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Molecular Structure and Spectroscopic Properties of a Copper(II) Complex with Mugineic Acid, a Novel Amino Acid from Gramineous Plants

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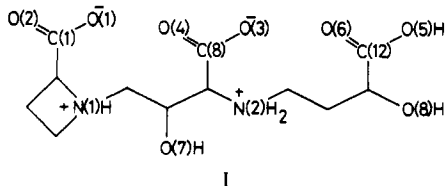
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The X-ray crystallographic analysis of the single-crystal mugineic acid-Cu^{II} complex showed that the mugineic acid acts as a hexadentate ligand. The coordination of Cu(II) involved the azetidine nitrogen, N(1), secondary amine nitrogen, N(2), and both terminal carboxylate oxygens, O(1) and O(5), in an approximate planar coordination, while the hydroxyl oxygen, O(8), and intermediate carboxylate oxygen, O(4), are bonded axially. Although the axial bond lengths are 2.477 (4) (Cu-O(8)) and 2.557 (4) Å (Cu-O(4)), the axial Cu-O bonds markedly deviate from the normal of the basal plane. The electron spin resonance (ESR), electronic, and circular dichroism (CD) spectral characteristics for the mugineic acid-Cu^{II} complex were as follows: $g_{\parallel} = 2.277$, $g_{\perp} = 2.060$, and $A_{\parallel} = 175.9 \times 10^{-4} \text{ cm}^{-1}$ (ESR); $\lambda_{\text{max}} = 14600 \text{ cm}^{-1}$ (ϵ 65) (electronic); $\lambda_{\text{max}} = 16950$ ($\Delta\epsilon$ +0.09) and 13330 cm^{-1} (-0.32) (CD). Mugineic acid is one of the low molecular weight naturally occurring hexadentate chelators.

Introduction

In an aerobic environment, iron exists exclusively in the ferric state and, as such, quantitatively forms insoluble ferric hydroxide at neutral pH. So that the biological unavailability of this vital element could be combated, microbes have developed powerful low molecular weight chelators known as siderophores which generally contain three secondary hydroxamate or catecholate groups.¹ On the other hand, several higher plants such as rice and oats also excrete a novel iron-chelating agent from their roots in order to effectively absorb iron under the condition of its deficiency.² The salient example of this class is mugineic acid ((2*S*,2'*S*,3'*S*,3''*S*)-*N*-[3-((3-carboxy-3-hydroxypropyl)amino)-3-carboxy-2-hydroxypropyl]azetidine-2-carboxylic acid) isolated from the roots of water-cultured barley (*Hordeum vulgare* L. var. Minorimugi).³ This novel amino acid is capable of solubilizing ferric hydroxide effectively within the pH range 4-9, and its addition to the medium of the water-cultured rice plant at pH 7 increases the content of chlorophyll. The iron-solubilizing action of mugineic acid is strongly inhibited by the presence of divalent metal ions, especially Cu(II) ion.^{2,4} However, nothing is known of the coordination chemistry of this compound. As part of our program to elucidate the metal complexes of mugineic acid, a naturally occurring metal chelator, we report here the molecular structure and spectroscopic properties of a single crystal of mugineic acid-Cu^{II} complex. Of special interest is the fact that mugineic acid is one of the natural hexadentate chelators with the low molecular weight.

In this paper, the coordination donor atoms of mugineic acid are numbered in the same manner as used in reporting the crystal structure as shown in I.



Experimental Section

Crystal Preparation of the Mugineic Acid-Cu^{II} Complex. The isolation and purification of mugineic acid and its related compounds were carried out according to procedures reported previously.³ Ni-

Table I. Crystal Data for the Mugineic Acid-Cu^{II} Complex Cu(C₁₂H₁₈N₂O₈)

cryst system: monoclinic	space group: $P2_1$
$a = 6.069$ (1) Å	$\beta = 106.4$ (1) ^o
$b = 13.617$ (1) Å	$V = 714.1$ (1) Å ³
$c = 9.005$ (1) Å	$Z = 2$
$D_m = 1.768 \text{ g cm}^{-3}$	$\mu(\text{Cu K}\alpha) = 26.5 \text{ cm}^{-1}$
$D_x = 1.776 \text{ g cm}^{-3}$	

cotianamine was synthesized by using the method of Kristensen et al.⁵ The obtained compounds were checked by elemental analysis and IR and proton NMR spectra. An aqueous solution of 1.0 mM CuSO₄·5H₂O was added to an equimolar mugineic acid solution with the pH neutral. After 10 min at room temperature, the reaction mixture was evaporated to give a blue residue that was crystallized as a platelike crystal from ethanol-isopropyl alcohol. The microanalysis of the mugineic acid-Cu^{II} complex satisfied the molecular formula Cu(C₁₂H₁₈N₂O₈).

Spectroscopic Measurements. Electronic and circular dichroism (CD) spectra of the isolated mugineic acid-Cu^{II} complex were recorded on a Shimadzu double-beam spectrophotometer, Model UV 210-A, and a JASCO J-20c spectropolarimeter, respectively. So that the overlap of electron spin resonance (ESR) hyperfine structures due to naturally abundant copper isotopes (⁶³Cu and ⁶⁵Cu, both $I = 1/2$) could be avoided, the ⁶⁵Cu-enriched complexes were used. ⁶⁵CuSO₄ (99.87%) was obtained from Oak Ridge National Laboratory. The ESR measurements were carried out at 77 K in a glass consisting of 25% ethylene glycol aqueous mixture with the use of a JES-FE-3X spectrometer operating with a 100-kHz magnetic field modulation. The g values were determined with Li-TCNQ ($g = 2.0026$) taken as a standard, and the magnetic field was calibrated against the splitting of Mn(II) in MnO ($\Delta H_{3-4} = 86.9 \text{ G}$).

Crystallographic Data. A single crystal with dimensions of ca. 0.4 × 0.1 × 0.4 mm was used for X-ray study. The diffraction angles and the intensities were measured on a Rigaku-Denki automatic

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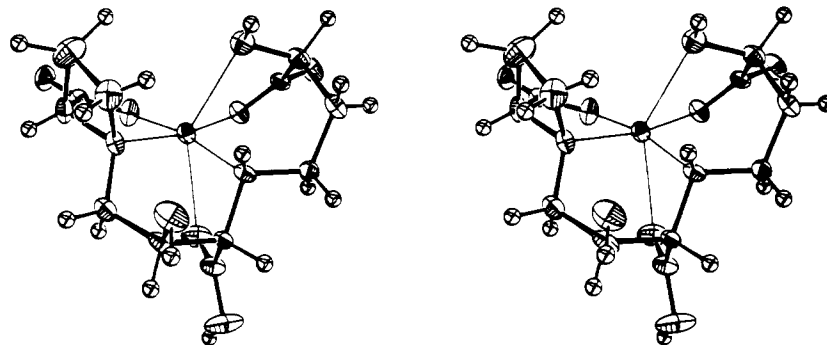


Figure 1. Stereoscopic drawing of the mugineic acid-Cu^{II} complex.

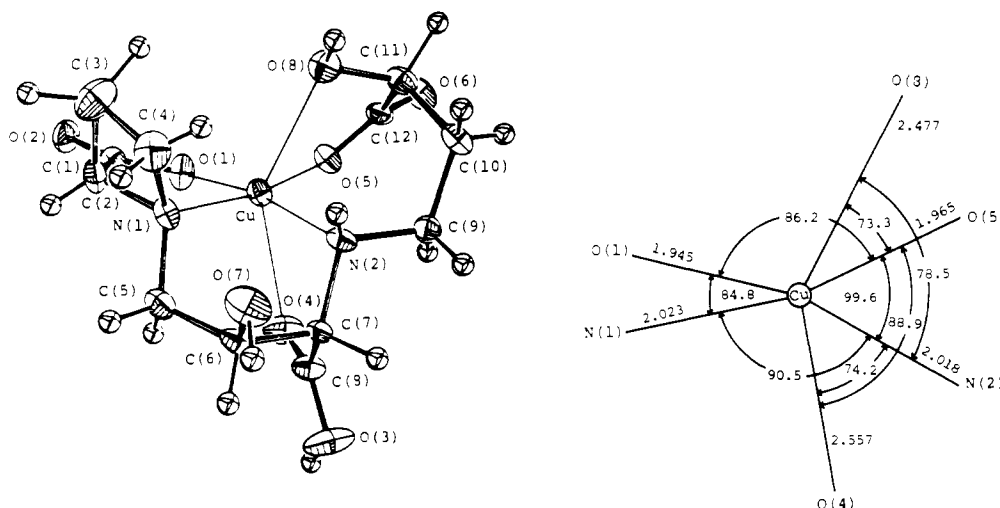


Figure 2. Bond lengths and angles of the Cu(II) coordination site in the mugineic acid-Cu^{II} complex.

four-circle diffractometer with graphite-monochromatized Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$) using the ω - 2θ scan technique. Crystal data are listed in Table I. The intensities of 1384 ($F_o \geq 3\sigma(F_o)$) independent reflections were measured up to a limit of $(\sin \theta)/\lambda = 0.588 \text{ \AA}^{-1}$ ($\theta = 64.99^\circ$).

Structure Determination by X-ray Diffraction. The position of the cupric ion was indicated on a three-dimensional Patterson function. Positions for all the other nonhydrogen atoms were found by successive cycles of Fourier and difference Fourier syntheses coupled with structure factor calculations. The coordinates and anisotropic thermal parameters were refined by the block-diagonal least-squares method, and the difference Fourier syntheses revealed the positions of all hydrogen atoms. The further least-squares refinement, including hydrogen atoms with isotropic temperature factors, was performed with a weighting scheme as follow: $w = 0.579$ for $F_o = 0$, $w = 1/(\sigma[F_o]^2 - 0.859|F_o| + 0.039|F_o|^2)$. The final R value was 0.052, including $F_o = 0$.

Results and Discussion

Description of the Structure. As shown in Figure 1, mugineic acid coordinates with Cu(II) ion as a hexadentate chelator. The X-ray crystallographic analysis of the isolated mugineic acid-Cu^{II} complex indicates a distorted octahedral configuration in which the azetidine nitrogen, N(1), secondary amine nitrogen, N(2), and both terminal carboxylate oxygens, O(1) and O(5), coordinate to Cu(II) as planar donor atoms and the hydroxyl oxygen, O(8), and intermediate carboxylate oxygen, O(4), as axial donors. The coordination of Cu(II) ion is illustrated in Figure 2. The bond lengths and valency angles are summarized in Tables II and III. The equatorial bond lengths to the copper atom are 1.945 (4) (Cu-O(1)), 1.965 (3) (Cu-O(5)), 2.018 (4) (Cu-N(2)), and 2.023 (4) \AA (Cu-N(1)). The axial bond lengths are normal and correspond well to those of usual amino acid-Cu^{II} and peptide-Cu^{II} complexes (1.90–2.04 and 2.30–2.82 \AA for equatorial and axial bonds, respectively). Several comments should be made on the dis-

Table II. Bond Lengths^a (\AA)

Metal-Ligand Bonds			
Cu-O(1)	1.945 (4)	Cu-O(4)	2.557 (4)
Cu-O(5)	1.965 (3)	Cu-O(8)	2.477 (4)
Cu-N(1)	2.023 (4)	Cu-N(2)	2.018 (4)
Ligand Molecule Bonds			
C(1)-C(2)	1.486 (7)	C(1)-O(1)	1.303 (6)
C(1)-O(2)	1.214 (6)	C(2)-C(3)	1.540 (8)
C(2)-N(1)	1.509 (7)	C(3)-C(4)	1.535 (8)
C(4)-N(1)	1.514 (7)	C(5)-C(6)	1.556 (7)
C(5)-N(1)	1.469 (7)	C(6)-C(7)	1.532 (7)
C(6)-O(7)	1.403 (6)	C(7)-C(8)	1.489 (7)
C(7)-N(2)	1.507 (6)	C(8)-O(3)	1.283 (7)
C(8)-O(4)	1.221 (6)	C(9)-C(10)	1.525 (7)
C(9)-N(2)	1.486 (6)	C(10)-C(11)	1.492 (7)
C(11)-C(12)	1.510 (7)	C(11)-O(8)	1.451 (6)
C(12)-O(5)	1.249 (6)	C(12)-O(6)	1.286 (6)

^a Standard deviations are given in parentheses.

tortions of the coordination geometry. As seen in Table IV, which lists the deviations of the donor atoms from the basal plane (root-mean-square deviation is 0.143), the deviation of Cu(II) (0.038 \AA) is less than those of the ligand atoms. Indeed, the deviations of the donor atoms from the basal plane are 0.101, 0.184, -0.110, and -0.160 \AA for N(1), O(5), N(2), and O(1). The valency angles N(2)-Cu-O(1) (168.8°) and N(1)-Cu-O(5) (168.6°) suggest that the coordination geometry around the copper atom slightly distorts from square planar toward tetrahedral. Also, the axial Cu-O bonds markedly deviate from the normal of the basal plane. The inclination angles are 22.2° for O(8) and 14.7° for O(4), and angle O(4)-Cu-O(8) is 144.3° . Probably, these distortions can be accounted for by the steric constraints of both a six-membered chelate ring, CuN(1)C(5)C(6)C(7)N(2), and a

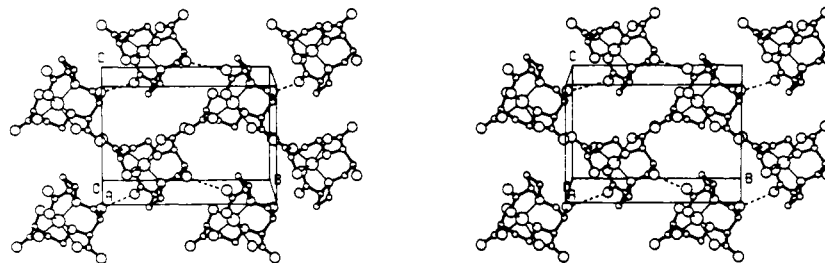


Figure 3. Stereoview of the structure, illustrating the packing of the complexes within the unit cell. Hydrogen bonds are shown by broken lines.

Table III. Bond Angles^a (Deg)

Metal-Ligand Bonds			
O(1)-Cu-O(4)	96.4 (1)	O(1)-Cu-O(5)	86.2 (2)
O(1)-Cu-O(8)	112.5 (1)	O(1)-Cu-N(1)	84.8 (2)
O(1)-Cu-N(2)	168.8 (2)	O(5)-Cu-O(4)	88.9 (1)
O(5)-Cu-O(8)	73.3 (1)	O(8)-Cu-O(4)	144.3 (1)
N(1)-Cu-O(4)	99.0 (2)	N(1)-Cu-O(5)	168.6 (2)
N(1)-Cu-O(8)	103.8 (2)	N(1)-Cu-N(2)	90.5 (2)
N(2)-Cu-O(4)	74.2 (2)	N(2)-Cu-O(5)	99.6 (2)
N(2)-Cu-O(8)	78.5 (2)		
Ligand Molecule Bonds			
C(2)-C(1)-O(1)	115.5 (4)	C(2)-C(1)-O(2)	121.2 (5)
O(1)-C(1)-O(2)	123.3 (5)	C(1)-C(2)-C(3)	115.3 (5)
C(1)-C(2)-N(1)	114.4 (4)	C(3)-C(2)-N(1)	89.0 (4)
C(2)-C(3)-C(4)	87.9 (4)	C(3)-C(4)-N(1)	89.0 (4)
C(6)-C(5)-N(1)	113.6 (4)	C(5)-C(6)-C(7)	114.6 (4)
C(5)-C(6)-O(7)	109.9 (4)	C(7)-C(6)-O(7)	109.9 (4)
C(6)-C(7)-C(8)	110.7 (4)	C(6)-C(7)-N(2)	110.1 (4)
C(8)-C(7)-N(2)	111.1 (4)	C(7)-C(8)-O(3)	111.8 (4)
C(7)-C(8)-O(4)	122.3 (5)	O(4)-C(8)-O(3)	125.9 (5)
C(10)-C(9)-N(2)	112.0 (4)	C(9)-C(10)-C(11)	117.6 (4)
C(10)-C(11)-C(12)	109.1 (4)	C(10)-C(11)-O(8)	113.0 (4)
C(12)-C(11)-O(8)	105.3 (4)	C(11)-C(12)-O(5)	120.7 (4)
C(11)-C(12)-O(6)	116.6 (4)	O(5)-C(12)-O(6)	122.7 (5)
Cu-O(1)-C(1)	115.9 (3)	Cu-O(4)-C(8)	102.9 (3)
Cu-O(5)-C(12)	121.1 (3)	Cu-O(8)-C(11)	98.9 (3)
Cu-N(1)-C(2)	105.9 (3)	Cu-N(1)-C(4)	116.9 (3)
Cu-N(1)-C(5)	110.6 (3)	C(2)-N(1)-C(4)	89.9 (4)
C(2)-N(1)-C(5)	116.5 (4)	C(4)-N(1)-C(5)	115.4 (4)
Cu-N(2)-C(7)	107.9 (3)	Cu-N(2)-C(9)	114.3 (3)
C(7)-N(2)-C(9)	111.8 (4)		

^a Standard deviations are given in parentheses.

seven-membered ring, CuN(2)C(9)C(10)C(11)C(12)O(5). In the violet glutathione-Cu^{II} complex with a distorted square-pyramidal configuration, a direction of the apical Cu^{II}-S bond is known to be bent by 22° from the perpendicular C_{4v} axis of the square-planar basal plane.⁸ The distortion of the equatorial rings should also be noted. The small angle of about 85° is found for the five-membered chelate rings, while the large angle of about 100° is observed for the seven-membered ring. The conformation of each chelate rings is denoted by the endocyclic torsion angle (see Table V). The equatorial five-membered ring (CuO(1)C(1)C(2)N(1)) adopts a nearly planar conformation, whereas the axial rings take an envelope form with a flap atom N(2) or C(11). Both six-membered rings adopt a chair conformation. On the other hand, both seven-membered rings adopt a boat conformation at C(11), Cu-N(2) and C(6), C(8)-O(4), respectively. A detailed analysis of the bonding between the complexes revealed that the monomers are linked through the hydrogen bonds (O(6)···O(3) 2.478 (6), O(7)···O(2) 2.877 (6), O(8)···O(1) 2.838 (5) Å) within the unit cell (see Figure 3). This interaction serves to stabilize the crystal packing of the Cu(II) complex.

Table IV. Deviations (Å) of Atoms from the Least-Squares Plane^a

Deviations from the Basal Plane formed by the Four Equatorial Ligand Atoms			
O(1)	-0.160	O(5)	0.184
N(1)	0.101	N(2)	-0.110
Cu*	0.038	C(1)*	0.153
C(2)*	0.365	C(3)*	1.834
C(4)*	1.403	C(5)*	-1.108
C(6)*	-1.266	C(7)*	-1.392
C(8)*	-2.551	C(9)*	-0.019
C(10)*	1.393	C(11)*	2.040
C(12)*	1.085	O(2)*	0.277
O(3)*	-3.633	O(4)*	-2.447
O(6)*	1.216	O(7)*	-0.199
O(8)*	2.331		
Deviations from Chelate Ring			
Cu	0.131	O(1)	-0.093
C(1)	0.030	C(2)	0.066
N(1)	-0.129	O(2)*	0.119
Cu	-0.152	O(4)	0.132
C(8)	-0.017	C(7)	-0.303
N(2)	0.359	O(3)*	0.029
Cu	0.016	O(5)	-0.101
C(12)	0.053	C(11)	0.419
O(8)	-0.348	O(6)*	-0.029
Azetidine Ring and Carboxyl Group			
C(2)	-0.105	C(3)	0.098
C(4)	-0.099	N(1)	0.108
C(1)	-0.002	C(2)	0.001
O(1)	0.001	O(2)	0.001
C(8)	0.005	C(7)	-0.001
O(3)	-0.001	O(4)	-0.002
C(12)	-0.016	C(11)	0.005
O(5)	0.004	O(6)	0.008

^a Atoms marked with an asterisk are not included in least-squares calculations.

Table V. Endocyclic Torsion Angles (Deg) Calculated for Various Chelate Rings

Cu-O(1)-C(1)-C(2)	-11	O(1)-C(1)-C(2)-N(1)	-4
C(1)-C(2)-N(1)-Cu	15	C(2)-N(1)-Cu-O(1)	-16
N(1)-Cu-O(1)-C(1)	16	Cu-O(4)-C(8)-C(7)	1
O(4)-C(8)-C(7)-N(2)	-33	C(8)-C(7)-N(2)-Cu	52
C(7)-N(2)-Cu-O(4)	-37	N(2)-Cu-O(4)-C(8)	22
Cu-O(5)-C(12)-C(11)	4	O(5)-C(12)-C(11)-O(8)	-39
C(12)-C(11)-O(8)-Cu	44	C(11)-O(8)-Cu-O(5)	-35
O(8)-Cu-O(5)-C(12)	18	Cu-N(1)-C(5)-C(6)	63
N(1)-C(5)-C(6)-C(7)	-62	C(5)-C(6)-C(7)-N(2)	66
C(5)-C(6)-C(7)-C(8)	-58	C(6)-C(7)-N(2)-Cu	-71
C(7)-N(2)-Cu-N(1)	63	N(2)-Cu-N(1)-C(5)	-59
Cu-N(2)-C(9)-C(10)	71	N(2)-C(9)-C(10)-C(11)	-54
C(9)-C(10)-C(11)-O(8)	67	C(9)-C(10)-C(11)-C(12)	-49
C(10)-C(11)-O(8)-Cu	-75	C(11)-O(8)-Cu-N(2)	68
O(8)-Cu-N(2)-C(9)	-68	C(6)-C(7)-C(8)-O(4)	90
C(8)-O(4)-Cu-N(1)	-66	O(4)-Cu-N(1)-C(5)	15
C(10)-C(11)-C(12)-O(5)	82	C(12)-O(5)-Cu-N(2)	-57
O(5)-Cu-N(2)-C(9)	2		

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X-ray structural studies of numerous amino acid- and peptide-Cu^{II} complexes have demonstrated that the coordi-

Table VI. ESR Parameters for Cu(II) Complexes of Mugineic Acid and Its Related Amino Acid

ligand		g_{\parallel}	g_{\perp}	$10^4 A_{\parallel}$, cm^{-1}	N-hfs line ^a
mugineic acid (MA)		2.277	2.060	175.9	5
2'-deoxymugineic acid (deoxy MA)		2.277	2.065	172.9	5
distichonic acid A (glycine-type MA)		2.277	2.063	178.9	5
nicotianamine		2.236	2.054	190.4	7

^a hfs = hyperfine splitting.

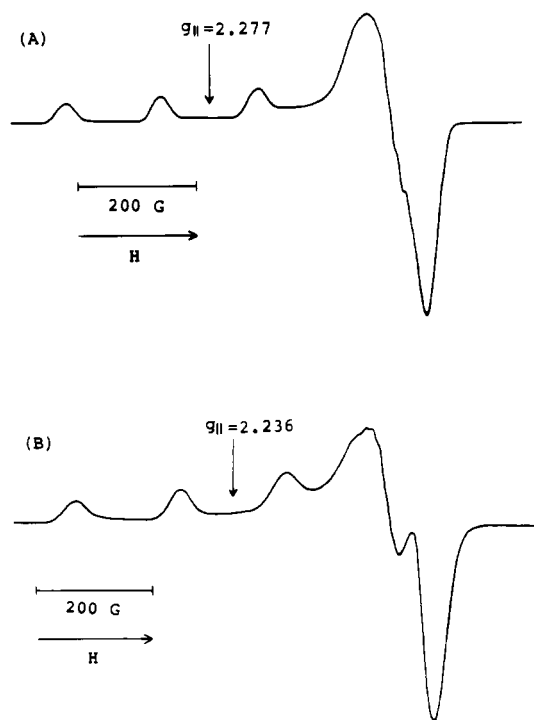


Figure 4. ESR spectra for the Cu(II) complexes of mugineic acid (A) and nicotianamine (B) in 1:3 ethylene glycol-water solution.

nated copper atom usually has tetragonal geometry and that the one or two weaker apical bonds are linked either to donor groups of an adjacent ligand molecule or solvent molecules such as water.⁷ Of special interest is the fact that mugineic acid with a low molecular weight is capable of forming an intramolecular hexadentate Cu(II) complex. In the mugineic acid-Cu^{II} complex, the binding of the azetidine ring nitrogen, N(1), and the axial coordination of the alcoholic hydroxyl oxygen, O(8), are also salient features. The present result clearly shows the azetidine ring carbons, C(3) and C(4), and the hydroxyl oxygen, O(7), are not participating in the Cu(II) complexation. Indeed, amino acids lacking the azetidine ring carbons, C(3) and C(4), or the hydroxyl oxygen, O(7), have been found to possess biological activity similar to mugineic acid.⁹

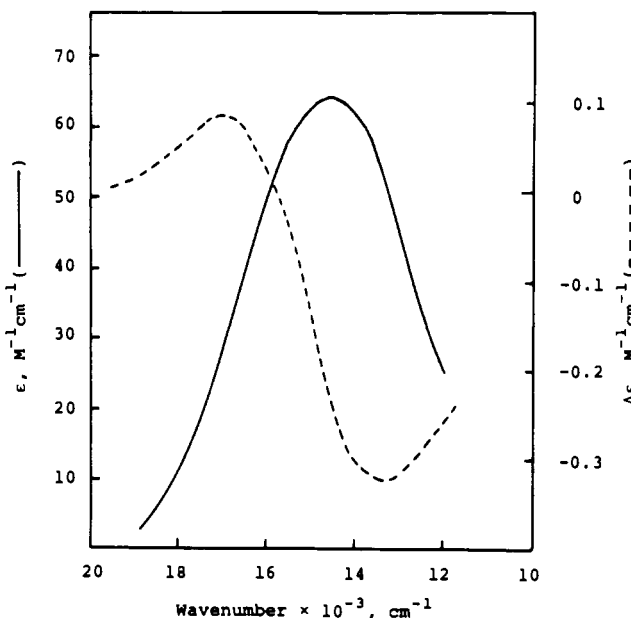


Figure 5. Visible (—) and circular dichroism (---) spectra of the 1:1 mugineic acid-Cu^{II} complex.

Spectroscopic Properties. The ESR spectrum of the mugineic acid-⁶⁵Cu^{II} complex at pH 7 and 77 K is shown in Figure 4, together with that of the 1:1 nicotianamine-⁶⁵Cu^{II} complex. Nicotianamine is different from mugineic acid by lack of the intermediate hydroxyl group and by replacement of the terminal hydroxy one with amino group.^{5,10} Both ESR spectra exhibit a typical copper hyperfine pattern with approximately axial symmetry ($g_x \approx g_y$). In addition, the ⁶⁵Cu(II) complexes of mugineic acid and nicotianamine show the five and seven nitrogen (¹⁴N, $I = 1$) superhyperfine splittings ($A^N = 13-14$ G) in the perpendicular region, suggesting the coordination of two and three nitrogen donor atoms to the Cu(II) ion, respectively. Table VI lists the ESR parameters estimated for the 1:1 Cu(II) complexes of mugineic

(9) Nomoto et al., manuscript in preparation.

(10) Noma, M.; Noguchi, M.; Tamaki, E. *Tetrahedron Lett.* 1971, 2017-2020.

Table VII. Fractional Atomic Coordinates

atom	x	y	z
Cu	0.9207 (1)	0.7500 ^a	0.8458 (6)
C(1)	1.2807 (8)	0.7319 (4)	1.1139 (5)
C(2)	1.1393 (9)	0.8116 (4)	1.1528 (5)
C(3)	0.953 (1)	0.7778 (5)	1.2275 (6)
C(4)	0.7826 (9)	0.8435 (4)	1.1111 (6)
C(5)	0.9871 (9)	0.9488 (4)	0.9614 (5)
C(6)	0.7809 (8)	0.9862 (4)	0.8282 (6)
C(7)	0.7271 (6)	0.9239 (3)	0.6806 (5)
C(8)	0.9309 (8)	0.9177 (3)	0.6199 (6)
C(9)	0.5262 (8)	0.7714 (3)	0.5666 (5)
C(10)	0.3953 (8)	0.6817 (4)	0.5973 (5)
C(11)	0.5255 (8)	0.6075 (4)	0.7103 (5)
C(12)	0.7439 (8)	0.5816 (3)	0.6703 (5)
O(1)	1.2173 (6)	0.7025 (3)	0.9704 (4)
O(2)	1.4426 (6)	0.6972 (3)	1.2112 (4)
O(3)	0.9353 (7)	0.9884 (3)	0.5265 (5)
O(4)	1.0743 (6)	0.8528 (3)	0.6590 (4)
O(5)	0.9176 (5)	0.6350 (2)	0.7135 (4)
O(6)	0.7368 (6)	0.5053 (3)	0.5849 (4)
O(7)	0.5849 (6)	0.9941 (3)	0.8806 (4)
O(8)	0.5991 (6)	0.6444 (3)	0.8677 (4)
N(1)	0.9527 (6)	0.8500 (3)	1.0167 (4)
N(2)	0.6473 (7)	0.8232 (3)	0.7119 (4)

^a The y coordinate of Cu was fixed at 0.75 by reason of arbitrary $P2_1$ symmetry.

acid, 2'-deoxymugineic acid (deoxymugineic acid), distichonic acid A (glycine-type mugineic acid), and nicotianamine.¹¹ Except for the nicotianamine-Cu^{II} complex, the three Cu(II) complexes have remarkably similar ESR parameters, indicating the similarity of Cu(II) coordination structure for these three ligands. The changes of the nitrogen hyperfine splitting, g , and A_{\parallel} values noted in the nicotianamine-Cu^{II} complex appear to be reasonably interpreted in terms of the coordination of the terminal amino nitrogen toward Cu(II). Because the bonding of axial nitrogen is generally too weak to produce superhyperfine features, however, the change of superhyperfine splittings at g_{\perp} as well as g_{\parallel} and A_{\parallel} value for the nicotianamine-Cu^{II} complex may suggest binding of ligands different from those of the mugineic acid-Cu^{II} complex. The colorless mugineic acid-Cu^I complex formed by reduction of the corresponding Cu(II) complex with sodium dithionite was ESR negative and was reoxidized by air to give the original mugineic acid-Cu^{II} complex.¹²

(11) At pH 2.5, the ESR parameters ($g_{\parallel} = 2.272$, $g_{\perp} = 2.078$, and $A = 168.2$ G) of the mugineic acid-Cu^{II} complex are somewhat different from those at pH 4.0–11.0.

Figure 5 shows the electronic and circular dichroism (CD) spectra of the isolated mugineic acid-Cu^{II} complex at pH 7, which gave an absorption maximum at $14\,600\text{ cm}^{-1}$ ($\epsilon\ 65$) and CD extrema at $16\,950$ ($\Delta\epsilon +0.09$) and $13\,330\text{ cm}^{-1}$ (-0.32), respectively. The visible bands at $16\,950$ ($d_{xz,yz} \rightarrow d_{x^2-y^2}$) and $13\,330\text{ cm}^{-1}$ ($d_{xy} \rightarrow d_{x^2-y^2}$) seen in the present complex are characteristic of d-d bands for tetragonally distorted octahedral Cu(II) type complexes. In general, the d-d transitions for Cu(II) complexes with an octahedral geometry occur in rather lower energy than those of the corresponding square-planar Cu(II) complexes. A band in the ultraviolet region occurred at $40\,300\text{ cm}^{-1}$ ($\epsilon\ 4500$), which can be assigned to a $N(\sigma) \rightarrow \text{Cu}^{\text{II}}$ charge-transfer (CT) transition. The 1:1 nicotianamine-Cu^{II} complex showed an absorption maximum at $16\,050\text{ cm}^{-1}$ ($\epsilon\ 95$). In comparison with that of the mugineic acid-Cu^{II} complex, the shift of the λ_{max} to higher wavenumber is attributed to the replacement of one hydroxyl oxygen with amino nitrogen toward the Cu(II) coordination.

In conclusion, the present X-ray crystallographic study clarified the unique structure for the Cu(II) complex of mugineic acid, a new amino acid ligand of biological origin. Mugineic acid coordinates with Cu(II) ion in a hexadentate fashion which is achieved by the azetidine nitrogen, N(1), secondary amine nitrogen, N(2), both terminal carboxylate oxygens, O(1) and O(5), hydroxyl oxygen, O(8), and intermediate carboxylate oxygen, O(4). Although the axial bond lengths are normal, 2.474 \AA for Cu-O(8) and 2.557 \AA for Cu-O(4), both axial Cu-O bonds markedly deviate from the basal plane. Indeed, the inclination angles are 22.2 and 14.7° for O(8) and O(4), respectively. Several spectroscopic properties are also characteristic of a distorted-octahedral Cu(II) complex with N_2O_4 donor set. On the basis of the present valuable information, the structural and spectroscopic investigations of biologically more important mugineic acid-Fe^{III} complex are now under way.

Atomic coordinates for the structural analysis appear in Table VII.

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Supplementary Material Available: Tables of thermal parameters, fractional atomic coordinates and thermal parameters for the hydrogen atoms and observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

(12) The cyclic voltammogram (CV) of the mugineic acid-Cu^{II} complex showed a reversible redox reaction and E_p (pH 6.9) = -0.159 V vs. NHE.