Inorg. Chem. **1985**, *24*, 3621-3626 **3621**

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Coordination Behavior of L-Glutamic Acid: Spectroscopic and Structural Properties of (L-Glutamato)(imidazole)copper(II), (L-Glutamato)(2,2′-bipyridine)copper(II), and Aqua(L-glutamato)(1,10-phenanthroline)copper(II) Trihydrate Complexes

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Received April 23, 1985

The synthesis and structural and spectroscopic characterization of three ternary copper(II)–L-glutamate complexes of formulas Cu(L-glu)(im), Cu(L-glu)(bpy), and Cu(L-glu)(*o*-phen)·$4H_2O$ (L-glu = L-glutamate ion; im = imidazole; bpy = 2,2′-bipyridine; *o*-phen = 1,10-phenanthroline) are described. The Cu(L-glu)(im) complex has a one-dimensional polymeric structure, due to the bridging by the glutamate ligand between square-planar copper ions. The same polymeric structure and the same metal binding by the glutamate ion occur in the Cu(L-glu)(bpy) complex, but in a square-pyramidal geometry. The structure of [Cu(L-glu)(*o*-phen)H_2O]·$3H_2O$ is made up of discrete mononuclear units, in which the glutamate ion acts as a simple bidentate ligand toward a square-pyramidal Cu atom. Crystal data are as follows. [Cu(L-glu)(im)]: orthorhombic, space group $P2_12_12_1$, a = 24.286 (2) Å, b = 8.604 (1) Å, c = 5.075 (1) Å, Z = 4, R = 0.044 for 831 observed reflections. [Cu(L-glu)(bpy)]: orthorhombic, space group $P2_12_12_1$, a = 7.674 (1) Å, b = 17.738 (4) Å, c = 21.761 (5) Å, Z = 8, R = 0.077 for 2129 reflections. [Cu(L-glu)(*o*-phen)·H_2O]·$3H_2O$: monoclinic, space group $P2_1$, a = 12.168 (2) Å, b = 22.222 (3) Å, c = 7.591 (1) Å, β = 106.10 (2)°, Z = 4, R = 0.049 for 3554 reflections. Spectroscopic (EPR, IR, and vis) properties of the complexes are interpreted in the light of the known structures. The polymeric ability of the L-glutamate and L-aspartate ions in the presence of the copper(II) ion is also discussed.

Introduction

Metal–aspartate and –glutamate complexes and their adducts with amine have been extensively investigated in solution.[2] It is generally accepted that aspartate usually seems to act as a tridentate ligand to the same metal ion, whereas mononuclear complexes with tridentate glutamate have never been well established.[2]

The formation of polynuclear complexes, which in solution are not considered (since they are important only at very high concentrations), becomes a relevant problem when the solid state is taken into account. In fact, in solid complexes glutamate has invariably been found to act as a ligand bridging, in an extended-chain configuration, two or three metal ions, giving rise to polymeric compounds,[2,4] and aspartate, although presenting a great variety in coordinative behavior,[2,5] in one case, too, forms a polymeric entity, bridging three copper(II) ions in an extended configuration.[5d]

In order to rationalize the conditions that may favor polynuclear aspartate and glutamate species, in this paper we report the synthesis and spectroscopic and structural investigations on polymeric (L-glutamato)(imidazole)copper(II) and (L-glutamato)(2,2′-bipyridine)copper(II) and mononuclear aqua(L-glutamato)(1,10-phenanthroline)copper(II) trihydrate complexes.

The choice of aromatic amines is made by considering the ability of the aromatic moieties to give rise to intra- or intermolecular hydrophobic and stacking interactions. Such interactions, observed in solution[6] and in the solid state[7-9] and recognized to be very important in nature,[6] which stabilized ternary complexes, are suggested as responsible for the creation of distinct structures.[6]

A further interest in this work derives from a coordination point of view, since the square-pyramidal geometry of the copper metal ion found in the known copper(II)–aspartate and –glutamate complexes[3,7,8] seems to be a distinctive feature of these amino acids.

Experimental Section

Preparation of the Complexes. All the complexes were prepared by dissolving Cu(L-glu)·$2H_2O$, prepared as reported in ref 3, and the amine in a 1:1 or 1:1.5 molar ratio, in hot water or water/methanol (3:1) (70 °C). When the solutions were allowed to stand for some days, crystals precipitated.

[Cu(L-glu)(im)]: Anal. Calcd for $C_8H_{11}CuN_3O_4$: C, 34.57; H, 4.36; N, 15.14. Found: C, 34.42; H, 4.31; N, 15.17. Color: violet.

[Cu(L-glu)(bpy)]: Anal. Calcd for $C_{15}H_{15}CuN_3O_4$: C, 49.09; H, 4.67; N, 11.46. Found: C, 48.92; H, 4.65; N, 11.39. Color: deep blue.

[Cu(L-glu)(*o*-phen)(H_2O)]·$3H_2O$. Anal. Calcd for $C_{17}H_{23}CuN_3O_8$: C, 44.28; H, 5.03; N, 9.12; H_2O, 15.64. Found: C, 44.25; H, 4.98; N, 9.22; H_2O, 15.31. Color: blue.

Physical Measurements. Spectroscopic and magnetic measurements were made as reported in ref 5.

X-ray Crystallography. Details of data collection and processing are given in Table I.

Systematic absences from a survey of the complete data sets (and the presence of optically active L-glu ligand for the [Cu(L-glu)(*o*-phen)H_2O]·$3H_2O$ complex) enabled the space groups to be determined uniquely.

All data were corrected for Lorentz and polarization effects; the absorption correction was neglected for the [Cu(L-glu)(im)] and [Cu(L-glu)(*o*-phen)H_2O]·$3H_2O$ complexes, in view of their small absorption coefficients, and their small and almost isotropic crystal dimensions. Only the observed reflections were used in structure determinations.

The structures were solved by conventional Patterson and Fourier techniques and refined by full-matrix least-squares calculations.[10]

All pertinent information relating to the structure determinations is reported in Table I. In all cases, the enantiomeric models were chosen by assigning the known *S*-configuration, according to the Cahn–Ingold notation, to the L-aspartate ions.[11]

Complex neutral-atom scattering factors[12] were used throughout. Major calculations were carried out on a CDC Cyber 7600 computer by using the SHELX 76 program package[13] and the ORTEP plotting program.[14]

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0020-1669/85/1324-3621$01.50/0

Table I. X-ray Experimental Data

	[Cu(L-glu)(im)]	[Cu(L-glu)(bpy)]	[Cu(L-glu)(*o*-phen)H_2O]·$3H_2O$
		(A) Crystal Parameters[a] at ~20 °C	
cryst system	orthorhombic	orthorhombic	monoclinic
space group	$P2_12_12_1$ (D_2^4, No. 19)	$P2_12_12_1$	$P2_1$ (C_2^2, No. 4)
a, Å	24.286 (2)	7.674 (1)	12.168 (2)
b, Å	8.604 (1)	17.738 (4)	22.222 (3)
c, Å	5.075 (1)	21.761 (5)	7.591 (1)
β, deg	90	90	106.10 (2)
V, Å^3	1060.4	2962.1	1972.1
mol formula	$C_8H_{11}CuN_3O_4$	$C_{15}H_{15}CuN_3O_4$	$C_{17}H_{23}CuN_3O_8$
mol wt	276.74	364.85	460.94
Z	4	8	4
F(000)	563.9	1495.9	955.9
ρ(calcd), g/cm^3	1.73	1.64	1.55
ρ(obsd),[b] g/cm^3	1.72	1.61	1.56
		(B) Data Collection	
diffractometer	Philips PW1100	Enraf-Nonius CAD4	Philips PW1100
radiation[c]	Cu Kα (λ = 1.541 78 Å)	Mo Kα (λ = 0.710 69 Å)	Cu Kα
reflcns measd	$+h,+k,+l$	$+h,+k,+l$	$\pm h,+k,+l$
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
θ range, deg	2–60	2–27	2–60
scan speed, deg/min	2.1	0.65–10.06	3.0
scan width, deg	1.2	0.68 + 0.35 (tan θ)	1.2
stds	1 every 50 reflcns (no changes)	3 every 2 h, total loss in intens of 17.6%	1 every 50 reflcns (no changes)
no. of collected reflcns	985	3641	4110
no. of obsd reflcns	831 ($I > 2\sigma(I)$)	2129 ($I > 3\sigma(I)$)	3554 ($I > 3\sigma(I)$)
cryst size, mm	~0.21 × 0.12 × 0.09	~0.35 × 0.14 × 0.10	~0.20 × 0.17 × 0.17
abs coeff, cm^{-1}	27.6	14.3	18.5
abs corr	not applied	based on ψ scan; 0.69 < T factor < 0.99	not applied
		(C) Structure Determination	
non-H atoms	Cu, O, N anisotropic C isotropic	Cu, O, N anisotropic C isotropic	Cu, O, N anisotropic C isotropic
H atoms	riding at ideal positions	riding at ideal positions	riding at ideal positions and in obsd locations (water)
no. of variable params	105	265	352
w	$1.0/(\sigma^2(F) + 0.0033F_o^2)$	$1.0/(\sigma^2(\mathrm{F}) + 0.006F_o^2)$	$1.0/(\sigma^2(F) + 0.00066F_o^2)$
R	0.0436	0.0775	0.0492
R_w	0.0476	0.0767	0.0551
$\lvert\Delta\rho_{max}\rvert$, e Å^{-3}	0.46	1.52	0.54
sec extinction	zero wt to 8 strong low-order reflcns	no evidence	zero wt to 6 strong low-order reflcns

[a] Unit cell parameters were derived from least-sqaures fits to the setting angles of 25 reflections from different regions of the reciprocal space. [b] By flotation. [c] Graphite monochromated.

Final positional parameters are given in Tables II–IV. Atomic temperature factors, hydrogen atom parameters, and tables of observed and calculated structure factors are available as supplementary material.

Analysis. Nitrogen, carbon, and hydrogen were analyzed with a C. ERBA elemental analyzer instrument, Model 1106, by G. Goldoni.

Results and Discussion

Description of the Structures. Selected bond distances and bond angles are reported in Table V. Tables of complete bond distances and angles, hydrogen bonding interactions, shortest interatomic aromatic-ring-stacking separations, and selected least-squares planes are available as supplementary material. For the sake of comparison, a summary of structural parameters for the known L-aspartate and L-glutamate Cu(II) complexes is reported in Table VI.

[Cu(L-glu)(im)]. A drawing of the structure, showing the atom numbering, is given in Figure 1. The structure is made up of one-dimensional polymeric chains, due to the metal bridging by the glutamate ion acting as a bidentate ligand through its α-glycinate portion and bonding to a second metal atom through the side-chain carboxylate. The copper ion exhibits a very slightly distorted square-planar four-coordination, being nearly coplanar (0.023 Å) with its donor atoms, which are displaced ±0.014 Å from their mean plane. A weak axial nonbonding interaction, typical of a carboxylate group acting as monodentate ligand,[15] involves the γ-carboxylic O(4) atom (Cu···O(4) = 2.625 (6) Å, ∠O(3)–Cu···O(4) = 55.6 (2)°). Such a coordination geometry appears rather unusual for Cu(II) amino acid or small peptide

Table II. Final Positional Parameters for the [Cu(L-glu)(im)] Complex

atom	*x*	*y*	*z*
Cu	0.3695 (1)	0.6251 (1)	0.1577 (2)
O(1)	0.4228 (2)	0.4599 (6)	0.1425 (13)
O(2)	0.4446 (2)	0.2282 (7)	0.2828 (14)
C(1)	0.4144 (3)	0.3415 (9)	0.2866 (15)
C(2)	0.3613 (2)	0.3396 (7)	0.4515 (15)
N(1)	0.3336 (2)	0.4934 (6)	0.4302 (13)
C(3)	0.3251 (3)	0.2046 (8)	0.3599 (17)
C(4)	0.2786 (3)	0.1607 (8)	0.5452 (16)
C(5)	0.2263 (3)	0.2573 (8)	0.5337 (16)
O(3)	0.1878 (2)	0.2147 (5)	0.6881 (11)
O(4)	0.2230 (2)	0.3754 (6)	0.3903 (11)
N(2)	0.4102 (2)	0.7305 (7)	−0.1232 (13)
C(6)	0.4523 (3)	0.6754 (9)	−0.2491 (15)
N(3)	0.4687 (2)	0.7706 (8)	−0.4417 (15)
C(7)	0.4344 (3)	0.8960 (10)	−0.4365 (18)
C(8)	0.3987 (4)	0.8706 (11)	−0.2430 (17)

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Table III. Final Positional Parameters for the [Cu(L-glu)(bpy)] Complex

atom	*x*	*y*	*z*
Cu(1)	0.1686 (2)	0.1954 (1)	0.1787 (1)
N(1)	0.0986 (14)	0.0876 (6)	0.1971 (5)
C(1)	0.0409 (22)	0.0338 (8)	0.1586 (7)
C(2)	−0.0106 (24)	−0.0358 (9)	0.1770 (8)
C(3)	−0.0001 (25)	−0.0549 (9)	0.2385 (8)
C(4)	0.0570 (24)	−0.0008 (9)	0.2785 (8)
C(5)	0.1090 (20)	0.0691 (7)	0.2584 (6)
N(2)	0.1911 (13)	0.1979 (6)	0.2708 (5)
C(6)	0.2433 (20)	0.2559 (8)	0.3035 (7)
C(7)	0.2682 (25)	0.2521 (10)	0.3665 (8)
C(8)	0.2449 (24)	0.1851 (9)	0.3950 (8)
C(9)	0.1954 (25)	0.1233 (9)	0.3615 (8)
C(10)	0.1638 (19)	0.1304 (7)	0.2987 (6)
O(1)	0.1183 (12)	0.3036 (4)	0.1748 (4)
O(2)	0.0205 (14)	0.3926 (5)	0.1114 (4)
C(11)	0.0538 (16)	0.3252 (6)	0.1239 (5)
C(12)	0.0180 (16)	0.2659 (6)	0.0741 (5)
N(3)	0.1217 (13)	0.1995 (6)	0.0890 (4)
C(13)	−0.1802 (18)	0.2504 (7)	0.0703 (6)
C(14)	−0.2639 (19)	0.2294 (7)	0.1295 (6)
C(15)	−0.4619 (18)	0.2234 (7)	0.1258 (6)
O(3)	−0.5396 (11)	0.1965 (6)	0.1717 (5)
O(4)	−0.5350 (14)	0.2462 (8)	0.0778 (5)
Cu(2)	0.2167 (2)	0.4411 (1)	0.5425 (1)
N(4)	0.1496 (17)	0.4783 (7)	0.6269 (5)
C(16)	0.1023 (23)	0.5479 (8)	0.6405 (7)
C(17)	0.0422 (25)	0.5682 (10)	0.6975 (8)
C(18)	0.0305 (29)	0.5148 (10)	0.7429 (9)
C(19)	0.0771 (29)	0.4412 (11)	0.7296 (9)
C(20)	0.1382 (20)	0.4237 (8)	0.6697 (7)
N(5)	0.2285 (18)	0.3432 (7)	0.5885 (5)
C(21)	0.2742 (29)	0.2769 (10)	0.5645 (9)
C(22)	0.2797 (35)	0.2132 (13)	0.6021 (12)
C(23)	0.2426 (33)	0.2185 (12)	0.6603 (10)
C(24)	0.1938 (31)	0.2861 (11)	0.6874 (10)
C(25)	0.1929 (23)	0.3478 (8)	0.6483 (7)
O(5)	0.3042 (14)	0.3969 (5)	0.4678 (4)
O(6)	0.4232 (19)	0.4235 (6)	0.3766 (5)
C(26)	0.3681 (22)	0.4430 (9)	0.4294 (7)
C(27)	0.3870 (17)	0.5268 (6)	0.4482 (6)
N(6)	0.2964 (16)	0.5392 (6)	0.5069 (5)
C(28)	0.5786 (20)	0.5451 (7)	0.4527 (6)
C(29)	0.6707 (20)	0.4963 (8)	0.5016 (6)
C(30)	0.8675 (21)	0.5019 (8)	0.5011 (6)
O(7)	0.9473 (12)	0.4415 (6)	0.5139 (5)
O(8)	0.9376 (14)	0.5621 (6)	0.4878 (5)

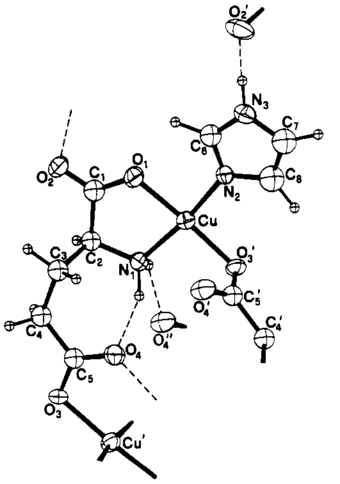

Figure 1. ORTEP view of [Cu(L-glu)(im)] showing the atom numbering and thermal motion ellipsoids (50%) for non-hydrogen atoms. The hydrogen atoms are represented as spheres of arbitrary radius. Hydrogen bonds are shown as dashed lines.

complexes, which most frequently show square-pyramidal pentacoordination, as found for all the copper aspartate or glutamate derivatives of known structure (see Table VI). The most relevant feature within the metal atom environment appears to be a very short Cu–O (α-carboxylate) bond distance (1.924 (5) Å), whose reported values in glycine chelate rings average 1.98 Å.[15] Corresponding Cu–O distances of 1.937 (4), 1.943 (9) (mean value), and 1.920 (4) Å (mean value) were found in [Cu(L-asp)(bpy)H_2O]·$3H_2O$,[5c] in [Cu(L-glu)(bpy)], and in [Cu(L-glu)(*o*-phen)H_2O]·$3H_2O$, respectively.

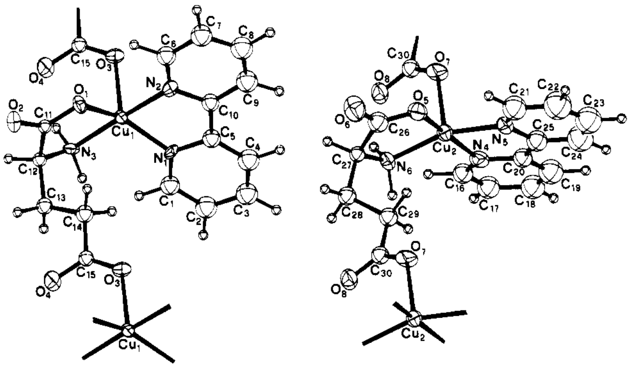

Figure 2. The two repetitive units in the linear-chain structure of [Cu(L-glu)(bpy)]. Non-hydrogen atoms are represented by 50% probability ellipsoids and hydrogen atoms by spheres of arbitrary radius.

These structural results are closely consistent with the main conclusion drawn from stability constant determinations: namely, that not only the pyridyl but also the imidazole group has a stability-increasing effect on the formation of ternary Cu^{2+} complexes containing O-donor atoms.[16–18] In the present complex, the coplanarity between the imidazole ring and the coordination plane (the dihedral angle between their mean planes being 5.2°) enables the π back-bonding from metal ion to aromatic amine, to which the increased stability of the ternary Cu^{2+} complexes has repeatedly been attributed.[18,19]

It is interesting to compare the structural features of our compound with those of the aqua(L-glutamato)copper(II) hydrate and (L-aspartato)(imidazole)copper(II) dihydrate.[5d] In the last two complexes, both showing a two-dimensional polymeric structure due to the bridging by the anionic ligands bonded to three different metal ions, the α-carboxylate group acts as a bridge (of syn–anti type) between two copper ions, whereas it acts as a simple unidentate ligand in the present complex. As a consequence, in the present compound a change of the copper coordination from square pyramidal to square planar occurs, and a one-dimensional polymeric structure is produced.

The crystal packing is mainly determined by strong hydrogen bonding interactions between the N-bonded hydrogen atoms and the uncoordinated carboxylate oxygens (see Figure 1).

[Cu(L-glu)(bpy)]. The structure is built up of two crystallographically independent one-dimensional polymeric chains, whose repetitive units are shown, together with the atom numbering, in Figure 2. A crystal packing diagram is presented in Figure 3.

Each Cu atom exhibits slightly distorted square-pyramidal five-coordination, with the bpy molecule and the L-glu^{2-} ion acting as bidentate ligands in the equatorial plane and a γ-carboxylate O atom from a second glutamate ion in the apical position. Although in a different copper stereochemistry, the glutamate ion shows the same metal binding and bridging observed in the imidazole derivative.

The dimensions of the two coordination polyhedra, as well as the extent of their deviations from ideal square-pyramidal geometry, are quite similar. Significant features appear to be a relevant tetrahedral distortion of the basal coordination planes (with atomic deviations of ±0.197 and ±0.137 Å, respectively, therefrom), the relevant displacements of the Cu atoms from the mean basal planes (0.289 and 0.238 Å, respectively) toward the apical O donor atoms, and the relatively short apical bond distances (2.245 (9) and 2.160

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Table IV. Final Positional Parameters for the [Cu(L-glu)(*o*-phen)H_2O]·$3H_2O$ Complex

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Cu(1)	0.4075 (1)	0.2500	0.2623 (1)	Cu(2)	0.9703 (1)	0.16717 (4)	0.6912 (1)
N(1)	0.4801 (4)	0.1748 (2)	0.1968 (7)	N(4)	0.8933 (4)	0.2394 (2)	0.7595 (7)
C(1)	0.4318 (6)	0.1229 (3)	0.1426 (9)	C(18)	0.9383 (6)	0.2919 (3)	0.8245 (10)
C(2)	0.4921 (6)	0.0762 (4)	0.0859 (10)	C(19)	0.8734 (7)	0.3369 (4)	0.8746 (11)
C(3)	0.6048 (6)	0.0838 (3)	0.0940 (10)	C(20)	0.7603 (6)	0.3270 (4)	0.8629 (10)
C(4)	0.6583 (5)	0.1395 (3)	0.1547 (8)	C(21)	0.7116 (6)	0.2716 (3)	0.7968 (9)
C(5)	0.5915 (5)	0.1833 (3)	0.2050 (8)	C(22)	0.7804 (5)	0.2288 (3)	0.7452 (8)
C(6)	0.7742 (6)	0.1526 (3)	0.1624 (9)	C(23)	0.5935 (6)	0.2555 (4)	0.7828 (10)
C(7)	0.8199 (6)	0.2077 (3)	0.2234 (9)	C(24)	0.5526 (7)	0.2003 (3)	0.7231 (10)
C(8)	0.7536 (5)	0.2535 (3)	0.2791 (8)	C(25)	0.6242 (6)	0.1559 (3)	0.6722 (9)
C(9)	0.6398 (5)	0.2405 (3)	0.2678 (8)	C(26)	0.7385 (5)	0.1715 (3)	0.6831 (7)
C(10)	0.6117 (5)	0.3338 (3)	0.3846 (8)	C(27)	0.7748 (6)	0.0773 (3)	0.5879 (9)
C(11)	0.7244 (5)	0.3505 (3)	0.3986 (9)	C(28)	0.6630 (7)	0.0586 (4)	0.5735 (11)
C(12)	0.7950 (6)	0.3102 (3)	0.3452 (9)	C(29)	0.5890 (7)	0.0977 (4)	0.6128 (11)
N(2)	0.5698 (4)	0.2807 (2)	0.3215 (7)	N(5)	0.8108 (4)	0.1321 (2)	0.6400 (7)
O(1)	0.2659 (3)	0.2081 (2)	0.2287 (7)	O(6)	1.1107 (4)	0.2112 (2)	0.7218 (7)
O(2)	0.0934 (4)	0.2115 (2)	0.2637 (8)	O(7)	1.2938 (4)	0.1975 (2)	0.7393 (7)
C(13)	0.1879 (5)	0.2338 (3)	0.2824 (8)	C(30)	1.1944 (5)	0.1795 (3)	0.7065 (8)
C(14)	0.2175 (5)	0.2944 (3)	0.3790 (8)	C(31)	1.1698 (5)	0.1130 (3)	0.6496 (8)
N(3)	0.3275 (4)	0.3180 (2)	0.3532 (8)	N(6)	1.0444 (4)	0.1077 (2)	0.5621 (8)
C(15)	0.1206 (5)	0.3397 (3)	0.3182 (9)	C(32)	1.2420 (6)	0.0898 (3)	0.5284 (9)
C(16)	0.1283 (6)	0.3925 (3)	0.4436 (10)	C(33)	1.2356 (6)	0.0224 (3)	0.5021 (10)
C(17)	0.0324 (5)	0.4380 (3)	0.3882 (9)	C(34)	1.3084 (5)	0.0018 (3)	0.3795 (9)
O(3)	0.0408 (4)	0.4848 (2)	0.4839 (7)	O(8)	1.4050 (4)	−0.0187 (3)	0.4498 (8)
O(4)	−0.0499 (4)	0.4271 (3)	0.2507 (8)	O(9)	1.2667 (5)	0.0076 (3)	0.2105 (8)
O(5)	0.3750 (5)	0.2885 (3)	−0.0280 (8)	O(10)	1.0092 (7)	0.1320 (3)	0.9763 (12)
				O(11)	0.7065 (9)	0.4475 (5)	0.0771 (12)
				O(12)	0.5087 (6)	0.4599 (3)	0.1855 (10)
				O(13)	0.9541 (6)	0.5111 (3)	0.9770 (10)
				O(14)	0.4473 (6)	0.4031 (4)	0.6537 (11)
				O(15)	0.3144 (8)	0.4057 (3)	0.9910 (17)
				O(16)	0.1486 (6)	0.4904 (3)	0.8502 (10)

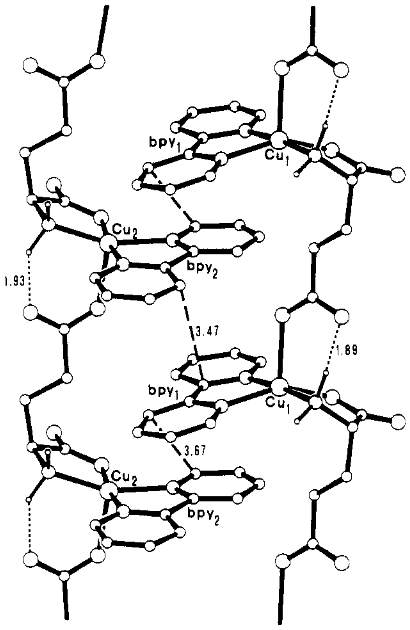

Figure 3. Crystal-packing diagram of [Cu(L-glu)(bpy)] showing intrachain hydrogen bond (dotted lines) distances (Å) and shortest interatomic ring-stacking interactions (dashed lines) between bpy ligands.

(10) Å, respectively). Corresponding values of ±0.159, 0.086, and 2.37 (2) Å, respectively, in [Cu(L-asp)(im)]·$2H_2O$,[5d] and of ±0.175, 0.126, and 2.368 (5) Å, respectively, in [Cu(L-asp)(bpy)H_2O]·$3H_2O$[5c] were previously observed.

The individual pyridine rings of the bpy ligands, planar within ±0.018 Å, are twisted about the 2–2′ bond by 5.8 and 5.0°, respectively, hence within the 0–11° range previously reported for this coordinated ligand.[20-22]

A further interesting structural feature is the crystal packing of the polymeric chains, mainly determined by ring-stacking interactions between bpy ligands of the –A–B–A–B– type (A = bpy(1), B = bpy(2); see Figure 3). It may be stressed that these interactions, observed either in solution[6,19] or in the solid state,[7-9,23] have been recognized as enhancing the stability of mixed ternary complexes, but, more importantly, as creating specific structures.[18,24] In the present case, the dihedral angle between bpy(1) and bpy(2) mean planes is 7.8°, and the shortest interatomic stacking distances range from 3.47 to 4.52 Å for bpy(1)–bpy(2) interactions and from 3.67 to 4.34 Å for the bpy(1)–bpy(2^i) ones (i = *x* − 1, *y*, *z*).

Further interactions between polymeric chains are due to two hydrogen bonds involving aminic groups and uncoordinated carboxylate oxygens.

[Cu(L-glu)(*o*-phen)H_2O]·$3H_2O$. The structure consists of two crystallographically independent [Cu(L-glu)(*o*-phen)H_2O] discrete molecules (Figure 4) linked by a complex network of hydrogen bonds involving six lattice water molecules and by aromatic ring-stacking interactions between *o*-phen ligands (Figure 5).

The coordination of the copper atoms is distorted square pyramidal with the organic ligands acting as bidentate in the equatorial plane and with water molecules in apical position. There are no significant differences between the dimensions of the two coordination polyhedra, whose distortions from the ideal geometry appear less large than those of the other L-aspartate or L-glutamate square-pyramidal copper complexes. The four equatorial donor atoms are nearly coplanar, with atomic deviations from the mean planes of ±0.007 and ±0.076 Å, respectively; the displacements of the copper atoms toward the apical ligand are 0.123 and 0.186 Å, respectively, with related apical Cu–O bond lengths of 2.294 (6) and 2.225 (8) Å.

Major contributors to the molecular packing are the ring-stacking interactions between aromatic ligands, which are of the

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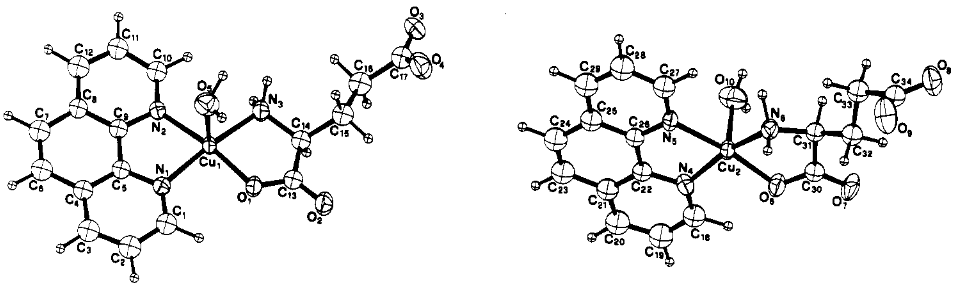

Figure 4. Atom numbering and thermal motion ellipsoids (50%) for the two crystallographically independent molecules of $[Cu(L\text{-}glu)(o\text{-}phen)H_2O]\cdot 3H_2O$. The spheres corresponding to the hydrogen atoms are on an arbitrary scale.

Table V. Bond Distances (Å) and Bond Angles (deg) Involving Copper Atoms[a]

	(A) [Cu(L-glu)(im)]		
Cu–O(1)	1.924 (5)	Cu–N(2)	1.957 (6)
Cu–N(1)	1.989 (6)	Cu–O(3^{i})	1.965 (5)
O(1)–Cu–N(1)	84.4 (2)	N(1)–Cu–O(3^{i})	92.0 (2)
O(1)–Cu–O(3^{i})	176.3 (2)	N(1)–Cu–N(2)	172.6 (2)
O(1)–Cu–N(2)	88.5 (2)	N(2)–Cu–O(3^{i})	95.1 (2)
	(B) [Cu(L-glu)(bpy)]		
Cu(1)–N(1)	2.026 (10)	Cu(2)–N(4)	2.019 (12)
Cu(1)–N(2)	2.011 (11)	Cu(2)–N(5)	2.008 (12)
Cu(1)–O(1)	1.960 (8)	Cu(2)–O(5)	1.926 (9)
Cu(1)–N(3)	1.987 (10)	Cu(2)–N(6)	1.999 (10)
Cu(1)–O(3^{ii})	2.245 (9)	Cu(2)–O(7^{iii})	2.160 (10)
N(1)–Cu(1)–N(2)	81.2 (4)	N(4)–Cu(2)–N(5)	80.8 (5)
N(1)–Cu(1)–O(1)	151.7 (4)	N(4)–Cu(2)–O(5)	172.0 (5)
N(1)–Cu(1)–N(3)	100.4 (4)	N(4)–Cu(2)–N(6)	98.4 (5)
N(1)–Cu(1)–O(3^{ii})	106.6 (4)	N(4)–Cu(2)–O(7^{iii})	91.0 (5)
N(2)–Cu(1)–O(1)	92.2 (4)	N(5)–Cu(2)–O(5)	93.0 (5)
N(2)–Cu(1)–N(3)	173.5 (4)	N(5)–Cu(2)–N(6)	158.8 (5)
N(2)–Cu(1)–O(3^{ii})	89.0 (4)	N(5)–Cu(2)–O(7^{iii})	100.9 (5)
O(1)–Cu(1)–N(3)	83.4 (4)	O(5)–Cu(2)–N(6)	85.5 (4)
O(1)–Cu(1)–O(3^{ii})	100.6 (4)	O(5)–Cu(2)–O(7^{iii})	95.3 (5)
N(3)–Cu(1)–O(3^{ii})	96.5 (4)	N(6)–Cu(2)–O(7^{iii})	100.3 (4)
	(C) $[Cu(L\text{-}glu)(o\text{-}phen)H_2O]\cdot 3H_2O$		
Cu(1)–N(1)	2.015 (5)	Cu(2)–N(4)	1.997 (5)
Cu(1)–N(2)	2.018 (5)	Cu(2)–N(5)	2.027 (5)
Cu(1)–O(1)	1.913 (4)	Cu(2)–O(6)	1.926 (4)
Cu(1)–N(3)	2.020 (5)	Cu(2)–N(6)	2.003 (6)
Cu(1)–O(5)	2.294 (6)	Cu(2)–O(10)	2.225 (8)
N(1)–Cu(1)–N(2)	82.4 (2)	N(4)–Cu(2)–N(5)	82.2 (2)
N(1)–Cu(1)–O(1)	90.2 (2)	N(4)–Cu(2)–O(6)	91.4 (2)
N(1)–Cu(1)–N(3)	171.9 (2)	N(4)–Cu(2)–N(6)	164.7 (2)
N(1)–Cu(1)–O(5)	92.5 (2)	N(4)–Cu(2)–O(10)	91.1 (2)
N(2)–Cu(1)–O(1)	169.7 (2)	N(5)–Cu(2)–O(6)	171.4 (2)
N(2)–Cu(1)–N(3)	101.9 (2)	N(5)–Cu(2)–N(6)	100.9 (2)
N(2)–Cu(1)–O(5)	89.2 (2)	N(5)–Cu(2)–O(10)	89.2 (3)
O(1)–Cu(1)–N(3)	84.7 (2)	O(6)–Cu(2)–N(6)	83.7 (2)
O(1)–Cu(1)–O(5)	98.3 (2)	O(6)–Cu(2)–O(10)	96.8 (3)
N(3)–Cu(1)–O(5)	94.5 (2)	N(6)–Cu(2)–O(10)	103.9 (3)

[a] Superscripts refer to the following symmetry transformations of the reference coordinates: (i) $^1/_2 - x, 1 - y, z - {}^1/_2$; (ii) $x + 1, y, z$; (iii) $x - 1, y, z$.

same –A–B–A–B– type observed in the above-reported bpy Cu complex and (but not pointed out) in the $[Cu(L\text{-}asp)(bpy)H_2O]\cdot 3H_2O$ derivative.[5c] As expected, the replacement of the bpy ligand by the larger and more planar *o*-phen molecule determines stronger ring-stacking interactions, with shorter interatomic separations, ranging from 3.33 to 3.73 Å for the *o*-phen(1)–*o*-phen(2) interactions and from 3.45 to 4.79 Å for *o*-phen(1)–*o*-phen(2^{i}) ones. The dihedral angle between the *o*-phen molecules, planar within ±0.03 and ±0.05 Å, respectively, is 1.4°.

Further contribution to the crystal-packing forces comes from hydrogen-bonding interactions, which involve the aminic groups, the uncoordinate *α*- and *β*-carboxylic oxygen atoms, and all the water molecules. The shortest contacts occur at the carboxylate oxygens, with O···N or O···O separations in the 2.72–2.91 Å range.

It is of interest to note that the present complex is isostructural with the $[Cu(L\text{-}asp)(bpy)H_2O]\cdot 3H_2O$ derivative,[5c] which displays the same metal binding by the amino acid, the same type of ring-stacking interactions, and a similar hydrogen-bonded network.

L-Glutamato Ion. In all the above described complexes the carbon skeleton of the glutamate ion shows an almost planar conformation, with maximum atomic deviations from mean planes ranging from ±0.086 to ±0.413 Å. Bond distances and bond angles are normal, and within the carboxylate groups, as expected,[15] the C–O bond lengths for coordinated O atoms (mean value 1.268 Å) are significantly longer than those involving uncoordinated oxygens (average 1.244 Å).

Despite the small number of available structural data (see Table VI), a correlation between the coordination ability of the glutamate or aspartate ligand toward the Cu^{2+} ion water contents of their salts or amino adducts could be tentatively suggested. In the anhydrous [Cu(L-glu)(im)] and [Cu(L-glu)(bpy)] complexes, the glutamate ion binds one Cu atom through the glycinate ring and bridges a second metal atom through the solid-chain carboxylate group. In addition, a third Cu^{2+} ion is bridged through the *α*-carboxylate function in both complexes containing two water molecules, i.e. $[Cu(L\text{-}glu)H_2O]\cdot H_2O$[3] and $[Cu(L\text{-}asp)(im)]\cdot 2H_2O$.[5d] Finally, in the $[Cu(L\text{-}asp)(bpy)H_2O]\cdot 3H_2O$[5c] and $[Cu(L\text{-}glu)(o\text{-}phen)H_2O]\cdot 3H_2O$ complexes the amino acid acts as a simple bidentate ligand, giving rise to mononuclear species in which a water molecule replaces an apical carboxylate atom in the copper coordination sphere.

Spectroscopic Results. All the complexes are stable in air and are soluble in polar solvents.

The thermogravimetric behavior of the hydrated *o*-phen complex shows that the three uncoordinated water molecules are lost in the 35–100 °C temperature range, while the loss of the coordinated water molecule in the 110–150 °C temperature range, is immediately followed by the decomposition of the complex.

The room-temperature magnetic moments of all the complexes (μ_{eff}(293 K) = 1.82–1.86 μ_B) are "normal" and typical of "magnetically dilute" complexes;[25] their polycrystalline EPR spectra ($g_{\parallel}$ = 2.226–2.244; $g_{\perp}$ = 2.079–2.113) closely resemble those of synthetic copper(II) peptides and of ternary complexes having similar environment and chromophore, reported in the literature,[26-30] for which an essentially $d_{x^2-y^2}$ ground state has been suggested.[31-32]

Their electronic spectra may be considered of particular relevance in the light of the utility of electronic spectroscopy in elucidating the probable coordination geometry of a metal ion site

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Table VI. Comparative Structural Parameters of the Known L-Aspartate and L-Glutamate Cu(II) Complexes[a]

	[Cu(L-asp)(im)]·$2H_2O$	[Cu(L-asp)(bpy)H_2O]·$3H_2O$	[Cu(L-glu)H_2O]·H_2O	[Cu(L-glu)(im)]	[Cu(L-glu)(bpy)]	[Cu(L-glu)(*o*-phen)H_2O]·$3H_2O$
space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_1$
Z	4	4	4	4	8	4
structure	2-D polymer	discrete molecules	2-D polymer	1-D polymer	1-D polymer	discrete molecules
coord geometry	square pyramidal	square pyramidal	square pyramidal	square planar	square pyramidal	square pyramidal
amino acidate binding sites	O, N (α-gly ring) O (α-carboxyl) O (β-carboxyl)	O, N (α-gly ring)	O, N (α-gly ring) O (α-carboxyl) O (γ-carboxyl)	O, N (α-gly ring) O (γ-carboxyl)	O, N (α-gly ring) O (γ-carboxyl)	O, N (α-gly ring)
Cu–O(gly ring),[b] Å	1.99 (2)	1.937 (4)	1.967 (4)	1.924 (5)	1.943 (9)*	1.920 (4)*
Cu–N(gly ring), Å	1.98 (2)	1.989 (5)	1.998 (4)	1.989 (6)	1.99 (1)*	2.011 (6)*
mean Cu–N(amine), Å	1.98 (2)	2.001 (5)		1.957 (6)	2.01 (1)	2.014 (5)
Cu–O(apical), Å	2.37 (2)	2.368 (5)	2.299 (4)		2.20 (1)*	2.258 (7)*
ref	5d	5c	3	this work	this work	this work

[a] Attempts to obtain a crystal of [Cu(L-asp)] or [Cu(L-asp)(*o*-phen)] suitable for X-ray analysis were unsuccessful. [b] Values marked with an asterisk represent averaged bond lengths.

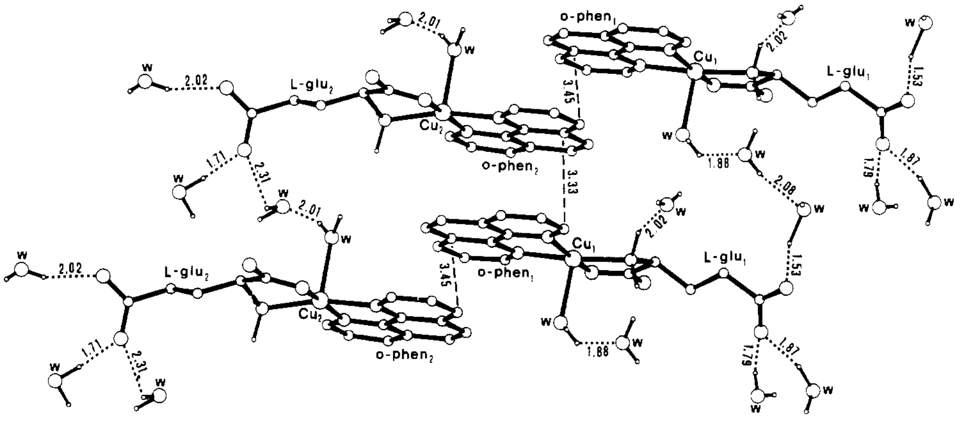

Figure 5. Molecular packing in [Cu(L-glu)(*o*-phen)H_2O]·$3H_2O$. Dotted lines correspond to the shortest interatomic ring-stacking separations between *o*-phen ligands.

in a protein[33–34] insofar as our complexes represent realistic mimics of the natural systems.[33–35] The room-temperature electronic spectrum of the imidazole complex (15 870 sh, 17 540 cm^{-1}) presents a d–d band maximum falling in a narrower energy of 17 500–18 200 cm^{-1} found for truly discrete square-planar systems, containing imidazoles and N-protected amino acids, having a CuN_2O_2 chromophore.[30,36]

The room-temperature electronic spectrum of the [Cu(L-glu)(*o*-phen)H_2O]·$3H_2O$, presenting an absorption maximum at 16 530 cm^{-1}, compares well that of the [Cu(L-asp)(bpy)H_2O]·$3H_2O$ (16 390 cm^{-1})[5c] and those of similar square-pyramidal copper(II) complexes.[28,29,37,38] The d–d band maximum in [Cu(L-glu)(bpy)], at lower energy than those of the [Cu(L-asp)(bpy)H_2O]·$3H_2O$ and [Cu(L-glu)(*o*-phen)H_2O]·$3H_2O$ compounds, having a similar environment and chromophore (CuN_3O_2), agrees with a greater tetrahedral distortion of the basal coordination plane and a greater displacement of the Cu atom from the mean basal plane in the former than in the latter.

Relevant, in the infrared spectral region, is the presence of multiple bands in the range characteristic of the asymmetric and symmetric modes of the carboxylate groups,[39,40] since in the complexes these groups are differently (both or only one) involved in the metal ion coordination. The lack of spectral differences, already observed for the L-aspartato complexes,[5c] may arise from the low symmetry of the free COO^-.[37]

Conclusion

(1) In solid complexes with copper(II) thus far studied crystallographically, the aspartate and glutamate ions always present an extended configuration, which favours square-planar or square-pyramidal metal ion geometry.

(2) Polymeric chain structures, where aspartate and glutamate ions bridge two or three different copper(II) ions, prevail in anhydrous or low-hydrate complexes.

(3) Only highly hydrate ternary complexes, containing four water molecules, give rise to isolated monomeric species. This suggests that when those systems are studied in aqueous solution, although the amino acid may exist in an extended form, the presence of polymeric species can probably be discounted.

Acknowledgment. The authors are grateful to the Centro di Calcolo Elettronico dell'Università di Modena for computing support and the Centro Strumenti dell'Università di Modena for recording the EPR and IR spectra.

Registry No. [Cu(L-glu)(im)], 97920-96-2; [Cu(L-glu)(bpy)], 98048-09-0; [Cu(L-glu)(*o*-phen)(H_2O)]·$3H_2O$, 97920-97-3.

Supplementary Material Available: Listings of bond distances and angles involving O, N, and C atoms, bond distances and angles involving water protons, hydrogen-bonding distances and angles, selected least-squares planes, stacking interactions, thermal parameters, hydrogen atom positions, and observed and calculated structure factors (56 pages). Ordering information is given on any current masthead page.

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