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Contribution from the Department of Chemistry,
University of North Carolina, Chapel Hill, North Carolina 27514

Oxidative Decarboxylation of Glycylglycyl-L-histidine by Copper(II) Hydroxide: X-Ray Structural Characterization of α,β-Didehydroglycylglycylhistaminatocopper(II) Dihydrate

PATRICE DE MEESTER and DEREK J. HODGSON*

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Red crystals of the title complex were obtained by the reaction of copper(II) hydroxide with glycylglycyl-L-histidine in water (ratio of metal:ligand 1:1). The structure of this complex, $C_9H_{11}O_2N_5Cu\cdot 2H_2O$, has been determined from three-dimensional x-ray counter data by Patterson and Fourier methods. The compound crystallizes in the triclinic space group $P\bar{1}$, with two formula units per cell. The cell constants are a = 7.315 (2) Å, b = 10.110 (3) Å, c = 9.609 (3) Å, α = 71.59 (3)°, β = 86.66 (2)°, and γ = 110.74 (2)°. Full-matrix least-squares refinement using 1636 independent reflections has reached R = 0.038. The central copper(II) atom is square planar, coordinating to four nitrogen atoms of the ligand. The metal does not show any weak interaction (less than 3.0 Å) with any fifth or sixth donor atom. The distances Cu–N(amino), Cu–N(peptide 1), Cu–N(peptide 2), and Cu–N(imidazole) are 2.028 (4), 1.898 (3), 1.960 (3), and 1.941 (3) Å, respectively. The two trans N–Cu–N angles are 165.9 (1) and 177.0 (1)°. The shortest separation between copper atoms in neighboring molecules is 3.946 Å. The major feature of the structure is that the original ligand has undergone an oxidative decarboxylation. The C^α atom of the histidine residue has lost its carboxylate group and the observed C^α–C^β distance of 1.340 (6) Å, much shorter than the value of 1.536 (3) Å in histidine, is consistent with a formal double bond between these atoms. All other distances in the ligand are normal. The two water molecules, while not involved in the copper coordination sphere, participate in several hydrogen bonds.

Introduction

Since the tripeptide glycylglycyl-L-histidine (glyglyhis) contains the same potential metal binding sites as the terminal portion of serum albumin,[1-3] there has been an enormous amount of recent chemical research on the interactions of copper(II) ions with this tripeptide.[4-7] A recent crystallographic study of the *N*-methylamide derivative of the complex confirmed the earlier postulate[4] that the complex has a square-planar structure with the copper atom coordinated to four nitrogen atoms of the tripeptide.[7] In reacting the tripeptide with freshly prepared copper(II) hydroxide, we obtained excellent crystals of what we initially assumed to be the parent complex, Cu(glyglyhis). Upon crystallographic examination, however, we discovered that the tripeptide had undergone decarboxylation, but that the complex retained the square-planar geometry at copper.[8] The results of our

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structural study are reported here.

Experimental Section

Synthesis. The title complex was prepared in the following manner: 0.5×10^{-3} mol of freshly prepared and wet copper(II) hydroxide was mixed with 0.5×10^{-3} mol of glycylglycyl-L-histidine in 15 mL of water. (Glycylglycyl-L-histidine was obtained from Fox Chemical Co. Its purity was verified by amino acid analysis which confirmed the correct 2:1 ratio of gly to his.) The resulting solution became violet, and after 15 h red prismatic crystals appeared. The crystals can be recrystallized after redissolution in boiling water. Our choice of the metal hydroxide as a starting material was guided by our success in preparing single crystals of Cu^{II}(L-methionine)$_2$ and Zn^{II}(L-methionine)$_2$[9] in a similar fashion, and also because this method has been proved useful in the preparation of other Cu(II)–peptide complexes.[10,11]

Collection and Reduction of the X-Ray Data. On the basis of precession and Weissenberg photographs, the crystals were assigned to the triclinic system. The presence of the L-isomer of histidine in the starting ligand suggested to us the noncentrosymmetric space group $P1$, but the subsequent successful solution and refinement of the structure showed that the histidine underwent an oxidative decarboxylation resulting in the loss of its chirality. Therefore, the correct space group was assigned as $P\bar{1}$. The cell constants, obtained by least-squares methods, are $a = 7.315$ (2) Å, $b = 10.110$ (3) Å, $c = 9.609$ (3) Å, $\alpha = 71.59$ (3)°, $\beta = 86.66$ (2)°, and $\gamma = 110.74$ (2)°. A density of 1.72 g cm^{-3} calculated for two formula units in the cell, compares well with a value of 1.70 (3) g cm^{-3} observed by flotation in a bromoform/carbon tetrachloride solution. Data were collected on a Picker FACS-I diffractometer from a crystal with faces (100), ($\bar{1}$00), (010), (0$\bar{1}$0), (001), and (00$\bar{1}$). The distances between these opposite pairs of faces were approximately 0.06, 0.19, and 0.25 mm, respectively. The crystal was mounted approximately parallel to the c axis. Intensity data using Mo Kα radiation (graphite monochromator) were collected at a takeoff angle of 1.3°. At this angle, the intensity of a typical reflection was approximately 90% of maximum as a function of the takeoff angle. The data were collected by the θ–2θ scan technique at a scan rate of 1°/min. Allowance was made for the presence of both Kα_1 and Kα_2 radiations, the peaks being scanned from −0.85° in 2θ below the calculated Kα_1 peak position to +0.85° above the calculated Kα_2 position. Stationary–counter, stationary–crystal background counts of 20 s were taken at each end of the scan. A unique data set having $2 \leq 2\theta \leq 50°$ was gathered. A total of 2313 intensities was recorded. The intensities of three standard reflections, measured after every 100 reflections, showed no statistically significant decline. Data processing was carried out as described by Corfield et al.[12] After correction for background, the intensities were assigned standard deviations according to the formula[12]

$$\sigma(I) = [C + 0.25(t_s/t_b)^2(B_H + B_L) + (pI)^2]^{1/2}$$

and the value of p was chosen as 0.04. The values of I and $\sigma(I)$ were corrected for Lorentz–polarization effects. In view of the modest size of the crystal and the small value of its absorption coefficient [μ(Mo Kα) = 18.5 cm^{-1}], the data were not corrected for absorption. Of the 2313 data collected, 1636 were greater than 2.6 times their estimated standard deviations. Only these data were used in the subsequent structure analysis.

Table I. Fractional Coordinates with Esd's in Parentheses

Atom	x	y	z
Cu	0.23481 (8)	0.87314 (6)	0.12859 (6)
N(1)	0.2375 (5)	0.6919 (4)	0.1004 (4)
C(1)	0.2286 (7)	0.5620 (5)	0.1998 (5)
N(2)	0.2390 (6)	0.4666 (4)	0.1341 (4)
C(2)	0.2524 (7)	0.5356 (5)	−0.0148 (5)
C(3)	0.2529 (6)	0.6764 (5)	−0.0381 (5)
C(4)	0.2603 (7)	0.7891 (5)	−0.1772 (5)
C(5)	0.2654 (7)	0.9281 (5)	−0.1989 (5)
N(3)	0.2626 (5)	0.9849 (4)	−0.0846 (4)
C(6)	0.2628 (7)	1.1238 (5)	−0.1194 (5)
O(1)	0.2733 (6)	1.2120 (4)	−0.2469 (3)
C(7)	0.2463 (6)	1.1755 (4)	0.0106 (4)
N(4)	0.2245 (5)	1.0517 (4)	0.1478 (4)
C(8)	0.2180 (6)	1.0671 (5)	0.2754 (5)
O(2)	0.2271 (5)	1.1839 (3)	0.3020 (3)
C(9)	0.1934 (7)	0.9257 (5)	0.4057 (5)
N(5)	0.1974 (5)	0.8025 (4)	0.3545 (4)
W(1)	0.4831 (5)	0.2669 (4)	0.4840 (3)
W(2)	0.1910 (5)	0.4588 (4)	0.6085 (5)

Table II. Fractional Coordinates of the Hydrogen Atoms

Atom	Attached to	x	y	z
H(1)	C(1)	0.211	0.544	0.312
H(2)	N(2)	0.217	0.368	0.184
H(3)	C(2)	0.254	0.479	−0.083
H(4)	C(4)	0.258	0.752	−0.267
H(5)	C(5)	0.229	0.985	−0.292
H(6)	C(7)	0.124	1.204	−0.004
H(7)	C(7)	0.386	1.272	−0.002
H(8)	C(9)	0.053	0.880	0.489
H(9)	C(9)	0.319	0.953	0.444
H(10)	N(5)	0.071	0.720	0.407
H(11)	N(5)	0.309	0.782	0.392
H(12)	W(1)	0.376	0.229	0.438
H(13)	W(1)	0.415	0.272	0.562
H(14)	W(2)	0.334	0.559	0.572
H(15)	W(2)	0.246	0.397	0.654

Solution and Refinement of the Structure. The structure was solved by standard Patterson and difference Fourier methods. All least-squares refinement in this analysis was carried out on F, the function minimized being $\sum w(|F_o| - |F_c|)^2$ and the weights w being taken as $4F_o^2/\sigma^2(F_o^2)$. In calculations of F_c, the atomic scattering factors for Cu, O, N, and C were from International Tables[13] and those for H from Stewart, Davidson, and Simpson.[14] The effects of the anomalous dispersion of Cu were included in the calculation of F_c, the values of $\Delta f'$ and $\Delta f''$ being taken from Cromer and Liberman.[15] The structure was first solved and refined in the noncentrosymmetric space group $P1$, with two independent molecules totaling 38 atoms. Isotropic least-squares refinement of these atoms led to values of the conventional agreement factors

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$$

and

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$$

of 0.257 and 0.285. A subsequent difference Fourier map failed to show any carboxylate group on each of the two independent ligands. Further, the arrangement of the two molecules was essentially centrosymmetric. At this point, it was evident that the molecule had lost its chirality, and isotropic least-squares refinement in space group $P\bar{1}$ of only one independent formula unit reduced R_1 and R_2 to 0.097 and 0.107, respectively. After anisotropic refinement, the 15 independent hydrogen atoms could be located and were included in refinement as fixed atom contributions with B's set at 4.0 Å^2. Inspection of the observed and calculated structure amplitudes near the end of the refinement indicated that there were significant errors in the data due to secondary extinction. A correction of the type derived by Zachariasen[16] was therefore applied. The refined value of the extinction coefficient was 1.6 (4) $\times 10^{-7}$. No parameter shift in the final cycle of least-squares refinement was greater than 0.02σ, which demonstrates that the refinement had converged. A final difference Fourier revealed no significant electron density, with no peak higher than 0.45 e Å^{-3}. The final agreement factors R_1 and R_2 are 0.038 and 0.042, respectively. The positional parameters for all atoms are presented in Tables I and II. A list of the anisotropic thermal parameters for all nonhydrogen atoms and a compilation of observed and calculated structure factors are available as supplementary material.

Description of the Structure and Discussion

The complex, referred to hereafter as CuGGHd, is shown in Figure 1. The copper atom binds to four nitrogen atoms of the ligand arranged in an approximate square plane. The distances Cu–N(5)(amino), Cu–N(4)(peptide 1), Cu–N(3)(peptide 2), and Cu–N(1)(imidazole) are 2.028 (4), 1.898 (3), 1.960 (3), and 1.941 (3) Å, respectively. The Cu–N distances are compared in Table III to those found in other related complexes.[7,10,17,18] Our results confirm the observation[10] that the Cu–N distances depend on the nature of that nitrogen

Table III. Comparison of the Copper Coordination in CuGGHd with Other Complexes

Complex	Cu-N (amino)	Cu-N (peptide 5,5)^a	Cu-N (peptide 5,6)	Cu-N (imidazole)
CuGGHd^b	2.028 (4)	1.898 (3)	1.960 (3)	1.941 (3)
CuGGHa	2.047 (4)	1.904 (4)	1.950 (4)	1.962 (4)
CuGH	2.043 (7)		1.991 (8)	1.977 (8)
CuGHG	1.997 (3)		1.951 (3)	1.957 (3)
CuGHG·NaClO$_4$	2.01		1.93	1.93
CuGGGGG	2.033 (7)	1.913 (7)	1.950 (7)^c	

[a] The numbers indicate the size of the rings shared by the nitrogen atoms. [b] Abbreviations used in this table and Table V, and the text: CuGGHd, the title complex; CuGGHa, copper(II) glycylglycyl-L-histidine-*N*-methylamide;[7] CuGH, glycyl-L-histidinatocopper(II);[10a] CuGHG, glycyl-L-histidinylglycinatocopper(II)-2.5-water;[17] CuGHG·NaClO$_4$, glycyl-L-histidinylglycinatocopper(II)-sodium perchlorate-water;[18] CuGGGGG, disodium tetraglycylglycinatocopper(II)-4.5-water.[10b] [c] For CuGGGGG, this N atom is shared by a five-membered ring and a terminal glycyl group.

Table IV. Least-Squares Planes in CuGGHd

Plane no.	Description	Atom^a	Δ, Å
I	Copper environment	N(1)	−0.003
		N(3)	0.003
		N(4)	−0.004
		N(5)	0.003
		[Cu]	0.027
II	Imidazole	N(1)	0.001
		C(1)	−0.004
		N(2)	0.005
		C(2)	−0.004
		C(3)	0.002
III	Peptide 1	C(7)	−0.019
		C(6)	0.011
		O(1)	0.004
		N(3)	0.029
		C(5)	−0.024
IV	Peptide 2	C(9)	−0.003
		C(8)	0.005
		O(2)	−0.001
		N(4)	−0.002
		C(7)	0.001
V	Vinyl group	C(3)	0.001
		C(4)	−0.002
		C(5)	0.002
		N(3)	−0.001

[a] In brackets, the atom not used in defining the plane.

atom (amino, peptide, or imidazole) and the size of the rings in which it is involved (five- and five- or five- and six-membered rings). All distances in Table III agree well, but those reported for CuGH (see Table III for abbreviations) and CuGHG·NaClO$_4$ are less consistent. These discrepancies probably reflect the inherent standard deviations in these two structures (the former has been refined from visually estimated data while no standard deviations have been reported for the latter). The cis angles at the copper atom range from 83.0 (1) to 99.4 (1)° and the trans angles are 165.9 (1) and 177.0 (1)°. In CuGGHa, the corresponding values for the trans angles are 165.0 (2) and 176.0 (2)°. As is shown in Table IV, the copper atom is displaced 0.027 Å out of the mean plane formed by N(1), N(3), N(4), and N(5) (plane I in Table IV). In Table V are compared the Cu–N–C angles found in this structure with those in other pertinent complexes. This comparison shows that the angle at the nitrogen atom depends on the same factors mentioned above: its nature and the ring size involved. All details concerning bond lengths and angles in this structure are given in Table VI. Within the ligand, all bond lengths are normal and not significantly different from those found in CuGGHa, except for the three bonds C(3)–C(4), C(4)–C(5), and C(5)–N(3) affected by the oxidative decarboxylation. Decarboxylation at C(5) and dehydrogenation at C(4) have occurred, resulting in a formal double bond of length 1.340 (6) Å between these two atoms. In CuGGHa and CuGHG, the corresponding bond length is 1.517 (6) and 1.536 (5) Å, respectively. In L-histidine itself, it is 1.536 (3) Å. As expected, the adjacent bonds C(3)–C(4) and C(5)–N(3) are slightly shorter than in L-histidine and these other copper complexes. The planarity of the group C(3), C(4), C(5), and N(3) can be estimated from Table IV (plane V). The angle between this plane and the imidazole plane (plane II) is 3.1°. Because these two planes are almost parallel the angle of 2.1° between the imidazole ring and the plane formed by the four-coordinated nitrogen atoms is considerably smaller than those found in CuGGHa and CuGHG, where they are 19 and 15°, respectively.

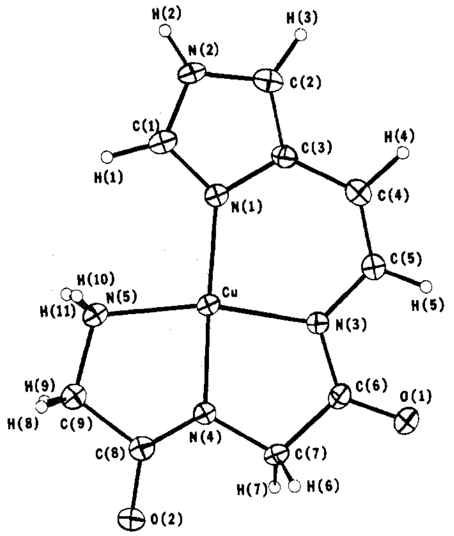

Figure 1. View of the complex α,β-didehydroglycylglycylhistaminatocopper(II), CuGGHd. Hydrogen atoms are drawn as spheres of arbitrary size; other ellipsoids are at the 40% probability level.

The only other bond which differs significantly in CuGGHd and CuGGHa is the C–N(amino) bond, which has the values of 1.485 (5) and 1.454 (6) Å, respectively. In CuGGHa, the terminal amino nitrogen atom is not hydrogen bonded, while in the title complex it is. In CuGHG, where the amino ni-

Table V. Comparison between Angles Cu-N-C in CuGGHd and in Other Systems

	Angle Cu-N-C				
Complex	N (amino *5*)^a	N (peptide *5,5*)	N (peptide 5,*6*)	N (peptide *5*,6)	N (imidazole *6*)
CuGGHd^b	110.2 (2)	117.2–120.8 (3)	115.8 (3)	125.9 (3)	123.8 (3)
CuGGHa	110.0 (3)	117.0–119.0 (3)	116.0 (3)	126.0 (3)	
CuGH	110.7 (6)		115.9 (7)	127.1 (6)	122.6 (8)
CuGHG	109.2 (2)		116.3 (2)	126.8 (2)	124.7 (3)
CuGGGGG	109.4 (5)	115.1–119.6 (5)	117.5 (5)^c	125.5 (5)^c	

[a] The numbers indicate the size of the rings at the N atom. The ring concerned is italicized. [b] See abbreviations and references in Table III. [c] For CuGGGGG, this N atom is shared by a five-membered ring and by a terminal glycyl group.

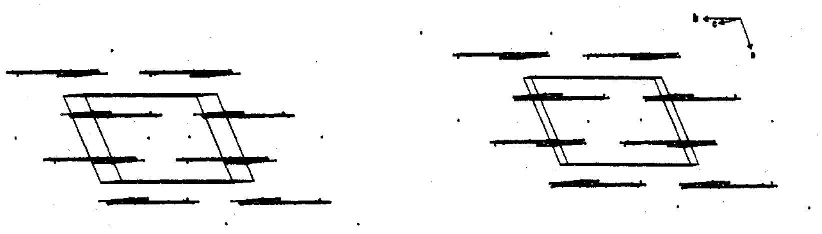

Figure 2. Stereoscopic view of the packing in the crystals of CuGGHd·$2H_2O$; water molecules are shown as the unbonded open circles.

Table VI. Bond Lengths (Å) and Bond Angles (deg) with Esd's in Parentheses

	Lengths		
Cu-N(1)	1.941 (3)	Cu-N(4)	1.898 (3)
Cu-N(3)	1.960 (3)	Cu-N(5)	2.028 (4)
N(1)-C(1)	1.335 (5)	N(3)-C(6)	1.336 (5)
C(1)-N(2)	1.329 (5)	C(6)-O(1)	1.246 (5)
N(2)-C(2)	1.360 (6)	C(6)-C(7)	1.513 (6)
C(2)-C(3)	1.368 (6)	C(7)-N(4)	1.457 (5)
C(3)-N(1)	1.391 (5)	N(4)-C(8)	1.285 (5)
C(3)-C(4)	1.440 (6)	C(8)-O(2)	1.265 (5)
C(4)-C(5)	1.340 (6)	C(8)-C(9)	1.518 (6)
C(5)-N(3)	1.393 (5)	C(9)-N(5)	1.485 (5)
	Angles		
N(1)-Cu-N(3)	94.6 (1)	N(5)-Cu-N(1)	99.4 (1)
N(3)-Cu-N(4)	83.0 (1)	N(1)-Cu-N(4)	177.0 (1)
N(4)-Cu-N(5)	83.0 (1)	N(3)-Cu-N(5)	165.9 (1)
Cu-N(1)-C(1)	130.3 (3)	C(5)-N(3)-C(6)	118.1 (3)
Cu-N(1)-C(3)	123.8 (3)	N(3)-C(6)-O(1)	126.3 (4)
C(3)-N(1)-C(1)	105.9 (3)	N(3)-C(6)-C(7)	115.7 (3)
N(1)-C(1)-N(2)	111.4 (4)	O(1)-C(6)-C(7)	118.0 (4)
C(1)-N(2)-C(2)	107.4 (3)	C(6)-C(7)-N(4)	108.3 (3)
N(2)-C(2)-C(3)	107.8 (4)	C(7)-N(4)-C(8)	121.6 (3)
N(2)-C(2)-C(3)	107.8 (4)	C(7)-N(4)-C(8)	121.6 (3)
C(2)-C(3)-N(1)	107.5 (4)	Cu-N(4)-C(7)	117.2 (3)
C(2)-C(3)-C(4)	127.9 (4)	Cu-N(4)-C(8)	120.8 (3)
N(1)-C(3)-C(4)	124.6 (4)	N(4)-C(8)-O(2)	127.3 (4)
C(3)-C(4)-C(5)	127.2 (4)	N(4)-C(8)-C(9)	114.1 (4)
C(4)-C(5)-N(3)	123.6 (4)	O(2)-C(8)-C(9)	118.6 (4)
Cu-N(3)-C(5)	125.9 (3)	C(8)-C(9)-N(5)	111.7 (3)
Cu-N(3)-C(6)	115.8 (3)	Cu-N(5)-C(9)	110.0 (2)

Hydrogen Bonding, A–H···B

A–H···B[a]	A···B	H···B	A–H–B
N(2)–H(2)···O(2)^{I}	2.770 (5)	1.880	166
N(5)–H(11)···W(1)^{II}	3.043 (5)	2.083	167
W(1)–H(12)···O(2)^{I}	2.733 (4)	1.814	163
W(1)–H(13)···O(1)^{III}	2.716 (5)	1.856	159
W(2)–H(14)···W(1)^{II}	2.771 (5)	1.684	166
W(2)–H(15)···O(1)^{III}	2.737 (5)	1.899	159

[a] Roman superscripts refer to atom in the following positions: I, $x, y-1, z$; II, $1-x, 1-y, 1-z$; III, $x, y-1, 1+z$.

Table VII. Dihedral Angles in CuGGHd

Atoms	Angle, deg
N(1)-C(3)-C(4)-C(5)	4.1[a]
C(3)-C(4)-C(5)-N(3)	−0.5
C(4)-C(5)-N(3)-C(6)	−178.2
C(5)-N(3)-C(6)-O(1)	−3.1
C(5)-N(3)-C(6)-C(7)	176.2
N(3)-C(6)-C(7)-N(4)	−2.6
O(1)-C(6)-C(7)-N(4)	176.8
C(6)-C(7)-N(4)-C(8)	176.2
C(7)-N(4)-C(8)-O(2)	0.5
C(7)-N(4)-C(8)-C(9)	179.6
N(4)-C(8)-C(9)-N(5)	4.2
O(2)-C(8)-C(9)-N(5)	−176.6

[a] Values are taken as positive when far atom rotates anticlockwise relative to near atom to be eclipsed.

trogen is also hydrogen bonded, one finds a bond length of 1.469 (5) Å. This suggests that hydrogen bonding at the terminal amino nitrogen atom may slightly increase the C–N bond length. The planarity of the two peptide groups can be estimated from Table IV (planes III and IV). The main dihedral angles are listed in Table VII.

At the molecular level, the complexes CuGGHd and CuGGHa present many similarities, despite the differences discussed above. At the crystal level, these two structures, which contain two similar complex molecules and two water molecules per cell, would be expected to have a very similar type of packing. This is, however, not the case. The packing in the title complex is represented in Figure 2. It can be seen that individual complex molecules are arranged in a parallel manner and that these molecules partially overlap. The distance between two molecules related by a center of inversion at the origin is 3.38 Å. One of the two water molecules, W(2), is almost in the same plane (0.08 Å away). In CuGGHa, the water molecules are weakly bonded to the copper atoms at distances of 2.61 and 2.88 Å for the two independent ligands, and each water molecule is situated in the direction opposite to the terminal *N*-methylamide group, resulting in the absence of overlapping between the two independent molecules or any of their neighbors.

There are several hydrogen bonds in the structure of the title complex. The terminal amino nitrogen is involved in one hydrogen bond of length 3.043 (5) Å with a water molecule. The protonated, uncoordinated imidazole nitrogen atom N(2) forms a hydrogen bond of length 2.770 (5) Å with a carboxylate oxygen atom of an adjacent molecule. All hydrogen atoms belonging to the water molecules are also involved in hydrogen bonding. W(1) forms hydrogen bonds of lengths 2.733 (4) and 2.716 (5) Å with two carboxylate oxygen atoms. W(2) is hydrogen bonded to W(1) and to a carboxylate oxygen atom with bonds of lengths 2.771 (5) and 2.737 (5) Å, respectively. Other details concerning these hydrogen bonds are given in Table VI.

The oxidative decarboxylation of glycylglycyl-L-histidine by copper(II) hydroxide was not anticipated by us but is not without precedent. The copper(II)-catalyzed decarboxylation of histidine to histamine and carbon dioxide has been proposed[19] to involve the formation of the six-membered Cu–N(1)–C(3)–C(4)–C(5)–N(3) ring observed here. Moreover, it has been noted that in the metal-catalyzed decarboxylation of histidine concomitant oxidation of the imidazole ring occurs.[20] In the present case, as a result of the crystallographic experiment, we are able to demonstrate that oxidation occurs in the histidine side chain. It is also noteworthy that oxidative decarboxylations of organic acids by metal salts (notably by lead tetraacetate in the presence of copper(II) acetate but also by other metal ions) have been described by other workers,[21-27] but in these previous examples the product is the stable, oxidized organic moiety (typically an olefin). The present example is the first, to our knowledge, in which the resulting product remains tightly coordinated to the metal. The essential stability of the complex is demonstrated by our ability to recrystallize it from boiling water.

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Supplementary Material Available: A table of anisotropic thermal parameters and listing of observed and calculated structure amplitudes (11 pages). Ordering information is given on any current masthead page.

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Contribution from the School of Chemical Sciences,
University of Illinois, Urbana, Illinois 61801

Magnetic Exchange Interactions in Transition-Metal Dimers. 12. Structural and Magnetic Characterization of the Di-μ(1,3)-azido Complex $[Cu_2(Me_5dien)_2(N_3)_2](BPh_4)_2$ and Similar Di-μ(1,3)-azido Copper(II) Dimers. Unusual Zero-Field Splitting in the Electron Paramagnetic Resonance Spectra[1]

TIMOTHY R. FELTHOUSE and DAVID N. HENDRICKSON*[2]

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The crystal and molecular structure of $[Cu_2(Me_5dien)_2(N_3)_2](BPh_4)_2$, where Me_5dien is 1,1,4,7,7-pentamethyldiethylenetriamine, has been determined using heavy-atom, least-squares, x-ray methods for 3140 reflections measured on a computer-automated four-circle diffractometer. The complex crystallizes as dark green prisms belonging to the space group $P2_1/n$ with two formula weights in a unit cell with $a = 12.798$ (2) Å, $b = 19.538$ (3) Å, $c = 13.072$ (2) Å, $\beta = 93.64$ (1)°, $\rho_{obsd} = 1.215$ g/cm^3, and $\rho_{calcd} = 1.218$ g/cm^3. The structure was refined to final discrepancy indices of $R_F = 0.051$ and $R_{wF} = 0.058$. The complex consists of discrete $[Cu_2(Me_5dien)_2(N_3)_2]^{2+}$ cations located about centers of inversion and BPh_4^- anions. The five-coordinate geometry about the copper(II) ion is intermediate between square pyramidal and trigonal bipyramidal. The two azide ions, which are parallel, are bridging in an end-to-end fashion between the two copper(II) ions. Each azide ion bonds at appreciably different distances, Cu–N = 1.985 (4) and 2.252 (5) Å, to the two copper(II) ions. The copper(II) ions are only 0.0504 (5) Å out of the azide plane and the Cu–Cu distance is 5.2276 (7) Å. Variable-temperature (4.2–270 K) magnetic susceptibility and EPR (X- and Q-band) data are reported for this Me_5dien and for five other analogous di-μ(1,3)-azido copper(II) dimers of the composition $[Cu_2(\text{"dien"})_2(N_3)_2](X)_2$, where "dien" is variously Et_5dien or dpt (dipropylenetriamine) and X^- is BPh_4^- or ClO_4^-. Antiferromagnetic exchange interactions are found for five of the six compounds with exchange parameters ranging from -3.1 cm^{-1} (Me_5dien, ClO_4^-) to -11.1 cm^{-1} (Et_5dien, ClO_4^-). These results are discussed in terms of the local copper(II) ion geometry which is enforced by the "dien" ligand and various other structural and electronic factors. The X-band EPR spectra for powdered *undoped* samples of the BPh_4^- salts exhibit copper(II) hyperfine structure as well as zero-filled splittings which are appropriate for the triplet state of such a dimer. The magnitude of zero-field splitting observed for these complexes greatly exceeds that calculated for purely dipolar interactions and, as such, the presence of pseudodipolar interactions is suggested. Pseudodipolar zero-field interactions, which result from spin–orbit admixture of excited states and depend on the exchange interactions in the excited states, were unexpected and indicate exchange interactions in the excited states that are greater than those observed for the ground state.

Introduction

In a previous paper in this series,[3] the magnitude of the magnetic exchange interaction between two copper(II) ions was found to be dependent upon the oribtal ground state composition of the copper(II) ions. A series of complexes of the type $[Cu_2(\text{"dien"})_2(C_2O_4)](BPh_4)_2$ was studied in which the relatively inflexible oxalate dianion ($C_2O_4^{2-}$) bridges the two copper(II) ions in a bis-bidentate fashion and in which "dien" is dien (diethylenetriamine), dpt (dipropylenetriamine), Me_5dien (1,1,4,7,7-pentamethyldiethylenetriamine), or Et_5dien (1,1,4,7,7-pentaethyldiethylenetriamine). Consequently, the local environment about the copper(II) ion could be changed from square pyramidal with dien to trigonal bipyramidal with Et_5dien.

When two azide ions are substituted for the oxalate dianion in the above complexes, two types of bridging modes could

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