θ range, deg	2 ≤ 2θ ≤ 50°
Range of h, k, l	±25, +7, +19
Reflections observed [$F_o \geq 6\sigma(F_o)$][b]	1366
Computer programs[c]	SHELX,[7] SDP[8]
Structure solution[d]	SHELX[7]
No. of parameters varied	153
Minimized function	$\Sigma w(|F_o| - |F_c|)^2$
Weights, w	$w = [\sigma^2(|F_o| + 0.001|F_o|^2]^{-1}$
GOF	2.04
$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$	0.075
$R_w = [\Sigma w(|F_o| - |F_c|)^2/ \Sigma w|F_o|^2]^{1/2}$	0.075
Largest feature final difference map[e]	2.4 e$^-$ Å^{-3}

[a] Least-squares refinement of [(sinθ)/λ]^2 values for 25 reflections in the 11.2 < 2θ < 36.2° range.
[b] Corrections: Lorentz and polarization.
[c] Neutral scattering factors and anomalous dispersion corrections.
[d] Structure solved by Patterson and Fourier methods and the final molecular model obtained by anisotropic full-matrix least-squares refinement of the non-hydrogen atoms.
[e] This artifact peak, probably due to the poor quality of the data, is at about 1 Å from the Cu ion.

the y and z axes of the sample holder, and a' = c × b along the x axis. This holder was positioned in an horizontal plane at the top of a pedestal in the center of the microwave cavity. The orientation uncertainties were about 2°. The magnetic field **B** was rotated in the xy, zx, and zy planes and the spectra were collected at intervals of 5° along 180°.

Cu(glyglygly)Cl·1·5H$_2$O single crystals of quality suitable for EPR measurements could not be grown. Therefore, powder EPR spectra of the chlorine and bromide compounds were obtained to compare their magnetic behavior. To this purpose, a computer simulation of powder EPR spectra as a function of the gyromagnetic tensor and the angular dependence of the linewidth was carried out. In the case of Cu(glyglygly)Br·1·5H$_2$O the parameters obtained from the single crystal EPR study were used in the simulation. Then we analyzed the changes of these values which simulate the spectrum of powdered Cu(glyglygly)Cl·1·5H$_2$O samples.

Results and discussion

Structural results

Fractional coordinates and isotropic temperature parameters[9] for the non-H-atoms in Cu(glyglygly)Br·1·5H$_2$O are given in Table 2. Relevant bond distances and angles around the copper ion and the tripeptide molecule are in Tables 3 and 4, respectively. Figure 1 is an ORTEP[10] drawing of the compound showing the labelling of the non-H-atoms.

Table 2. Fractional atomic coordinates and equivalent isotropic temperature parameters (Å^2) of Cu(glyglygly)Br·1·5H$_2$O

Atom	X/a	Y/b	Z/c	B_{iso} [a]
Cu	0.1612(1)	−0.0519(2)	0.7214(1)	2.44(5)
Br	0.2341(1)	−0.1071(2)	0.8493(1)	2.64(4)
C(1)	0.2037(6)	−0.053(2)	0.5606(8)	2.6(4)
C(2)	0.1449(6)	0.068(2)	0.5572(7)	2.1(4)
C(3)	0.0653(7)	0.259(2)	0.4667(7)	2.8(4)
C(4)	0.0729(7)	0.482(2)	0.4570(8)	2.5(4)
C(5)	0.0454(6)	0.762(2)	0.3650(7)	2.3(4)
C(6)	0.0952(6)	0.804(2)	0.3093(7)	2.1(4)
N(1)	0.2272(5)	−0.097(2)	0.6506(6)	2.7(3)
N(2)	0.1254(5)	0.157(2)	0.4841(6)	2.6(3)
N(3)	0.0417(5)	0.555(1)	0.3871(6)	2.3(3)
O(1)	0.1155(4)	0.077(1)	0.6170(5)	2.8(3)
O(2)	0.1065(6)	0.580(1)	0.5087(6)	4.4(4)
O(3)	0.0931(4)	0.985(1)	0.2823(5)	2.7(3)
O(4)	0.1331(5)	0.679(1)	0.2954(6)	3.2(3)
O(W1)	0.1190(4)	−0.357(1)	0.6840(6)	2.9(3)
O(W2)	0	0.291(2)	0.25	2.8(5)

[a] B_{iso} defined by:

$$B_{iso} = \frac{8\pi^2}{3} \sum_i \sum_j U_{ij}\, a_i^*\, a_j^*\, \mathbf{a}_i^* \cdot \mathbf{a}_j^*.$$

Table 3. Interatomic bond distances (Å) and angles (deg) in the environment of copper in Cu(glyglygly)Br·1·5H$_2$O[a]

Bond distances				
Cu	−	O(3^i)	1.931(9)	
Cu	−	Br	2.433(2)	
Cu	−	N(1)	1.97(1)	
Cu	−	O(1)	2.019(8)	
Cu	−	O(W1)	2.286(9)	
Bond angles				
Br	−	Cu	−	N(1)	92.4(3)
Br	−	Cu	−	O(1)	161.7(3)
Br	−	Cu	−	O(W1)	105.6(2)
Br	−	Cu	−	O(3^i)	92.5(3)
N(1)	−	Cu	−	O(1)	83.3(4)
N(1)	−	Cu	−	O(W1)	90.0(4)
N(1)	−	Cu	−	O(3^i)	173.7(4)
O(1)	−	Cu	−	O(W1)	92.2(3)
O(1)	−	Cu	−	O(3^i)	90.8(4)
O(W1)	−	Cu	−	O(3^i)	92.5(3)

[a] Symmetry code: (i) x, $1 - y$, $z + 1/2$.

Table 4. Interatomic bond distances (Å) and angles (deg) in the tripeptide molecule in Cu(glyglygly)Br·1·5H$_2$O[a]

Bond distances				
C(1)	−	C(2)	1.50(2)	
C(1)	−	N(1)	1.50(2)	
C(2)	−	N(2)	1.34(1)	
C(2)	−	O(1)	1.23(1)	
C(3)	−	C(4)	1.52(2)	
C(3)	−	N(2)	1.45(2)	
C(4)	−	N(3)	1.32(2)	
C(4)	−	O(2)	1.21(2)	
C(5)	−	C(6)	1.52(2)	
C(5)	−	N(3)	1.44(2)	
C(6)	−	O(3)	1.29(1)	
C(6)	−	O(4)	1.21(2)	
Bond angles				
C(2)	−	C(1)	−	N(1)	108(1)
C(1)	−	C(2)	−	N(2)	115(1)
C(1)	−	C(2)	−	O(1)	122(1)
N(2)	−	C(2)	−	O(1)	123(1)
C(4)	−	C(3)	−	N(2)	112(1)
C(3)	−	C(4)	−	N(3)	114(1)
C(3)	−	C(4)	−	O(2)	122(1)
N(3)	−	C(4)	−	O(2)	124(1)
C(6)	−	C(5)	−	N(3)	113(1)
C(5)	−	C(6)	−	O(3)	112(1)
C(5)	−	C(6)	−	O(4)	122(1)
O(3)	−	C(6)	−	O(4)	126(1)
Cu	−	N(1)	−	C(1)	111.4(8)
C(2)	−	N(2)	−	C(3)	123(1)
C(4)	−	N(3)	−	C(5)	122(1)
Cu	−	O(1)	−	C(2)	113.2(8)
C(6)	−	O(3)	−	Cu^{ii}	113.6(8)

[a] Symmetry code: (ii) x, $1 - y$, $z - 1/2$.
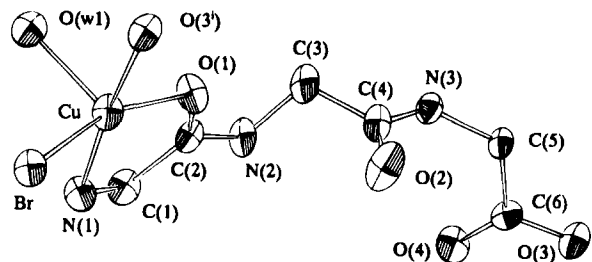
Fig. 1. Projection of Cu(glyglygly)Br·1·5H$_2$O showing the labeling of the non-hydrogen atoms, the environment of copper atom and the tripeptide molecule.

As expected, the Cu(glyglygly)Br·1·5H$_2$O is isomorphous to the chlorine-containing compound. The Cu(glyglygly)Cl·1·5H$_2$O structure was solved several years ago, employing visually estimated X-ray diffraction data and refined to $R = 0.12$.[6] For comparison, the present study uses essentially the same atom labeling scheme as in Ref. 6.

The tripeptide is attached to one Cu(II) ion through the nitrogen and oxygen atoms of one terminal glycine residue (see Fig. 1) and to another Cu(II) ion (symmetry related to the first one by a glide plane), through one terminal carboxyl oxygen atom. This generates covalently linked and infinite −Cu−tripeptide− −Cu−tripeptide− chains along c.

The Cu(II) ion is in a distorted tetragonal pyramidal coordination. At the corners of the pyramid base are a bromide ion [d(Cu−Br) = 2.433(2) Å], the terminal glycine nitrogen [d(Cu−N) = 1.97(1) Å] and oxygen [d(Cu−O)=2.019(8) Å] atoms of one peptide chain, and a terminal carboxylic oxygen atom [d(Cu−O) = 1.931(9) Å] of another (symmetry related through a glide plane) tripeptide. The fivefold coordination is completed with a water molecule at the top of the pyramid [d(Cu−Ow) = 2.286(9) Å]. The Cu(II) ion is at 0.197(2) Å from the least-squares plane through the four atoms of the pyramid base and towards the water oxygen atom, whose distance from this plane is 2.460(9) Å.

Within the tripeptide, bond distances and angles (Table 4), least-squares planes and dihedral angles are essentially in agreement with the corresponding data reported for Cu(glyglygly)Cl·1·5H$_2$O.[6] Both Cα−CO−N−Cα moieties and the terminal acetate Cα-COO group are planar to within experimental accuracy. The dihedral angle between the two amide planes is 96.9(4)°; the angle between adjacent amide and acetate planes is 91.2(4)°.

The −Cu−glyglygly−Cu−glyglygly− chains provide a path for magnetic superexchange interaction

between Cu(II) ions 10.98 Å apart through the high electron density σ-skeleton of the tripeptide. These chains are linked to one another by H-bonds. A screw-axis symmetry operation brings copper atoms on neighboring chains at the shortest distance of 5.06(1) Å, giving rise to an infinite −Cu−N−H··· Br−Cu−N−H···Br− pattern along **b** (see Fig. 2). This provides the shortest electron density path connecting neighboring Cu(II) ions in the lattice and therefore could be relevant in the transmission of the superexchange interaction between copper atoms detected by EPR measurements. Neighboring chains, symmetry related to one another through glide planes, are linked by a network of N(2)−H···Br (along **c**) and O(W1)−H···O(4) (along **b**) hydrogen bonds. The water oxygen O(W2), located on a two-fold axis, is in a nearly tetragonal bonding geometry where O(W2) acts as an hydrogen acceptor in a N(3)−H···O(W2) contact and as a donor in a O(W2)−H···O(3) hydrogen bond. These interactions link neighboring chains
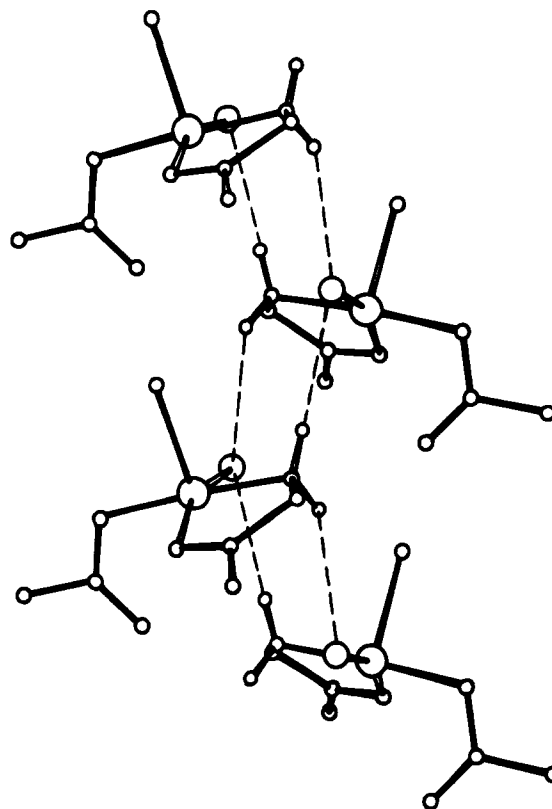
Fig. 2. View of molecular fragments around nearest copper atoms in Cu(glyglygly)Br·1·5H$_2$O. The fragments are symmetry related through an screw-axis along the vertical. The largest and second largest circles, denote copper and bromide atoms, respectively. Dashed lines indicate N−H···Br hydrogen bonds.

EPR results

Single crystal data. A single EPR line was observed for any orientation $h=B/|B|=(\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$ of the magnetic field B in the three orthogonal planes xy, zx, and zy. The angles θ and ϕ are related to the to the xyz axes system of the sample holder. The experimental values for the squared gyromagnetic factor $g^2(\theta,\phi)$ are displayed in Fig. 3. The angular variation of the position of the resonance is described by a spin Hamiltonian

$$H = \mu_B S \cdot g \cdot B, \qquad (1)$$

where μ_B is the Bohr magneton, S the effective spin ($S = 1/2$), and g the gyromagnetic tensor. The components of the g^2 tensor were calculated from the experimental data in Fig. 4 using a least squares procedure. The components, eigenvalues and eigenvectors of g^2 are given in Table 5. The solid lines in Fig. 4 were calculated with these values.

Since $Cu(glyglygly)Br\cdot1\cdot5H_2O$ crystallizes in the space group $C2/c$ with $Z = 8$, four copper complexes are obtained by translation of the other four, which are labeled as I, II, III, and IV. Therefore, both sets of four Cu(II) complexes must display identical EPR spectra. Besides, within each set, sites I and III are
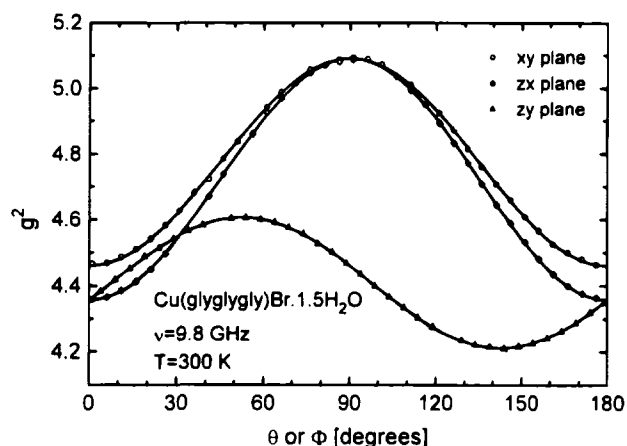

Fig. 3. Angular variation of the squared gyromagnetic factor measured at 300 K and 9.8 GHz in three orthogonal planes of Cu(glyglygly)Br·1·5H₂O single crystal. The solid lines were obtained by fitting the data with a symmetric g^2 second-order tensor. The parameters of the fit are included in Table 5a.

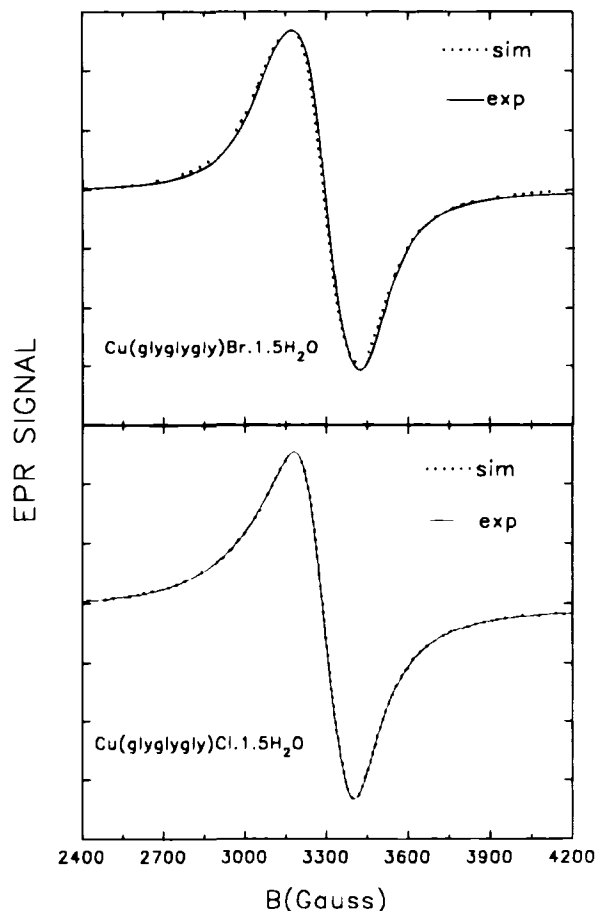Fig. 4. (a) Powder EPR spectrum of Cu(glyglygly)Br·1·5H₂O. The dotted line is a simulated spectrum obtained with the g-tensor and angular variation of the linewidth from single crystal EPR experiments. (b) Powder EPR spectrum of Cu(glyglygly)Cl·1·5H₂O. The dotted line spectrum was calculated assuming that the EPR behavior is similar to that of the bromide compound. The values of the parameters used are given in Table 6.

related to sites II and IV, respectively, by an inversion operation, and then the members of each of the pairs (I,II) and (III,IV) must also display identical spectra. Sites (I,II) are related to sites (III,IV) by a C_2 operation around the b axis, giving rise to two types of magnetically inequivalent copper ions in the unit cell, which will be called A = (I,II) and B = (III,IV). Two EPR lines are expected for B in the xy and zy planes. Only one signal is expected in the zx plane, perpendicular to the C_2 axis relating the A and B sites, and for B along the b axis. The fact that just a single EPR line was observed indicates the presence of exchange averaging effects which collapse the spectra of the A- and B-type coppers in the xy and zy planes.[5] By analyzing the structure of the compound it can be seen that the

Table 5. (a) Values of the components of the crystal gyromagnetic tensor g^2 obtained by a least-squares analysis of the data[a] and (b) Values of the components of the g_A^2 molecular tensor in site A[b]

(a) Crystal g^2 tensor

$(g^2)_{a'a'} = 4.4608(5)$
$(g^2)_{bb} = 5.0909(5)$
$(g^2)_{cc} = 4.3579(5)$
$(g^2)_{a'b} = 0.0000(6)$
$(g^2)_{a'c} = 0.1901(6)$
$(g^2)_{bc} = 0.0000(6)$

Eigenvalues	Eigenvectors
$(g^2)_1 = 5.0909(5)$	$(0, 1, 0)$
$(g^2)_2 = 4.2124(7)$	$(0.6081, 0, -0.7939)$
$(g^2)_3 = 4.6064(7)$	$(0.7939, 0, 0.6081)$

(b) Molecular g^2 tensor

$(g^2)_{XX} = 4.5113(1)$
$(g^2)_{YY} = 4.2327(1)$
$(g^2)_{ZZ} = 5.1655(1)$
$(g^2)_{XY} = -0.0934(1)$

Eigenvalues	Eigenvectors
$g_1 = 2.2728$	$(0, 0, 1)$
$g_2 = 2.0504$	$(0.2911, 0.9567, 0)$
$g_3 = 2.1307$	$(0.9567, -0.2911, 0)$

[a] Eigenvalues and eigenvectors are referred to $a'bc$ coordinate system.

[b] Eigenvalues and eigenvectors of the g^2 tensors in the XYZ molecular coordinate system as defined in the text.

paths for these interactions could be either the long σ-skeleton of the tripeptide, or the much shorter $N(1)-H\cdots Br$ hydrogen bonds. The g-factor corresponding to this single line should be the average $g(\theta,\phi)$ of the g-factors for the resonances corresponding to the A and B sites

$$g(\theta,\phi) = \frac{1}{2}[g_A(\theta,\phi) + g_B(\theta,\phi)], \quad (2)$$

with $g_A(\theta,\phi) = (h\cdot g_A\cdot g_A\cdot h)^{1/2}$ and $g_B(\theta,\phi) = (h\cdot g_B\cdot g_B\cdot h)^{1/2}$, where g_A and g_B are the gyromagnetic tensors corresponding to copper ions in sites A and B, respectively. For small g-anisotropies, i.e., for $(g_A - g_B)/2 << (g_A + g_B)$, it follows that[11]

$$g^2 \approx (g_A^2 + g_B^2)/2. \quad (3)$$

The observed values of $g^2(\theta,\phi)$ correspond to this collective resonance. To calculate the squared molecular gyromagnetic tensors g_A^2 and g_B^2, the method of Abe and Ono,[12] which assumes axial symmetry for g_A and g_B around the normals to the planes of equatorial ligands, was first employed. As it turns out, the angle

2α between these two normals, calculated from the components of g^2 by this method, does not agree with the value obtained from the crystallographic data. This discrepancy indicates departure from axial symmetry for the molecular g-tensors. This asymmetry of the local arrangement around copper ions is expected and should be mainly produced by the presence of the bromide ion as an equatorial ligand.

The distorted tetragonal pyramidal coordination around copper suggests that the direction of the normal to the equatorial ligands is a principal direction of the gyromagnetic molecular g-tensors g_A^2 and g_B^2. Therefore, g_A^2 was referred to a molecular system XYZ with Z along the normal to the $N(1)O(1)O(3^i)Br$ plane, X along $Cu-Br$ direction projected onto this plane, and the Y axis defined to complete a right-handed axes triad. The transformation matrix U which rotates this g_A^2 tensor from the crystal $a'bc$ axes to the XYZ molecular system was then calculated using the crystallographic data. The g_B^2 tensor, expressed in the $a'bc$ system, was obtained rotating g_A^2 $180°$ around b. Using eq (3), the unknown components of g_A^2 and g_B^2 expressed in the $a'bc$ system were evaluated from the set of lineal equations

$$U_{11}^2(g_A^2)_{XX} + U_{21}^2(g_A^2)_{YY} + U_{31}^2(g_A^2)_{ZZ} + U_{11}U_{21}(g_A^2)_{XY} = (g^2)_{a'a'}$$

$$U_{12}^2(g_A^2)_{XX} + U_{22}^2(g_A^2)_{YY} + U_{32}^2(g_A^2)_{ZZ} + U_{12}U_{22}(g_A^2)_{XY} = (g^2)_{bb}$$

$$U_{13}^2(g_A^2)_{XX} + U_{23}^2(g_A^2)_{YY} + U_{33}^2(g_A^2)_{ZZ} + U_{13}U_{23}(g_A^2)_{XY} = (g^2)_{cc},$$

$$U_{13}U_{11}(g_A^2)_{XX} + U_{23}U_{21}(g_A^2)_{YY} + U_{33}U_{31}(g_A^2)_{ZZ}$$
$$+ (U_{11}U_{23} + U_{13}U_{21})(g_A^2)_{XY} = (g^2)_{a'c} \quad (4)$$

where $(g^2)_{ij}$ are the components of the experimental tensor. This allowed to evaluate the components $(g_A^2)_{XX}$, $(g_A^2)_{YY}$, $(g_A^2)_{ZZ}$, and $(g_A^2)_{XY}$ of the g_A^2 tensor.[13] These results and the principal values of these tensors, are reported in Table 5b.

Powdered samples

Since $Cu(glyglygly)Cl\cdot1\cdot5H_2O$ single crystals of convenient size for EPR measurements were not available, powder EPR spectra of $Cu(glyglygly)Cl\cdot1\cdot5H_2O$ and $Cu(glyglygly)Br\cdot1\cdot5H_2O$ were obtained and compared. These spectra are displayed in Fig. 4. As expected for isomorphous compounds, they are quite similar. To evaluate the small differences between the EPR parameters, the powder spectrum corresponding to $Cu(glyglygly)Br\cdot1\cdot5H_2O$ was simulated using the

parameters determined in the single crystal study. This simulation is shown in Fig. 4a. Then, small changes in the components of the gyromagnetic tensor of the bromide compound were proposed and used to simulate the powder spectrum of $Cu(glyglygly)Cl \cdot 1 \cdot 5H_2O$. This simulated spectrum is represented in Fig. 4b (dotted line), and the corresponding parameters are given in Table 6. The similarity of the EPR results for the compounds strongly suggests a similar electronic structure of Cu(II) in both lattices. Differences between bromide and chlorine ligands to copper could not be detected in the powder EPR spectra.

Concluding remarks

The single EPR line for **B** in xy and zy planes indicates the presence of magnetic exchange coupling

$$H_{ex}^{AB} = \Sigma_{ij} J_{AB}^{ij} S_{iA} \cdot S_{jB}, \tag{5}$$

where the sum extends on the pairs of magnetically inequivalent Cu(II) ions at neighboring i,j copper sites A and B. It is possible to estimate a lower bound for the magnitude of J_{AB} from the experimental data through[14]

$$J_{AB} \geq \frac{1}{2} (g_A - g_B)\mu_B B = 0.01 \text{ cm}^{-1}. \tag{6}$$

Magnetically non-equivalent copper ions iA and jB are connected by two types of chemical pathways which could be important for the transmission of the

exchange interaction. One of them is a $H \cdots Br - Cu - N - H \cdots Br$ hydrogen bond net (see Fig. 2) which connects inequivalent neighbor copper ions 5.09 Å apart. The other also connects nonequivalents neighboring Cu(II) ions 10.98 Å apart though the σ-skeleton of the tripeptide molecule (see Fig. 1).

The role of hydrogen bonds as superexchange paths between copper ions has been studied recently by us in two systems.[15,16] In both cases pairs of H-bonds give rise to antiferromagnetic exchange parameters $J \sim 0.5$ K, much larger than needed to collapse into one band the EPR spectra of types A and B copper ions.

The role of the σ-skeleton of amino acids as superexchange paths has been studied for aspartic[17] and glutamic acid.[18] In the case of aspartic acid this coupling is $J \simeq -5.6$ K, surprisingly large for the number of diamagnetic atoms involved in the path (five). In the case of glutamic acid, with six diamagnetic ions in the path, the superexchange interaction parameter is $J \sim 1$ K. Because of the length and higher geometric complexity of the σ-skeleton of triglycine, it is not possible to estimate the value of J_{AB} through this path. However, we think that its role within the exchange network of $Cu(glyglygly)Br \cdot 1 \cdot 5H_2O$ and $Cu(glyglygly)Cl \cdot 1 \cdot 5H_2O$ is much less important than that of the H-bonds discussed above.

Acknowledgments

Table 6. Values of the parameters in the spin Hamiltonian used to calculate the powder EPR spectra of $Cu(glyglygly)X \cdot 1 \cdot 5H_2O$ (X = Br, Cl) isomorphous compounds

Gyromagnetic tensors

$Cu(glyglygly)Br \cdot 1 \cdot 5H_2O$	$Cu(glyglygly)Cl \cdot 1 \cdot 5H_2O$
$(g^2)_{a'a} = 4.4608$	$(g^2)_{a'a} = 4.4408$
$(g^2)_{bb} = 5.0909$	$(g^2)_{bb} = 5.1109$
$(g^2)_{cc} = 4.3579$	$(g^2)_{cc} = 4.3379$
$(g^2)_{a'c} = 0.1901$	$(g^2)_{a'c} = 0.1901$

Coefficients in the expansion of the angular variation of the EPR linewidth (ΔB) for both compounds.[a]

$A_1 = 143.4$
$A_2 = 194.4$
$A_3 = 136.2$
$A_4 = 0.9$
$A_5 = -17.1$
$A_6 = 2.0$

[a] ΔB is given by: $\Delta B(\theta, \phi) = A_1 \sin^2\theta\cos^2\phi + A_2\sin^2\theta\sin^2\phi + A_3\cos^2\theta + A_4\sin2\theta\cos\phi + A_5 [g_A (\theta, \phi) - g_B (\theta, \phi)] + A_6 \cos^4\theta$.

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