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Aqua(L-phenylalaninato)(L-prolinato)copper(II) monohydrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.010 Å
H-atom completeness 91%
R factor = 0.057
wR factor = 0.168
Data-to-parameter ratio = 11.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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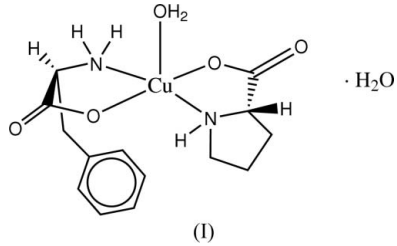
The title compound, $[Cu(C_5H_8NO_2)(C_9H_{10}NO_2)(H_2O)]\cdot H_2O$, is formed by the chelate coordination of L-prolinate and L-phenylalaninate anions. Both ligands bind through carboxylate O and amine N atoms to the Cu^{II} atom in a *trans* arrangement. The square pyramid is completed by an aqua ligand in the apical position.

Comment

Copper plays a key role in several biological processes, and several enzymes and proteins that contain this metal are widely distributed in animals and plants (Sigel, 1981). Aiming to contribute to the understanding of Cu–biomolecule interactions, several Cu complexes with the same two amino acids (Freeman *et al.*, 1964; Van der Helm & Franks, 1969; Van der Helm *et al.*, 1971; Van der Helm & Tatsch, 1972; Gramaccioli & Marsh, 1966; Gillard *et al.*, 1969; Weeks *et al.*, 1969; Ibarra *et al.*, 1972; Fawcet *et al.*, 1979; Calvo *et al.*, 1993; Rizzi *et al.*, 2000), with two different amino acids (Yamauchi *et al.*, 1989; Sasada *et al.*, 1983), and with an amino acid and a diamine ligand (Antolini *et al.*, 1985; Aoki & Yamazaki, 1987; Masuda *et al.*, 1991; Solans *et al.*, 1993; Moreno-Esparza *et al.*, 1995) have been synthesized and structurally characterized to serve as simple models of complex metalloproteins. In this paper we report the crystal structure of compound (I), [Cu(L-pro)(L-phe)(H_2O)]·H_2O (L-pro = L-prolinate, L-phe = L-phenylalaninate).



(I)

The coordination polyhedron around the Cu^{II} atom is a square pyramid formed by amino acid residues in the basal plane and an aqua ligand at the apical position (Fig. 1), showing the expected Cu—O and Cu—N bond distances and bond angles (Table 1). The sixth position of the coordination around the Cu atom is sterically shielded by a phenyl ring (C9–C14; centroid *Cg*), which is involved in an intramolecular C—H···π interaction. The C5—H5*D*···*Cg* angle is 168° and the H5*D*···*Cg* distance is 2.82 Å.

The H atoms of the solvent water molecule were not included in the refinement. They are probably involved in two hydrogen bonds, O6···O2^{i} [symmetry code (i) $\frac{1}{2}+x$, $\frac{1}{2}-y$,

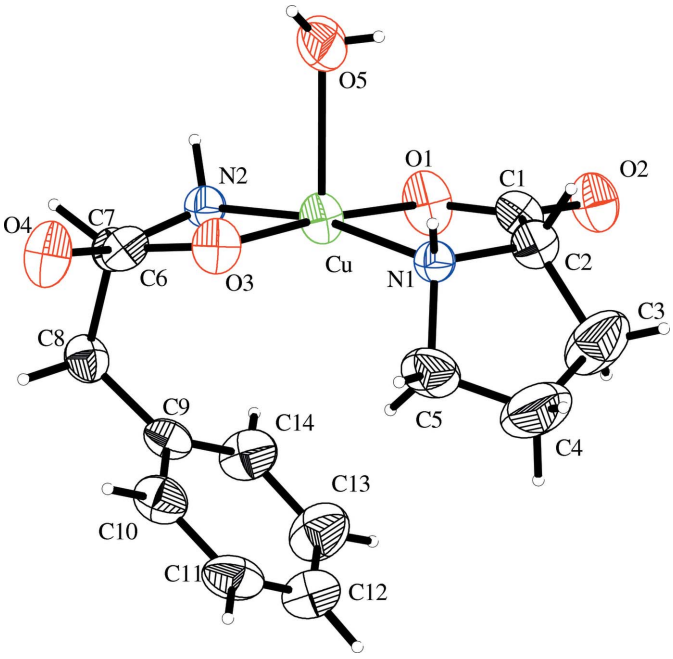


Figure 1
The structure of the [Cu(L-pro)(L-phe)(H_2O)] complex in (I) with the labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

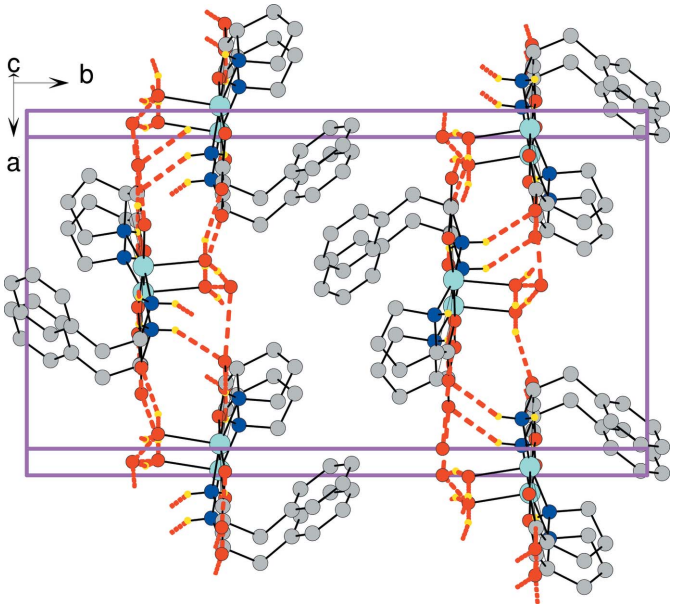


Figure 2
A view of the crystal structure of (I). Dashed lines indicate hydrogen bonds. H atoms not involved in these interactions have been omitted.

$1 - z$] and O6···O5, the O···O distances being 2.775 (7) and 3.158 (10) Å, respectively. The complex molecules and solvent water molecules are connected *via* N—H···O and O—H···O hydrogen bonds (Table 2), forming a two-dimensional network parallel to the (010) plane (Fig. 2). The hydrogen-bonded planes stack along the *b* axis through non-bonding dipolar interactions without any π–π stacking interaction between the L-phe ligands.

Experimental

A solution of optically pure L-proline (0.1 mmol) and L-phenylalanine (0.1 mmol) in water (20 ml) containing a few drops of 1.0 *M* NaOH aqueous solution was added to an aqueous solution (10 ml) containing $CuCl_2$ (0.1 mmol). The pH of the resulting solution was adjusted to 5.5 with 1.0 *M* NaOH aqueous solution. The sky-blue solid obtained was filtered off and discarded. Blue needle crystals of compound (I) were obtained by slow evaporation of the filtrate (yield 40%). Analysis calculated for $C_{14}H_{22}CuN_2O_6$: C 44.5, H 5.8, N 7.4%; found: C 44.9, H 5.5, N 7.6%.

Crystal data

$[Cu(C_5H_8NO_2)(C_9H_{10}NO_2)(H_2O)]\cdot H_2O$
M_r = 377.88
Orthorhombic, $P2_12_12_1$
a = 12.663 (3) Å
b = 22.894 (3) Å
c = 5.609 (3) Å
V = 1626.1 (10) Å^3
Z = 4
D_x = 1.544 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 1.38 mm^{-1}
T = 293 (2) K
Needle, blue
0.30 × 0.03 × 0.01 mm

Data collection

Rigaku AFC-7S diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.683, T_{max} = 0.986
2508 measured reflections
2415 independent reflections
1983 reflections with $I > 2\sigma(I)$
R_{int} = 0.045
θ_{max} = 27.5°
3 standard reflections
every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.168
S = 1.06
2415 reflections
215 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.118P)^2 + 1.1436P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 1.08 e Å^{-3}
$\Delta\rho_{min}$ = −0.65 e Å^{-3}
Absolute structure: Flack (1983), 235 Friedel pairs
Flack parameter: 0.01 (3)

Table 1
Selected geometric parameters (Å, °).

Cu—O3	1.949 (4)	Cu—N1	1.985 (5)
Cu—O1	1.955 (4)	Cu—O5	2.338 (5)
Cu—N2	1.971 (5)		
O3—Cu—O1	175.2 (2)	N2—Cu—N1	167.86 (18)
O3—Cu—N2	84.7 (2)	O3—Cu—O5	92.0 (2)
O1—Cu—N2	95.46 (19)	O1—Cu—O5	92.8 (2)
O3—Cu—N1	93.55 (19)	N2—Cu—O5	93.77 (19)
O1—Cu—N1	85.3 (2)	N1—Cu—O5	98.3 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^{i}	0.91	2.33	3.155 (7)	150
N1—H1···O2^{i}	0.91	2.57	3.243 (7)	131
N2—H2B···O3^{ii}	0.90	2.28	3.090 (7)	150
N2—H2A···O2^{iii}	0.90	2.27	3.084 (6)	150
O5—H5A···O4^{iv}	0.75 (6)	1.98 (7)	2.699 (7)	160 (11)
O5—H5B···O6^{i}	0.76 (6)	2.19 (9)	2.858 (10)	147 (11)

Symmetry codes: (i) $x, y, z-1$; (ii) $x, y, z+1$; (iii) $x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (iv) $x-\frac{1}{2}, -y+\frac{1}{2}, -z$.

H atoms bonded to C and N atoms were positioned geometrically and treated as riding with C—H = 0.93–0.98 Å, and N—H = 0.90–0.91 Å. H atoms bonded to tertiary C atoms (C2 and C7) and N atoms were refined with $U_{iso}(H) = 1.2U_{eq}(C,N)$, while for the rest $U_{iso}(H) = 1.5U_{eq}(C)$. H atoms of the coordinated water molecule (O5) were located in a difference map and their coordinates were freely refined with $U_{iso}(H) = 1.5U_{eq}(O)$. Their O—H distances are shown in Table 2. The H atoms of the solvent water molecule (O6) could not be located in difference maps, and were therefore not included. The anisotropic displacement ellipsoids of atoms C3 and C4 displayed a marked elongation in the direction perpendicular to the proline ring, which may be due to a conformational disorder. Restraints were applied to the anisotropic displacement parameters of atoms C2—C5 to reduce the difference between their U_{eq} values. The location of highest residual electron-density peak is 0.83 Å from Cu.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *MSC/AFC Diffractometer Control Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *PLATON* (Spek, 2003).

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