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Chloro(L-glutamato-κ^2N,O)-(1,10-phenanthroline-κ^2N,N')-copper(II) monohydrate

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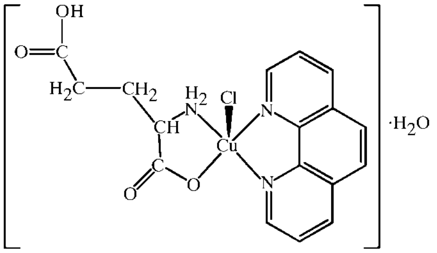
The crystal structure of the title compound, $[CuCl(C_5H_8NO_4)(C_{12}H_8N_2)]\cdot H_2O$ or $[CuCl(L\text{-Glu})(phen)]\cdot H_2O$ (where phen is 1,10-phenanthroline and L-Glu is L-glutamate), shows that the ternary complex consists of two neutral molecules, in which the Cu^{II} ions each have a distorted square-pyramidal coordination geometry comprised of one bidentate phenanthroline ligand, one *O*,*N*-bidentate L-glutamate anion and an apical Cl^- anion. The angles between the planes of the Cu–phenanthroline and the Cu–aminocarboxylate chelate rings are 6.1 (5) and 11.8 (5)° in the two molecules. The Cu—Cl bond lengths are 2.608 (3) and 2.590 (3) Å in the two molecules, slightly longer than the value of 2.546 Å observed for the Cu—Cl bond in the analogous chloro(L-glycinato)(1,10-phenanthroline)copper complex [Solans, Ruiz-Ramírez, Martinez, Gasque & Briansó (1983). *Acta Cryst.* C**44**, 628–631]. Additionally, the Cu ion is weakly coordinated at a sixth position by an α-carboxyl O atom from a neighbouring complex. A number of intra- and intermolecular hydrogen bonds stabilize the crystal structure.

Comment

In recent years, ternary copper(II) complexes have attracted significant attention due to their range of properties, which include interactions with DNA (Chikira *et al.*, 2002), anticonvulsant activity (Viossat *et al.*, 2003) nuclease activity (Garcýa-Raso *et al.*, 2003) and interactions of copper(II) with nucleotides and nucleosides (Gasowska, 2003; Lomozik & Jastrzáb, 2003). A variety of ternary complexes involving copper, 1,10-phenanthroline (phen) and α-amino acids have been described (Anitolini *et al.*, 1983, 1985; Moreno-Esparza *et al.*, 1995; Solans *et al.*, 1988; Venkatraman *et al.*, 1999). We report here the crystal structure of the novel title copper, phenanthroline and α-amino acid ternary complex, (I).

Some features of the molecular geometry of (I) are listed in Table 1, and the molecular conformation and crystal packing are illustrated in Figs. 1 and 2, respectively. In this ternary complex, there are two neutral molecules in the asymmetric unit. The Cu ions in each complex have distorted square-pyramidal coordination geometry comprised of one bidentate phenanthroline ligand, one *O*,*N*-bidentate L-glutamate monoanion (with protonated γ-carboxylate) and an apical Cl^- anion, in contrast with the structure of $[Cu(L\text{-glu})(phen)(H_2O)]$ (Anitolini *et al.*, 1985), in which the Cu ions also have distorted square-pyramidal coordination geometry comprised of a bidentate phenanthroline ligand, but an *O*,*N*-bidentate L-glutamate dianion (with ionized γ-carboxyl) and an apical coordinating water O atom.



(I)

The four equatorial donor atoms in (I) (N1, N2, N3 and O1, and N4, N5, N6 and O5, in the two independent molecules) are nearly coplanar, with respective r.m.s. deviations of 0.0347 and 0.0526 Å in the two independent molecules and displacements of the Cu atoms toward the apical Cl^- ligand of 0.191 (5) and 0.151 (5) Å, respectively. The angles between the planes of the Cu–phenanthroline (atoms C1–C12/N1/N2/Cu1 or C18–C29/N4/N5/Cu2) and the aminocarboxylate chelate ring (atoms C13/C14/Cu1/O1/N3 or C30/C31/Cu2/O5/N6) are 6.1 (5) and 11.8 (5)°, respectively, *i.e.* somewhat different in the two molecules. This variability in the angles between the planes defined by the chelate rings is also observed in ternary copper

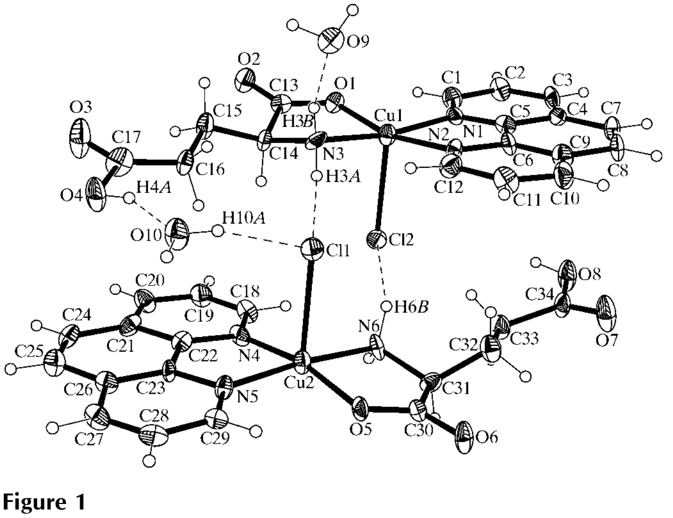


Figure 1
The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii.

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complexes with phenanthroline and other amino acids (Anitolini *et al.*, 1985; Moreno-Esparza *et al.*, 1995).

The Cu coordination distances are listed in Table 1. The Cu—N coordination bond lengths to the phenanthroline ligand are in the range 1.986 (11)–2.057 (9) Å; these and the other Cu coordination distances are as typically observed in related structures (Anitolini *et al.*, 1983, 1985; Moreno-Esparza *et al.*, 1995; Solans *et al.*, 1988; Venkatraman *et al.*, 1999). The Cu—Cl bond lengths are 2.608 (3) and 2.590 (3) Å in the two molecules, slightly longer than the value of 2.546 Å observed for the Cu—Cl bond in the analogous chloro(glycinato)(1,10-phenanthroline)copper complex (Solans *et al.*, 1988), but similar to that observed in the complex $[Cu_2(phen)_2(OH)_2(H_2O)_2][Cu_2(phen)_2(OH)_2Cl_2]Cl_2·6H_2O$ (2.602 Å; Lu *et al.*, 2003). In addition, Fig. 2 shows that the Cu ions are coordinated by the O atom of an α-carboxylate group from a neighbouring asymmetric unit, forming a weak sixth coordination ligand, with $Cu2—O2^{i}$ and $Cu1—O6^{ii}$ distances of 3.275 and 3.215 Å, respectively [symmetry codes: (i) $x, y-1, z$; (ii) $x, y+1, z$]. Therefore, the overall coordination geometry is actually octahedral. This octahedral coordination geometry is also found in a similar L-proline ternary complex (Venkatraman *et al.*, 1999), in which the weak sixth coordinating α-carboxyl O atom is from another ternary complex in same asymmetric unit.

The hydrogen-bonding geometry in (I) is listed in Table 2. As illustrated in Figs. 1 and 2 and in Table 2, a number of intra- and intermolecular hydrogen bonds stabilize the crystal structure of (I). These hydrogen bonds are formed mainly between water molecules and α-amino N atoms, α-carboxyl and γ-carboxyl O atoms, and O atoms and the coordinating Cl^- anions. Hydrogen bonds also exist between α-amino N atoms and the Cl^- ligands. It is worthy of mention that atom H10*B* is involved in an intermolecular three-centred hydrogen bond with atoms O1 and O2. Furthermore, the weak coordination by the sixth ligand also contributes to the intermolecular interactions observed in the crystal packing. The Cl^- and carboxylate ligands together contribute to the extension of the intermolecular packing interactions throughout the crystal structure. Additionally, the complex molecules are arranged in such a way that symmetry-related phenanthroline planes of neighbouring complexes [the plane containing atoms C1–C12/N1/N2 and that containing atoms $C18^{iii}$–$C31^{iii}$/$N4^{iii}$/$N5^{iii}$; symmetry code: (iii) $x, y+1, z-1$] are orientated in parallel planes, with phen–phen separations of about 3.42 Å, indicating significant π–π stacking interactions.

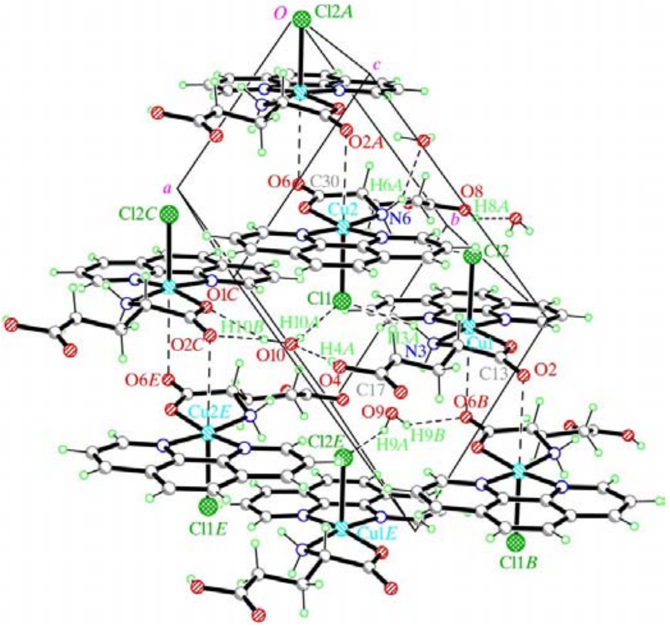

Figure 2
The hydrogen-bonding network and octahedral coordination geometry of (I). Atoms labelled with the suffixes *A*, *B*, *C* or *E* are at the symmetry positions $(x, y-1, z)$, $(x, y+1, z)$, $(x+1, y-1, z)$ and $(x+1, y, z)$, respectively.

Experimental

All chemicals were of reagent grade and commercially available from the Beijing Chemical Reagents Company of China, and were used without further purification. $CuCl_2·2H_2O$ (1.705 g, 10.0 mmol) was dissolved in water (80 ml). 1,10-Phenanthroline (1.98 g, 10 mmol) was separately dissolved in water (20 ml) with a few drops of HCl. L-Glutamic acid (1,47 g, 10.0 mmol) was then added to the copper(II) chloride solution with stirring at 333 K until all the L-glutamic acid had dissolved. The two solutions were then mixed, the pH adjusted to 3 with HCl and the solution stirred at room temperature for 2 h. The resulting blue solution was filtered and the filtrate left at 277 K. Blue crystals of (I) appeared after several weeks, by slow evaporation of the aqueous solvent. Elemental analysis, calculated for $C_{17}H_{16}ClCuN_3O_4·H_2O$: C 46.06, H 4.09, N 9.48%; found: C 45.98, H 4.17, N 9.35%.

Crystal data

$[CuCl(C_5H_8NO_4)(C_{12}H_8N_2)]·H_2O$
$M_r = 443.33$
Triclinic, $P1$
$a = 8.3022\ (14)$ Å
$b = 10.0591\ (17)$ Å
$c = 12.393\ (2)$ Å
$\alpha = 66.730\ (2)°$
$\beta = 72.047\ (2)°$
$\gamma = 68.828\ (2)°$
$V = 869.9\ (3)$ Å^3
$Z = 2$
$D_x = 1.693$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3499 reflections
$\theta = 2.3$–$27.2°$
$\mu = 1.45$ mm^{-1}
$T = 183\ (2)$ K
Block, blue
0.55 × 0.40 × 0.40 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
$T_{min} = 0.474$, $T_{max} = 0.561$
4229 measured reflections
3578 independent reflections
3455 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 25.0°$
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 8$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.121$
$S = 1.10$
3578 reflections
506 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2 + 2.5194P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.52$ e Å^{-3}
$\Delta\rho_{min} = -0.75$ e Å^{-3}
Absolute structure: Flack (1983), 602 Friedel pairs
Flack parameter = −0.02 (3)

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.937 (8)	N3—C14	1.495 (12)
Cu1—N3	1.979 (11)	N6—C31	1.475 (12)
Cu1—N1	2.016 (10)	C13—O2	1.239 (13)
Cu1—N2	2.057 (9)	C13—O1	1.281 (13)
Cu1—Cl2	2.590 (3)	C17—O3	1.202 (14)
Cu2—O5	1.934 (8)	C17—O4	1.385 (15)
Cu2—N5	1.986 (11)	C30—O6	1.243 (14)
Cu2—N4	1.993 (10)	C30—O5	1.269 (13)
Cu2—N6	2.004 (10)	C34—O7	1.204 (14)
Cu2—Cl1	2.608 (3)	C34—O8	1.313 (14)
O1—Cu1—N3	84.6 (4)	O5—Cu2—Cl1	97.8 (3)
N1—Cu1—N2	81.8 (4)	N5—Cu2—Cl1	94.6 (3)
O1—Cu1—Cl2	95.9 (3)	N4—Cu2—Cl1	94.2 (3)
N3—Cu1—Cl2	93.1 (3)	N6—Cu2—Cl1	91.0 (3)
N1—Cu1—Cl2	95.9 (3)	O2—C13—O1	123.6 (10)
N2—Cu1—Cl2	97.2 (3)	O3—C17—O4	113.7 (12)
O5—Cu2—N5	93.4 (3)	O6—C30—O5	124.0 (11)
O5—Cu2—N6	84.1 (4)	O7—C34—O8	120.3 (10)
O1—Cu1—N1—C5	171.7 (8)	O5—Cu2—N4—C22	73 (2)
Cl2—Cu1—N1—C5	−92.2 (7)	N6—Cu2—N4—C22	178.2 (8)
O1—Cu1—N1—C1	−9.6 (10)	N6—Cu2—N4—C18	−5.2 (11)
N3—Cu1—N2—C12	5.4 (11)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O10—H10*B*···O1$^{\mathrm{i}}$	0.89 (5)	2.56 (6)	3.313 (12)	143 (6)
O10—H10*B*···O2$^{\mathrm{i}}$	0.89 (5)	1.92 (5)	2.771 (13)	159 (7)
O9—H9*B*···O6$^{\mathrm{ii}}$	0.87 (5)	2.13 (7)	2.774 (12)	130 (7)
O8—H8*A*···O9$^{\mathrm{iii}}$	0.84 (4)	1.82 (6)	2.587 (12)	152 (8)
O4—H4*A*···O10	0.81 (5)	1.86 (6)	2.592 (13)	149 (9)
O10—H10*A*···Cl1	0.83 (5)	2.38 (6)	3.136 (10)	153 (8)
O9—H9*A*···Cl2$^{\mathrm{iv}}$	0.90 (5)	2.26 (6)	3.112 (10)	157 (7)
N6—H6*A*···O10$^{\mathrm{iii}}$	0.92	2.18	3.009 (14)	149
N3—H3*B*···O9	0.92	2.12	3.017 (14)	164
N3—H3*A*···Cl1	0.92	2.57	3.440 (10)	158

Symmetry codes: (i) $1+x, y-1, z$; (ii) $x, 1+y, z$; (iii) $x-1, y, z$; (iv) $1+x, y, z$.

H atoms attached to C and N atoms were placed in geometrically idealized positions, with Csp^3—H = 0.99 Å, Csp^2—H = 0.95 Å, α-Csp^3—H = 1.00 Å and Nsp^3—H = 0.92 Å, and constrained to ride on their parent atoms, with $U_{\rm iso}(\rm H) = 1.2U_{\rm eq}(\rm C,N)$. H atoms attached to O atoms (L-glutamic acid and solvent water) were located in difference Fourier maps and their global $U_{\rm iso}$ value was refined. The O—H distances are in the range 0.81 (5)–0.90 (5) Å.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*/*PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL*/*PC*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1128). Services for accessing these data are described at the back of the journal.

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