

catena-Poly[copper(II)- μ -L-tyrosyl-L-leucinato]

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In the title compound, $[\text{Cu}(\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_4)]_n$, the copper(II) coordination is square planar. The anionic L-tyrosyl-L-leucinate ligand binds in an N,N',O -tridentate mode to one Cu^{II} cation on one side and in an O -monodentate mode to a second Cu^{II} cation on the other side, thus defining $-\text{Cu}-\text{O}-\text{C}-\text{O}-\text{Cu}'-$ chains which run along the a axis. These chains are held together by a strong hydrogen bond involving the hydroxy H atom.

Comment

Weak and long non-covalent interactions are important in the structure and function of biological macromolecules (Lippard & Berg, 1994). They contribute to the structure, optimize molecular reactivity, allow molecular recognition, and more. In electron-transfer proteins, these bonds are conveniently tuned to regulate the kinetics of the transfer process, and thus the function of the protein.

The best known and probably most important weak interactions between metal ions, radicals or redox centres are hydrogen bonds (Jeffrey & Saenger, 1991). Real chemical paths are usually a sequence of weak interactions plus strong covalent bonds. They may be identified in protein structures (Perutz, 1993), assigned to a specific biological function (Calvo *et al.*, 2000) and in some cases reproduced in model systems (Costa-Filho *et al.* 2001, 2004; Santana *et al.*, 2005). Thus, characterization of these weak interactions in model systems is important, and metal compounds with amino acids and peptides are particularly relevant. In previous work (Costa-Filho *et al.*, 2001, 2004; Santana *et al.*, 2005), we have characterized the properties of weak interactions between metal ions using electron paramagnetic resonance (EPR) and magnetic measurements. Recently, our work allowed comparison with results obtained in an electron-transfer

protein (Calvo *et al.*, 2000; Santana *et al.*, 2005). Both structural and magnetic information about a compound are needed to progress in this direction. In line with the work performed by Costa-Filho *et al.* (2001, 2004), we are now involved in the study of magnetic interactions in the title compound, (I). So far, our EPR experiments have allowed the evaluation of the exchange interactions transmitted through a 13-step path (two coordination + ten covalent + one hydrogen bond), which connects Cu^{II} ions 9.735 (1) Å apart (see below). Magnetic measurements at very low temperature displayed a magnetic phase transition of the compound, intimately connected to this path. Thus, a detailed structural determination is essential in order to be able to analyze these magnetic data, and this is the scope of the present report.

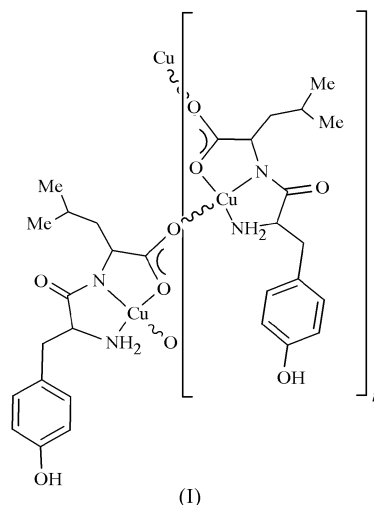


Fig. 1 presents a molecular view of complex (I). The L-tyrosyl-L-leucine (TyrLeu) ligand binds to atom Cu1 in a tridentate mode *via* amino atom N1, deprotonated peptide atom N2 and carboxylate atom O3. The square-planar coordination of the metal centre is completed through the binding of the second carboxylate atom O4ⁱ [symmetry code: (i) $x + \frac{1}{2}$,

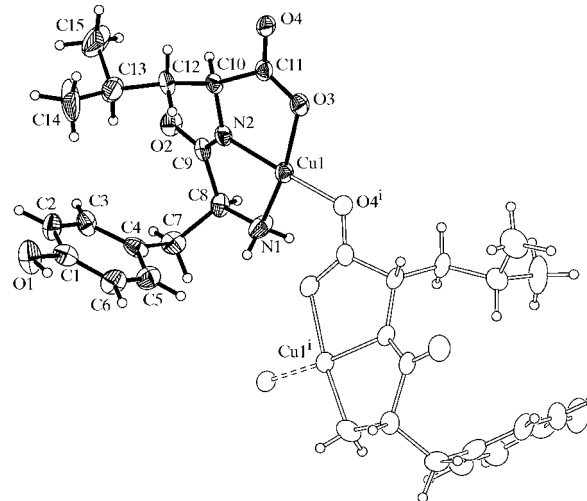


Figure 1
A view of (I), showing the independent part of the molecule in bold and the atom numbering. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code: (i) $x + \frac{1}{2}, \frac{1}{2} - y, 1 - z$.]

$\frac{1}{2} - y, 1 - z]$ of a neighbouring ligand. This particular coordination leads to CuN_2O_2 polyhedra mounted onto a 2_1 screw axis parallel to the a axis, with the Cu^{II} cations bridged by carboxylate groups in a $-\text{Cu}-\text{O}-\text{C}-\text{O}-\text{Cu}'-$ chain sequence. Similar one-dimensional structures have already been described in other Cu-dipeptide complexes [(II) (Nascimento *et al.*, 2001), (III) (Tiliakos *et al.*, 2002) and (IV) (Amirthalingam & Muralidharan, 1976)]. Table 1 presents selected bond distances and angles around the Cu^{II} cation in (I), which depart significantly from a regular pattern due to restraints imposed by chelation, a general trend ($\text{Cu}-\text{N}_{\text{peptide}} < \text{Cu}-\text{N}_{\text{amine}} \simeq \text{Cu}-\text{O}_{\text{carboxy}}$) which is shared by other dipeptide complexes. There are, however, some distortions which are intrinsic to each structure and which depend on the particular interaction scheme. One of these is the departure from planarity of the CuN_2O_2 group. The copper coordination plane in (I) presents a slight tetrahedral distortion, with the mean plane through atom Cu1 leaving the donor atoms alternately above and below the mean plane by a mean of 0.10 (1) Å. This value lies somewhere in between the distortions presented in complexes (II) [0.05 (1) Å], (III) [0.12 (1) Å] and (IV) [0.22 (1) Å].

Another distinctive feature is the shape that the two five-membered coordination loops adopt upon chelation. In the present case, the description is simplified by the fact that, in both five-membered loops, four atoms lie very nearly in the same plane, with the fifth atom departing significantly and thus giving each ring a well defined 'envelope' appearance, *viz.* in the Cu1/O3/C11/C10/N2 and N2/C9/C8/N1/Cu1 groups, the first four atoms depart by a mean of 0.01 (1) and 0.02 (1) Å from planarity, respectively, while the fifth atom is 0.14 (1) or 0.38 (2) Å away, respectively. An alternative way to evaluate this is through the torsion angles calculated around the loops (Table 1). It can be seen that, in each cycle, one of these torsion angles is distinctly smaller than the rest and corresponds to the quasi-planar part of the cycle.

From the two possible H-atom donor groups present in the dipeptide (OH and NH_2), the first provides a strong intermolecular interaction [$\text{O1}-\text{H1A} \cdots \text{O2}(1-x, y-\frac{1}{2}, \frac{1}{2}-z)$], while only one of the amino H atoms appears involved in a fairly weak contact, *viz.* $\text{N1}-\text{H1C} \cdots \text{O3}(x+\frac{1}{2}, \frac{1}{2}-y, 1-z)$ (Table 2).

In many related compounds where the Cu centre is complexed to dipeptides with aromatic groups in their side chains, some sort of $\text{Cu} \cdots \pi$ interaction has been observed [*viz.* glycyl-L-leucyl-L-tyrosine (Franks & Van der Helm, 1971), L-tyrosine (Van der Helm & Tatsch, 1972) and glycyl-L-tryptophan (Hursthouse *et al.*, 1971)]. This does not seem to be the case in (I), where the benzene ring is at an angle of $103.5(1)^\circ$ to the CuN_2O_2 mean plane, and the nearest $\text{Cu} \cdots \text{C}_{\text{ar}}$ approach is 3.84 (1) Å. There is, however, a close approach of a methyl H atom to the centroid (C_g) of the benzene ring (Table 2).

As already stated, the elemental packing units in the structure are the chains running along the a axis. The *syn-anti* carboxylate bridges link symmetry-related Cu^{II} ions to a nearest-neighbour distance along the chain of 4.981 (1) Å.

Fig. 2 presents a simplified view, showing the chain 'spine' in bold, as well as two intrachain non-bonding interactions providing the chain stability, namely the weak hydrogen bond involving the amino H atom (full broken lines) and the $\text{C}-\text{H} \cdots \pi$ interaction (double broken line).

These 'S'-shaped strips (Fig. 3) stack parallel to each other, the main link between neighbouring units being the strong hydrogen bond involving the hydroxy group. The bulky lateral wings act as effective chain spacers and, as a result, the second nearest-neighbour distance between cations [$\text{Cu1} \cdots \text{Cu1}(x+1, y, z) = 9.031(1) \text{ Å}$] is also achieved along the chain and corresponds to one full unit-cell translation along a . The shortest chemical path joining cations from different chains goes through the hydroxy hydrogen bond and links Cu^{II} centres 9.735 (1) Å apart *via* a 19.12 (1) Å path made up of 12 covalent/coordination steps plus one hydrogen bond. We have detected a weak interchain magnetic interaction through this path, of a still unknown character, exhibiting $J/k_{\text{B}} \sim 0.05 \text{ K}$. This should be compared with the direct link along the chain, $\text{Cu1} \cdots \text{Cu1}(x+\frac{1}{2}, \frac{1}{2}-y, 1-z)$, of 4.981 (1) Å, through a four-step path of 6.39 (1) Å, along which a ferromagnetic interaction takes place with $J/k_{\text{B}} \sim 3.5 \text{ K}$.

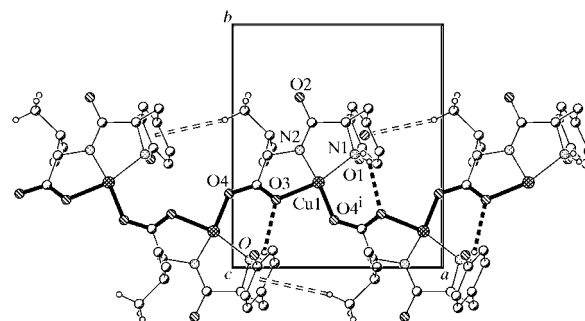


Figure 2

A lateral view of a chain, with the main path connecting Cu atoms shown in bold. Full broken lines denote the hydrogen bond involving the amino H atom and double broken lines indicate the $\text{C}-\text{H} \cdots \pi$ interactions. [Symmetry code: (i) $x+\frac{1}{2}, \frac{1}{2}-y, 1-z$].

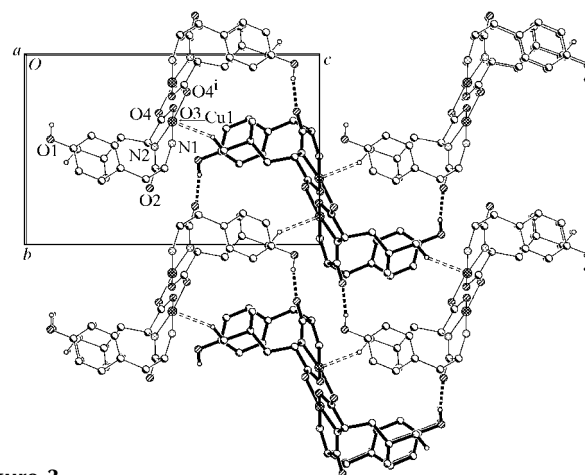


Figure 3

A packing view of (I) down the a axis. For clarity, chains are shown in alternate line weights. Full broken lines denote the hydrogen bond involving the hydroxy H atom and double broken lines indicate the short $\text{H} \cdots \text{Cu}$ contact (see *Comment*). [Symmetry code: (i) $x+\frac{1}{2}, \frac{1}{2}-y, 1-z$].

The way in which chains approach each other favours the appearance of a very short Cu...H contact [Cu1...H14B-($\frac{1}{2} - x, 1 - y, z + \frac{1}{2}$) = 2.50 (1) Å; shown as double broken lines in Fig. 3]. A survey of the Cambridge Structural Database (CSD; November 2003 update; Allen, 2002) showed this to be a rather infrequent case: out of 4060 reported cases with a CuN_nO_{4-n} polyhedra (0 ≤ n ≤ 4), only 30 presented shorter H...Cu distances, namely in the range 2.04–2.50 Å.

Experimental

To a solution containing cupric acetate monohydrate (0.25 mmol) (Merck, Darmstadt, Germany) and L-tyrosyl-L-leucine (0.25 mmol) (Sigma, St Louis, Missouri, USA) in water (20 ml) were added ethanol (20 ml) and 0.1 N NaOH (5 ml). After one week, a number of well shaped, though small and extremely poorly diffracting, needles appeared by evaporation of the solution at room temperature.

Crystal data

[Cu(C ₁₅ H ₂₀ N ₂ O ₄)]	Mo K α radiation
$M_r = 355.87$	Cell parameters from 25 reflections
Orthorhombic, $P2_12_12_1$	$\theta = 7.5\text{--}12.5^\circ$
$a = 9.0307$ (9) Å	$\mu = 1.45$ mm ⁻¹
$b = 10.4375$ (12) Å	$T = 295$ (2) K
$c = 16.1471$ (18) Å	Needle, blue
$V = 1522.0$ (3) Å ³	$0.55 \times 0.14 \times 0.12$ mm
$Z = 4$	
$D_x = 1.553$ Mg m ⁻³	

Data collection

Siemens R3m diffractometer	$R_{\text{int}} = 0.055$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 25.0^\circ$
Absorption correction: ψ scan	$h = 0 \rightarrow 10$
(SHELXTL/PC; Sheldrick, 1994)	$k = 0 \rightarrow 12$
$T_{\text{min}} = 0.785, T_{\text{max}} = 0.845$	$l = 0 \rightarrow 19$
1662 measured reflections	2 standard reflections
1557 independent reflections	every 98 reflections
1066 reflections with $I > 2\sigma(I)$	intensity decay: 2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0517P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.048$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.111$	$(\Delta/\sigma)_{\text{max}} = 0.05$
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.32$ e Å ⁻³
1557 reflections	$\Delta\rho_{\text{min}} = -0.36$ e Å ⁻³
202 parameters	Absolute structure: Flack (1983),
H atoms: see below	no Friedel pairs
	Flack parameter: -0.07 (5)

Table 1

Selected geometric parameters (Å, °).

Cu1—N2	1.887 (7)	Cu1—O3	1.969 (5)
Cu1—O4 ⁱ	1.922 (5)	Cu1—N1	1.975 (6)
N2—Cu1—O4 ⁱ	170.4 (3)	N2—Cu1—N1	83.2 (3)
N2—Cu1—O3	83.6 (3)	O4 ⁱ —Cu1—N1	104.2 (3)
O4 ⁱ —Cu1—O3	89.8 (2)	O3—Cu1—N1	164.2 (2)
Cu1—N1—C8—C9	-8.6 (8)	Cu1—O3—C11—C10	-1.9 (10)
N1—C8—C9—N2	-5.0 (10)	O3—C10—C11—N2	4.2 (10)
C8—C9—N2—Cu1	17.9 (9)	C10—C11—N2—Cu1	-172.0 (7)
C9—N2—Cu1—N1	-18.7 (7)	C11—N2—Cu1—O3	-2.7 (3)
N2—Cu1—N1—C8	14.0 (6)	N2—Cu1—O3—C10	4.5 (3)

Symmetry code: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$.

H atoms attached to C and N atoms were included in calculated positions, with idealized distances to their hosts [C—H(CH) = 0.98,

Table 2

Hydrogen-bond geometry (Å, °).

Cg is the centroid of the C1–C6 benzene ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1A...O2 ⁱⁱ	0.85 (4)	1.81 (4)	2.642 (8)	168 (12)
N1—H1C...O3 ⁱ	0.90	2.38	2.813 (7)	110
C15—H15B...Cg ⁱⁱⁱ	0.96	3.08	4.02	167

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

C—H(CH₂) = 0.97, C—H(CH₃) = 0.96, C—H(aromatic) = 0.93 and N—H(NH₂) = 0.92 Å] and allowed for as riding; in the case of terminal CH₃, they were allowed to rotate as well. The hydroxy H atom was found in a difference density map and refined with a restrained O—H distance of 0.82 (1) Å. The H atoms were given $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C})$ and $1.5U_{\text{eq}}(\text{C})$ for methyl and non-methyl H atoms, respectively.

Data collection: P3/P4-PC (Siemens, 1991); cell refinement: P3/P4-PC; data reduction: XDISK in SHELXTL/PC (Sheldrick, 1994); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XP in SHELXTL/PC.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1224). Services for accessing these data are described at the back of the journal.

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