Table IV. Angles L–O–L′ (deg, above the Diagonal) and Distances between the Ligands (Å, below the Diagonal) around the O and F Ions in $Te(OH)_6 \cdot 2KF$

O(1)	O(1)–L	H(1)	Te	K^a	K	K^e
H(1)	0.805		117.6	115.2	86.7	60.9
Te	1.903	2.39		126.1	95.2	98.1
K^a	2.766	3.19	4.18		97.9	97.7
K	2.931	2.99	3.64	4.30		147.5
K^e	3.225	2.92	3.97	4.52	5.91	

$\Sigma_3' = 358.9°$

O(2)	O(2)–L	H(2)	Te	K^b	K	K^f
H(2)	0.647		111.5	133.5	77.3	74.2
Te	1.911	2.23		114.7	88.7	99.5
K^b	2.776	3.25	3.97		108.6	92.8
K	3.136	3.06	3.64	4.81		151.4
K^f	3.149	3.04	3.94	4.30	6.09	

$\Sigma_3 = 359.7°$

O(3)	O(3)–L	H(3)	Te	K^c	K
H(3)	0.627		100.9	133.1	102.0
Te	1.902	2.11		113.5	95.6
K^c	2.780	3.24	3.94		105.1
K	2.918	3.11	3.64	4.52	

$\Sigma_3 = 347.5°$

F	F–L	$H(1)^g$	$H(2)^d$	$H(3)^h$	K	K^d
$H(1)^g$	1.734		133.5	121.1	100.2	66.9
$H(2)^d$	1.969	3.40		97.9	100.7	69.7
$H(3)^h$	2.017	3.27	3.01		94.9	164.1
K	2.591	3.36	3.53	3.42		97.1
K^d	3.125	2.92	3.06	5.09	4.30	

$\Sigma_3 = 352.5°$

[a] $\frac{1}{2} - x, y, -\frac{1}{2} + z$. [b] $-\frac{1}{2} + x, \frac{1}{2} - y, z$. [c] $x, -\frac{1}{2} + y, \frac{1}{2} - z$. [d] $\frac{1}{2} - x, y, \frac{1}{2} + z$. [e] $\frac{1}{2} - x, -\frac{1}{2} + y, -z$. [f] $-x, \frac{1}{2} - y, -\frac{1}{2} + z$. [g] $x, \frac{1}{2} + y, \frac{1}{2} - z$. [h] $\frac{1}{2} + x, \frac{1}{2} - y, z$.

be split threefold. For ν(OH), however, only one very broad band is found at 2720 cm^{-1}. This corresponds[12] to an O–H···O bridge of about 2.63 Å; i.e., because of the ~0.04 Å smaller ionic radius of F^- this bond indicates an O–H···F bridge of about 2.59 Å. This expected value agrees well with the found mean O···F distance of 2.58 Å.

The δ(TeOH) band (in plane) is somewhat structured: 1160 (s) cm^{-1} with a shoulder at 1190 cm^{-1}. The latter value should correspond to the shortest O–H···F bridge, whereas the other two O···F distances differ too little. Because of the anharmonicity of these vibrations the first overtones also appear at wavenumbers 2250 (m) and 2370 (w) cm^{-1}, which are not quite doubled.

The γ(TeOH) band (out of plane) is rather nicely split into three lines at 935 (m), 890 (m), and 815 (mw) cm^{-1}, which do not coincide with the ν(TeO) band as in the case of $Te(OH)_6$ and $Te(OH)_6 \cdot NaF$.[2]

The valence band ν(OH···F) corresponding to the hydrogen bonds shows up at 255 cm^{-1} as for $Te(OH)_6 \cdot NaF$.

Acknowledgment. We wish to thank Dr. R. Gruehn, Giessen, for performing the heating experiment in a Guinier camera and Dr. K. Dehnicke, Marburg, for taking the ir and Raman spectra and discussing their interpretation.

Registry No. $Te(OH)_6$, 7803-68-1; KF, 7789-23-3.

Supplementary Material Available: Listing of structure factor amplitudes (1 page). Ordering information is given on any current masthead page.

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Crystal Structure of a Mixed-Ligand Complex of Copper(II), 1,10-Phenanthroline, and Glycylglycine Dianion: Glycylglycinato(1,10-phenanthroline)copper(II) Trihydrate

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Received October 14, 1975 AIC507458

The crystal and molecular structures of glycylglycinato(1,10-phenanthroline)copper(II) trihydrate has been determined by single-crystal x-ray diffraction, using counter methods. In the mixed Cu(II) complex glycylglycine serves as a terdentate ligand with amino, ionized amide nitrogen, and carboxylate oxygen donor atoms approximately tetragonally disposed about Cu(II). The fourth tetragonal position about Cu(II) is occupied by one phen nitrogen atom while the other more distant nitrogen occupies a tilted apical position resulting in an overall distorted square-pyramidal geometry about Cu(II). The individual complex molecules are hydrogen bonded to their neighbors via the three water molecules, forming a polymeric hydrogen-bonded lattice. Visible absorption spectra results suggest that the structure found in the crystal persists in aqueous solution near pH 9. Crystal data: $CuO_6N_4C_{16}H_{20}$, space group $P\bar{1}$, $Z = 2$, $a = 7.842$ (1) Å, $b = 9.395$ (2) Å, $c = 13.763$ (4) Å, $\alpha = 74.64$ (2)°, $\beta = 72.00$ (2)°, $\gamma = 75.76$ (2)°, $V = 915$ Å^3, $R = 3.1\%$, 1664 reflections.

After amide nitrogen deprotonation, glycylglycine dianion (gg) serves as a terdentate ligand with amino, ionized amide nitrogen, and carboxylate oxygen donor atoms about tetragonal Cu(II). Originally deduced from potentiometric titrations,[2] this structure, which exists in neutral aqueous solutions[3,4] has been confirmed by optical[5] and calorimetric[6] results in solution and by an x-ray study in a crystal, where water molecules occupy the fourth position in the tetragonal plane and an axial position.[7] Due to the planar amide bond, terdentate gg with an ionized amide nitrogen never assumes a bent but only the planar conformation about a transition metal ion. In an aqueous solution study of mixed complexes of oligoglycines

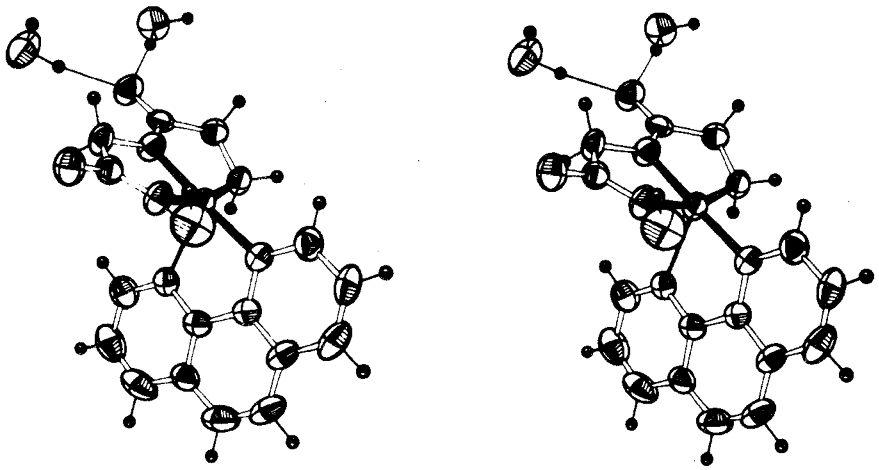


Figure 1. Stereoscopic pair of the mixed Cu(II) complex of phen and dianionic glycylglycine.

with Cu(II) and 2,2'-bipyridyl (bpy), it was suggested that gg is only bidentate through the two nitrogen atoms with a free carboxylate group since the opposite pair of positions about the tetragonal Cu(II) was presumed to be occupied by bpy nitrogens.[8] In this paper, we report from the results of an x-ray crystal structure of a mixed complex with 1,10-phenanthroline (phen) that the gg is terdenate and the Cu(II) five-coordinate square pyramidal with phen nitrogens occupying both near-tetragonal and near-apical positions. An effort is made from visible absorption spectra to deduce whether this structure persists in solutions.

Experimental Section

Preparation of Glycylglycinato(1,10-phenanthroline)copper(II) Trihydrate. An aqueous solution containing $Cu(NO_3)_2{\cdot}3H_2O$, 1,10-phenanthroline monohydrate, glycylglycine, and KOH in 1:1:1:2 molar ratio was left to evaporate at room temperature. Deep blue needle-shaped crystals slowly formed. They were collected by filtering the mixture on suction and washed with distilled water. The crystals once formed dissolved slowly in water. A small, approximately cubic fragment was broken from a larger single crystal for x-ray data collection.

Crystal data: mol wt 428, space group $P\bar{1}$, $Z = 2$, $a = 7.842$ (1) Å, $b = 9.395$ (2) Å, $c = 13.763$ (4) Å, $\alpha = 74.64$ (2)°, $\beta = 72.00$ (2)°, $\gamma = 75.76$ (2)°, $V = 915$ Å^3, $d_{\text{calcd}} = 1.55$ g cm^{-3}, $d_{\text{obsd}} = 1.52$ g cm^{-3}, $\mu(\text{Mo K}\alpha) = 12.8$ cm^{-1}, $F(000) = 442$; maximum, minimum crystal dimensions (calibrated microscope) 0.11, 0.09; maximum, minimum $e^{-\mu t}$ 0.28, 0.25.

The Enraf-Nonius program SEARCH was used to obtain 15 accurately centered reflections which were then used in the program INDEX to obtain an orientation matrix for data collection and also preliminary cell dimensions. Refined cell dimensions and their estimated standard deviations were estimated from least-squares refinement of 28 accurately centered reflections. The mosaicity of the crystal was examined by the ω-scan technique and judged to be excellent.

Collection and Reduction of Data. Diffraction data were collected at 292 K on an Enraf-Nonius low-circle CAD-4 diffractometer controlled by a PDP8/M computer, using Mo Kα radiation from a highly oriented graphite crystal monochromator. The θ–2θ scan technique was used to record all reflections for which $0° < 2\theta < 50°$. Scan widths (SW) were calculated from the equation $SW = A + B \tan\theta$ where A is estimated from crystal mosaicity and B allows for Kα_1 and Kα_2 splitting. The values of A and B were 0.60° and 0.20°, respectively. This scan angle is extended on each side by 25% for background determination (BG1 and BG2). The net count (NC) is then given by NC = TOT − 2(BG1 + BG2), where TOT is the integrated peak intensity. Reflection data were considered insignificant if intensities registered less than 10 counts above background on a rapid prescan, such reflections being rejected (coded as "unobserved") automatically by the computer.

The intensities of three standard reflections, monitored at 100-reflection intervals, showed no greater fluctuations during the data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz-polarization effects but not for absorption. The absence of absorption corrections for this small crystal should have at most a small effect on the temperature factors. After averaging of the intensities of equivalent reflections, the data were reduced to 2742 independent intensities of which 1664 had $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics.[9] These 1664 data were used in the final refinement of the structural parameters.

Determination and Refinement of the Structure. Full-matrix least-squares refinement was based on F, and the function was minimized as $\sum w(|F_o| - |F_c|)^2$, with weights w taken as $[2F_o/\sigma(F_o^2)]^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors were taken from Cromer and Waber[10] and those for hydrogen from Stewart et al.[11] The effects of anomalous dispersion for all nonhydrogen atoms were included in F_c using Cromer's values[12] for $\Delta f'$ and $\Delta f''$. Agreement factors are defined as $R = \sum\|F_o| - |F_c\|/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$. To minimize computer time, the initial calculations were carried out on the first 1000 reflections collected.

The coordinates of the copper and two of the ligand atoms (N(1), O(1)) were determined from a three-dimensional Patterson function and these phased the intensity data well enough to solve the structure. All of the nonhydrogen atoms were located from Fourier difference maps, and the remaining diffraction data were then added to the calculation ($R = 7.3\%$). Anisotropic temperature factors were introduced, and the phen hydrogen atoms and the methylene hydrogens of gg were inserted at their calculated positions with isotropic temperature factors of 5.0 Å^2, assuming C–H = 1.00 Å. After convergence of this model ($R = 3.8\%$), a Fourier difference map was used to locate the remaining eight hydrogen atoms (NH_2 and H_2O) and indicated extensive hydrogen bonding. These hydrogen atoms were subjected to one cycle of least-squares refinement with fixed temperature factors. The model was then refined with all hydrogens fixed and converged with $R = 3.1\%$, $R_w = 3.7\%$. A structure factor calculation with all observed and unobserved reflections included (no refinement) gave $R = 3.6\%$; on this basis it was decided that careful measurement of reflections rejected during the data collection would not significantly improve the results. No secondary extinction effects were observed in any of the strong low-angle reflections.

A final Fourier difference map was featureless. A table of the final observed and calculated structure factors is available.[13]

Results and Discussion

Final positional and thermal parameters for Cu(gg)phen·$3H_2O$ are given in Table I. Tables II and III contain the bond lengths and angles. The digits in parentheses in the tables are the estimated standard deviations in the least significant figures quoted and were derived from the inverse matrix in the course of least-squares refinement calculations. The labeling system of the atoms is indicated in i and ii. Figures 1 and 2 are stereoscopic pair views of the molecular unit and of the molecular packing in the unit cell, respectively.

The terdentate gg and the bidentate phen coordinate to the Cu in the form of a distorted square pyramid, whose base

Table I. Positional and Thermal[a] Parameters and Their Estimated Standard Deviations

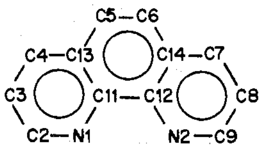
Atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Cu	0.1358 (1)	−0.036 20 (8)	0.314 06 (5)	0.0132 (1)	0.009 92 (8)	0.004 78 (4)	−0.0053 (2)	−0.0059 (1)	−0.001 05 (9)
O(1)	0.3312 (4)	0.073 4 (4)	0.306 1 (3)	0.0141 (7)	0.010 0 (5)	0.006 4 (2)	−0.0082 (9)	−0.0083 (6)	−0.000 2 (6)
O(2)	0.5888 (5)	0.039 4 (4)	0.352 1 (3)	0.0160 (7)	0.013 0 (6)	0.007 8 (3)	−0.0084 (10)	−0.0072 (7)	−0.003 5 (6)
O(3)	0.2005 (5)	−0.379 6 (4)	0.553 2 (3)	0.0201 (8)	0.013 6 (6)	0.005 9 (3)	−0.0078 (12)	−0.0083 (7)	0.004 3 (7)
O(5)	−0.0071 (6)	−0.567 1 (4)	0.719 3 (3)	0.0241 (10)	0.013 2 (6)	0.008 0 (3)	−0.0106 (12)	−0.0045 (9)	0.001 7 (7)
O(6)	0.3517 (6)	0.381 3 (4)	0.238 9 (3)	0.0309 (11)	0.011 4 (6)	0.009 5 (3)	−0.0078 (13)	−0.0068 (10)	−0.004 7 (7)
O(7)	0.5173 (6)	−0.478 3 (5)	0.621 7 (3)	0.0309 (10)	0.017 5 (7)	0.011 1 (3)	0.0040 (14)	−0.0223 (8)	−0.008 7 (7)
N(1)	0.0332 (5)	0.123 0 (4)	0.206 8 (3)	0.0150 (9)	0.008 8 (6)	0.005 2 (3)	−0.006 (1)	−0.0068 (8)	−0.001 6 (7)
N(2)	0.2795 (6)	−0.126 8 (5)	0.165 9 (3)	0.0134 (9)	0.008 8 (6)	0.005 4 (3)	−0.005 (1)	−0.0039 (8)	−0.001 9 (7)
N(3)	0.2311 (5)	−0.170 0 (5)	0.422 9 (3)	0.0138 (8)	0.012 2 (6)	0.005 2 (3)	−0.011 (1)	−0.0059 (8)	0.000 7 (7)
N(4)	−0.0669 (6)	−0.160 3 (5)	0.372 5 (3)	0.0131 (9)	0.011 1 (6)	0.005 6 (3)	−0.002 (1)	−0.0068 (8)	−0.001 9 (7)
C(2)	−0.0935 (8)	0.243 5 (6)	0.227 7 (4)	0.0185 (13)	0.011 5 (8)	0.007 3 (4)	0.002 (2)	−0.0076 (11)	−0.005 4 (10)
C(3)	−0.1547 (8)	0.354 3 (6)	0.150 1 (5)	0.0210 (13)	0.010 3 (9)	0.010 0 (5)	0.006 (2)	−0.0148 (12)	−0.003 8 (11)
C(4)	−0.0870 (8)	0.339 9 (6)	0.049 7 (5)	0.0255 (13)	0.010 4 (8)	0.008 9 (4)	−0.008 (2)	−0.0172 (12)	0.004 8 (10)
C(5)	0.1201 (7)	0.189 1 (7)	−0.081 1 (4)	0.0206 (11)	0.022 4 (11)	0.005 9 (4)	−0.027 (2)	−0.0121 (10)	0.007 9 (11)
C(6)	0.2411 (8)	0.063 8 (8)	−0.100 0 (4)	0.0218 (13)	0.028 2 (12)	0.004 6 (4)	−0.023 (2)	−0.0038 (11)	−0.004 8 (11)
C(7)	0.4246 (8)	−0.181 8 (7)	−0.034 5 (4)	0.0213 (4)	0.024 0 (10)	0.007 2 (4)	−0.018 (2)	0.0026 (12)	−0.015 6 (10)
C(8)	0.4685 (8)	−0.282 3 (7)	0.048 4 (5)	0.0194 (14)	0.016 3 (9)	0.010 3 (5)	−0.003 (2)	−0.0028 (13)	−0.014 2 (10)
C(9)	0.3950 (8)	−0.251 0 (6)	0.148 3 (4)	0.0185 (13)	0.011 7 (8)	0.007 4 (4)	−0.004 (2)	−0.0045 (12)	−0.005 3 (10)
C(11)	0.1015 (6)	0.107 3 (6)	0.105 5 (4)	0.0120 (9)	0.011 3 (7)	0.004 5 (3)	−0.012 (1)	−0.0041 (9)	−0.002 1 (8)
C(12)	0.2313 (6)	−0.025 8 (6)	0.084 3 (4)	0.0126 (10)	0.011 4 (7)	0.004 4 (3)	−0.013 (1)	−0.0024 (9)	−0.002 7 (8)
C(13)	0.0455 (7)	0.214 6 (6)	0.023 7 (4)	0.0163 (10)	0.013 7 (8)	0.005 3 (3)	−0.017 (1)	−0.0094 (9)	0.002 6 (9)
C(14)	0.3001 (7)	−0.047 4 (6)	−0.019 0 (4)	0.0129 (11)	0.018 2 (9)	0.005 2 (3)	−0.011 (2)	−0.0025 (10)	−0.006 5 (9)
C(15)	0.4481 (7)	−0.002 5 (6)	0.356 8 (4)	0.0131 (10)	0.010 3 (7)	0.004 9 (3)	−0.000 (1)	−0.0050 (9)	−0.006 5 (8)
C(16)	0.4082 (7)	−0.152 0 (6)	0.425 8 (4)	0.0112 (10)	0.012 5 (8)	0.006 0 (4)	−0.008 (1)	−0.0073 (9)	−0.000 4 (9)
C(17)	0.1424 (7)	−0.274 4 (6)	0.486 0 (4)	0.0156 (11)	0.011 0 (8)	0.003 2 (3)	−0.004 (2)	−0.0010 (10)	−0.003 2 (8)
C(18)	−0.0474 (7)	−0.259 5 (6)	0.473 6 (4)	0.0161 (12)	0.011 8 (8)	0.004 9 (4)	−0.006 (2)	−0.0040 (10)	−0.001 3 (9)

	x	*y*	*z*	*B*, Å^2		*x*	*y*	*z*	*B*, Å^2
H(2)	−0.1482 (11)	0.2526 (9)	0.3024 (6)	5.0	H(181)	−0.1395 (10)	−0.2158 (9)	0.5318 (6)	5.0
H(3)	−0.2480 (11)	0.4429 (9)	0.1706 (7)	5.0	H(182)	−0.0690 (10)	−0.3610 (9)	0.4764 (6)	5.0
H(3)	−0.1327 (11)	0.4196 (9)	−0.0062 (7)	5.0	H(1N)	−0.1875 (63)	−0.1032 (53)	0.3809 (36)	5.0
H(5)	0.0823 (10)	0.2649 (10)	−0.1418 (6)	5.0	H(2N)	−0.0475 (63)	−0.2251 (52)	0.3228 (35)	5.0
H(6)	0.2925 (11)	0.0484 (11)	−0.1736 (6)	5.0	H(105)	−0.1233 (63)	−0.5116 (52)	0.7304 (36)	5.0
H(7)	0.4803 (12)	−0.2014 (10)	−0.1100 (7)	5.0	H(205)	0.0415 (65)	−0.5094 (53)	0.6671 (36)	5.0
H(8)	0.5523 (12)	−0.3804 (9)	0.0382 (7)	5.0	H(106)	0.3578 (64)	0.2796 (53)	0.2541 (35)	5.0
H(9)	0.4294 (11)	−0.3250 (9)	0.2089 (6)	5.0	H(206)	0.3593 (63)	0.4154 (53)	0.2890 (36)	5.0
H(161)	0.4060 (9)	−0.1536 (9)	0.4993 (6)	5.0	H(107)	0.4162 (63)	−0.4438 (52)	0.5917 (35)	5.0
H(162)	0.5027 (9)	−0.2354 (9)	0.3999 (6)	5.0	H(207)	0.4934 (64)	−0.3986 (52)	0.6572 (36)	5.0

[a] The form of the anisotropic thermal parameters is $\exp[-(B(1,1)h^2 + B(2,2)k^2 + B(3,3)l^2 + B(1,2)hk + B(1,3)hl + B(2,3)kl)]$.

Table II. Bond Distances (Å)

Cu-O(1)	2.008 (4)	C(2)-C(3)	1.391 (9)
Cu-N(1)	2.009 (5)	C(3)-C(4)	1.349 (9)
Cu-N(2)	2.275 (5)	C(4)-C(13)	1.409 (9)
Cu-N(3)	1.901 (5)	C(5)-C(6)	1.347 (10)
Cu-N(4)	2.040 (5)	C(6)-C(14)	1.418 (10)
O(1)-C(15)	1.283 (7)	C(7)-C(8)	1.351 (10)
O(2)-C(15)	1.238 (7)	C(7)-C(14)	1.414 (10)
O(3)-C(17)	1.263 (6)	C(8)-C(9)	1.396 (9)
N(1)-C(2)	1.340 (7)	C(11)-C(12)	1.439 (8)
N(1)-C(11)	1.365 (7)	C(11)-C(13)	1.401 (8)
N(2)-C(12)	1.352 (7)	C(12)-C(14)	1.407 (8)
N(3)-C(16)	1.453 (7)	C(15)-C(16)	1.517 (8)
N(3)-C(17)	1.308 (7)	C(17)-C(18)	1.519 (8)
N(4)-C(18)	1.484 (7)	C(5)-C(13)	1.440 (9)



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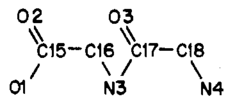

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Table III. Bond Angles (deg)

O(1)-Cu-N(1)	94.1 (2)	C(6)-C(5)-C(13)	120.5 (7)
O(1)-Cu-N(2)	96.2 (2)	C(5)-C(6)-C(14)	122.1 (7)
O(1)-Cu-N(3)	82.0 (2)	C(8)-C(7)-C(14)	119.7 (7)
O(1)-Cu-N(4)	161.3 (2)	C(7)-C(8)-C(9)	119.9 (7)
N(1)-Cu-N(2)	78.3 (2)	N(2)-C(9)-C(8)	122.4 (7)
N(1)-Cu-N(3)	173.8 (2)	N(1)-C(11)-C(12)	117.9 (6)
N(1)-Cu-N(4)	99.9 (2)	N(1)-C(11)-C(13)	121.9 (6)
N(2)-Cu-N(3)	106.9 (2)	C(12)-C(11)-C(13)	120.2 (6)
N(2)-Cu-N(4)	98.7 (2)	N(2)-C(12)-C(11)	117.9 (6)
N(3)-Cu-N(4)	82.9 (2)	N(2)-C(12)-C(14)	122.7 (6)
Cu-O(1)-C(15)	114.5 (4)	C(11)-C(12)-C(14)	119.3 (6)
Cu-N(1)-C(2)	124.7 (5)	C(4)-C(13)-C(5)	123.5 (7)
Cu-N(1)-C(11)	116.9 (4)	C(4)-C(13)-C(11)	117.5 (7)
C(2)-N(1)-C(11)	118.3 (5)	C(5)-C(13)-C(11)	118.9 (7)
Cu-N(1)-C(9)	132.5 (5)	C(6)-C(14)-C(7)	124.3 (7)
Cu-N(2)-C(12)	108.7 (4)	C(6)-C(14)-C(12)	119.0 (7)
C(9)-N(2)-C(12)	118.7 (4)	C(7)-C(14)-C(12)	116.6 (7)
Cu-N(3)-O(3)	146.2 (3)	O(1)-C(15)-O(2)	123.9 (6)
Cu-N(3)-C(16)	115.6 (4)	O(1)-C(15)-C(16)	116.8 (6)
Cu-N(3)-C(17)	120.2 (4)	O(2)-C(15)-C(16)	119.3 (6)
C(16)-N(3)-C(17)	124.2 (5)	N(3)-C(16)-C(15)	108.4 (5)
Cu-N(4)-C(18)	109.5 (4)	O(3)-C(17)-N(3)	126.0 (6)
N(1)-C(2)-C(3)	122.6 (7)	O(3)-C(17)-C(18)	120.3 (6)
C(2)-C(3)-C(4)	119.3 (7)	N(3)-C(17)-C(18)	113.7 (6)
C(3)-C(4)-C(13)	120.3 (7)	N(4)-C(18)-C(17)	110.9 (5)

contains the three gg donors and one of the phen nitrogen atoms. The other phen nitrogen atom forms the apex of the pyramid, with a significantly tilted and elongated Cu–N bond. This, together with the other noteworthy features of the coordination sphere, is shown in Figure 3. The square base of the coordination pyramid is reasonably planar (plane IX of Table IV), with the gg amide nitrogen atom and the phen nitrogen slightly raised with respect to the other gg donors. As expected for a square-pyramidal structure,[14-16] the Cu is raised (0.15 Å) above this plane toward the other phen nitrogen. The two ligands are only approximately orthogonal, with an angle of 83.7° between Cu(phen) and Cu(gg) (Table IV). The N···N "bite" of phen is 2.71 Å, which lies in the normal range.[17-23] The bite angle N–Cu–N is 78.3° compared with 80.6, 81.0° for bpy in square-pyramidal copper(II)

Table IV. Coefficients of Least-Squares Planes $AX + BY + CZ = D$

Plane	Atoms in plane	A	B	C	D	Distances (Å) from plane
I	N(1), C(2), C(3), C(4), C(13), C(11)	0.8678	0.4874	−0.0966	1.7870	N(1), 0.0075; C(2), −0.0077; C(3), 0.0053; C(4), −0.0029; C(13), 0.0028; C(11), −0.0050
II	C(11), C(12), C(13), C(14), C(5), C(6)	0.8820	0.4547	−0.1236	1.7279	C(11), −0.0022; C(12), 0.0028; C(13), 0.0011; C(14), −0.0023; C(5), −0.0006; C(6), 0.0012
III	N(2), C(12), C(14), C(7), C(8), C(9)	0.8949	0.4295	−0.1209	1.7655	N(2), 0.0024; C(12), −0.0043; C(14), −0.0008; C(7), 0.0076; C(8), −0.0095; C(9), 0.0046
IV	Cu, O(1), N(1), N(3), N(4)	0.2358	−0.7017	−0.6723	−2.6395	Cu, 0.1206; O(1), −0.0853; N(1), 0.0122; N(3), 0.0354; N(4), −0.0829
V	Cu, N(3), N(4), C(17), C(18)	0.1294	−0.8026	−0.5823	−2.4116	Cu, −0.0435; N(3), −0.0056; N(4), 0.0921; C(17), 0.0689; C(18), −0.1120
VI	Cu, O(1), N(3), C(15), C(16)	0.2237	−0.6560	−0.7208	−2.8114	Cu, 0.0926; O(1), −0.0849; N(3), −0.1136; Cu(15), 0.0300; C(16), 0.0759
VII	Cu, N(3), N(4), C(17), C(18), O(1), C(15), C(16)	0.1662	−0.7321	−0.6606	−2.8112	Cu, 0.1624, N(3), 0.0587; N(4), 0.1109; C(17), −0.0090; C(18), −0.2261; O(1), −0.1964; C(15), −0.0554; C(16), 0.1549
VIII	Cu, N(1), N(2), C(2)-C(9), C(11)-C(14)	0.8801	0.4592	−0.1209	1.7014	Cu, 0.0880; N(1), −0.0005; N(2), 0.0075; C(2), −0.0622; C(3), −0.0550; C(4), −0.0200; C(5), 0.0276; C(6), 0.0222; C(7), −0.0213; C(8), −0.0657; C(9), −0.0331; C(11), 0.0311; C(12), 0.0284; C(13), 0.0358; C(14), 0.0172
IX	O(1), N(1), N(3), N(4)	0.2347	−0.7010	−0.6734	−2.6765	O(1), −0.0561; N(1), 0.0458; N(3), 0.0625; N(4), −0.0523

Interplanar angles, Deg

I-II	I-III	II-III	V-VI	VII-VIII
2.6	3.9	1.6	12.8	83.7

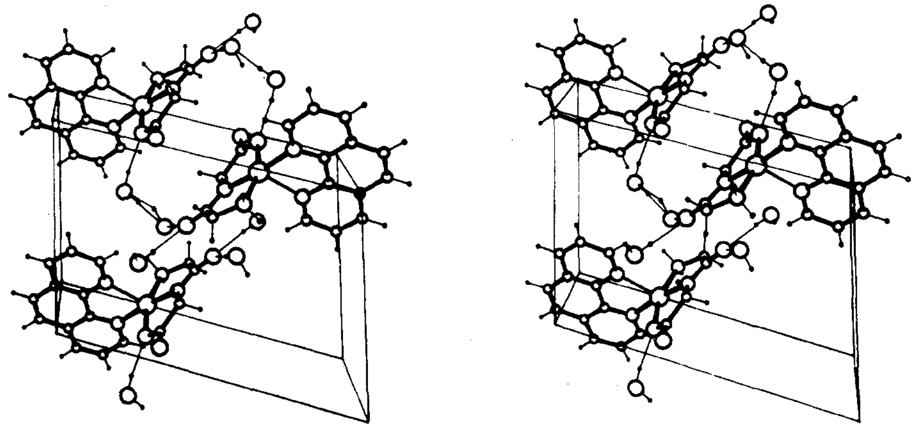

Figure 2. Stereoscopic view of the molecular packing in the unit cell.

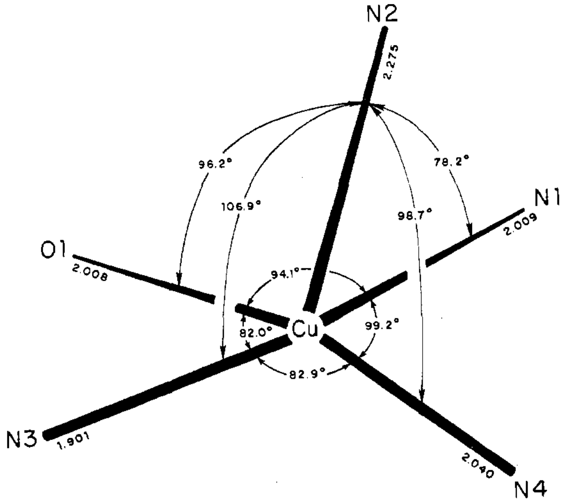

Figure 3. Dimensions of the mixed Cu(II) complex of phen and dianionic glycylglycine.

complexes with bpy joining two corners of the pyramid base.[14,15]

Table V. Hydrogen-Bonded Contacts (Å)

Atom 1	Atom 2	Distance	H atom
O(1)	O(6)	2.82	H(106)
O(2)	N(4)	2.93[a]	H(1N)
O(3)	O(7)	2.79	H(107)
O(5)	N(4)	3.00	H(2N)
O(5)	O(6)	2.82	H(105)

[a] Intermolecular.

The gg ligand deviates significantly from planarity: the two five-membered rings in Cu(gg) are inclined at 12.8° to each other. The phen is also distorted (planes I, II, and III), mostly near the apical nitrogen atom. The angle between the two C_5N fragments is 3.9°.

The individual Cu(gg)phen molecules are hydrogen bonded to their neighbors via the three H_2O molecules, forming a polymeric hydrogen-bonded lattice (Table V and Figure 2).

The structure reported in this paper bears similarities to that of Cu(gg)·$3H_2O$ with a similarly coordinated gg ligand.[7] In the water complex, the Cu(II) to gg distances are as follows: O(1), 1.98 Å; N(3), 1.89 Å; N4, 2.02 Å. These values are less than those given in this paper for the phen complex. Intraligand gg bond distances are similar in the two structures.

In addition the Cu(II) to H_2O distance of 1.96 Å in the tetragonal plane is shorter than that to N(1) while that to apical water of 2.35 Å is longer than that to N(2). Except for those involving the restricted N(1) and N(2) atoms in the phen ligand, bond angles in the two structures are similar.

The crystal structure result indicates that phen does not displace the carboxylate group of gg from a tetragonal position about Cu(II) but adopts a seemingly more awkward position with near-tetragonal and tilted axial nitrogen donors. Due to the planarity of the amide bond, it is not feasible for the carboxylate group of gg to adopt an apical position. In the Cu(II) complex of triglycine with two ionized amide nitrogen atoms, hydroxide is able to displace the carboxylate oxygen atom in the fourth tetragonal position at pH 12.[24] The preference of phen to form a square-pyramidal mixed complex rather than displace the gg carboxylate in the crystal structure to form a mixed complex with four tetragonally disposed nitrogen donors may be due to the lesser tetragonal field provided by one vs. two ionized amide nitrogens.

In order to assess whether the five-coordinate mixed complex found in the crystal persists in solution, visible absorption spectra are compared under a variety of conditions. The absorption spectrum of the crystal dispersed in a Nujol mull and mounted on a strip of filter paper exhibits a broad maximum at 615 nm with considerable absorption still appearing at 850 nm. The crystal was dissolved in several solvents at about 10^{-2} M where an absorption maximum occurs at 616 nm in DMSO, at 629 nm in methanol, and at 640 nm (ϵ 102) in water. In all three solvents an appreciable absorption approaching that of a shoulder occurs at about 850 nm. The absorptivity at 850 nm as a percentage of the absorptivity at the maximum wavelength is 34, 38, and 41%, respectively, for the three solvents. The spectrum in water at pH 9.3 is unaffected by increasing the temperature from 23 to 60 °C. The corresponding solution containing 1:1:1 mole ratios of 2,2'-bpy:Cu:gg in water at pH 9.5 exhibits a similar absorption spectrum with a maximum at 642 nm (ϵ 103) with the absorptivity at 850 nm 47% of that at the maximum. In contrast to these high relative absorptivities near 850 nm, a solution containing 1:1:1 mole ratios of bpy:Cu:glycinamide at pH 8.7, where the amide nitrogen atom is deprotonated, displays an absorption maximum at 618 nm (ϵ 60) with the absorptivity at 850 nm only 24% that at the maximum. A solution containing 1:1:1 ratios of phen:Cu:glycinate exhibits an absorption maximum at 617 nm (ϵ 50) with the absorptivity at 850 nm only 16% of that at the maximum. The binary complex of Cu(II) and glycylglycine with a deprotonated amide nitrogen exhibits an absorption maximum at 639 nm (ϵ 87) similar to that of other binary dipeptide complexes.[5] The absorptivity at 850 nm is only 10% of that at the maximum.

In judging whether the five-coordinate square-pyramidyl Cu(II) mixed complex of gg and phen exists in solutions, two aspects must be considered: the frequency with which a complex species of given composition occurs and the possibility of multiple structures for a species of set composition. The first point on compositions of solution complexes may often be solved by detailed computer-assisted interpretation of titration results over a range of conditions. Titration results from a similar solution with Cu(II), gg, and bpy[8] suggest that appreciable amounts of the binary complex of Cu(II) and dianionic gg without coordinated phen might exist but that the complex with mixed composition should predominate in aqueous solution.

Does then the structure found in the crystal for the complex of mixed composition persist in aqueous solution? The similarity of the absorption maximum and intensity of the 1:1:1 solution with that of a solution containing the binary Cu(II) complex of gg suggests that gg is also terdentate in the mixed complex. The presence of appreciable absorption at 850 nm in all solutions containing Cu, gg, and either phen or bpy suggests that in these solutions some Cu(II) is five-coordinate with a nitrogen donor in a near-apical position.[25] Thus the visible absorption spectra results suggest that an appreciable, perhaps predominant, fraction of the complexes of Cu, gg, and either phen or bpy in aqueous solution adopts the structure found in the crystal. It is anticipated that other mixed couples of Cu(gg) and bidentate ligands will adopt a comparable structure in the solid state and in solution.

Acknowledgment. This research was supported by two grants from the National Science Foundation, one from the Molecular Biology section and one from the Chemistry Section for the x-ray instrumentation.

Registry No. Glycylglycinato(1,10-phenanthroline)copper(II) trihydrate, 58188-52-6.

Supplementary Material Available: Listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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