

## Poly[[diaqua- $\mu$ -4,4'-bipyridine-di-nitratodi- $\mu$ -L-tyrosinato-dicopper(II)]: a chiral two-dimensional coordination polymer

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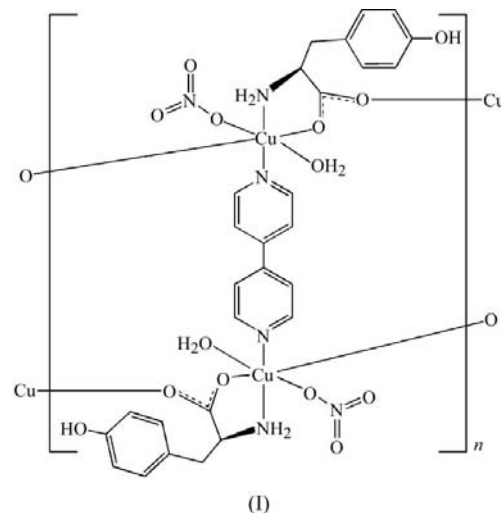
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The title compound,  $[\text{Cu}_2(\text{C}_9\text{H}_{10}\text{NO}_3)_2(\text{NO}_3)_2(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})_2]_n$ , contains  $\text{Cu}^{\text{II}}$  atoms and L-tyrosinate (L-tyr) and 4,4'-bipyridine (4,4'-bipy) ligands in a 2:2:1 ratio. Each Cu atom is coordinated by one amino N atom and two carboxylate O atoms from two L-tyr ligands, one N atom from a 4,4'-bipy ligand, a monodentate nitrate ion and a water molecule in an elongated octahedral geometry. Adjacent Cu atoms are bridged by the bidentate carboxylate groups into a chain. These chains are further linked by the bridging 4,4'-bipy ligands, forming an undulated chiral two-dimensional sheet. O—H...O and N—H...O hydrogen bonds connect the sheets in the [100] direction. This study offers useful information for the engineering of chiral coordination polymers with amino acids and 4,4'-bipy ligands by considering the ratios of the metal ion and organic components.

### Comment

There is considerable interest in chiral coordination polymers, owing to their potential application in asymmetric catalysis and chiral separation (Kesanli & Lin, 2003). Although these materials can be synthesized from single chiral or achiral organic components, self-assembly based on a mixed-ligand system containing both chiral and achiral ligands is an attractive approach to the construction of chiral framework materials since it allows for facile tuning of structural, topological and functional features derived from different molecular components (Dai *et al.*, 2005; Wang *et al.*, 2008; Zaworotko, 2001). The 4,4'-bipyridine (4,4'-bipy) molecule is a common building block, which has been used extensively as a rigid linear linker between metal centres (Biradha *et al.*, 2006). Amino acids such as L-tyrosine (L-tyr) are good candidates as chiral building blocks, with their amino and carboxylate groups being capable of binding to metal ions in flexible

modes (Vaidhyanathan *et al.*, 2006). We report here the title chiral two-dimensional coordination polymer, (I), which is assembled by connecting Cu–L-tyr units with 4,4'-bipy linkers.



The asymmetric unit of (I) consists of two  $\text{Cu}^{\text{II}}$  atoms, two deprotonated L-tyr ligands, one 4,4'-bipy ligand, two nitrate ions and two coordinated water molecules (Fig. 1). Each Cu atom is coordinated by one N atom and two carboxylate O atoms from two L-tyr ligands and one N atom from a 4,4'-bipy ligand in the equatorial plane, and by a monodentate nitrate ion and a water molecule in the axial positions. The nitrate ions and water molecules are weakly bonded to the Cu atoms, with Cu—O<sub>nitrate</sub> distances of 2.565 (5) and 2.808 (7) Å, and Cu—O<sub>water</sub> distances of 2.461 (4) and 2.627 (5) Å (Table 1). These axial Cu—O distances are longer than the sum of the ionic radii (Wells, 1975), but they are still within the range of 2.2–2.9 Å known for axial Cu—O bond lengths (Zhang *et al.*, 1996), thus displaying an elongated octahedral geometry around each Cu atom. The L-tyr ligand binds to the Cu atom in a  $\mu$ -( $\kappa^3\text{N},\text{O}:\text{O}'$ ) mode, that is, one carboxylate O atom chelates a Cu atom together with the amino N atom, and the other carboxylate O atom coordinates to another Cu atom. The hydroxyl O atom of the phenol group is uncoordinated. In this way, the L-tyr ligands bridge adjacent Cu atoms to form a chiral  $[\text{Cu}(\text{L-tyr})(\text{NO}_3)(\text{H}_2\text{O})]_n$  chain extending in the [001]

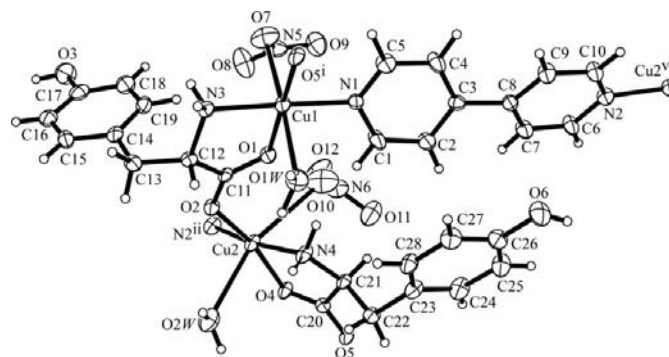
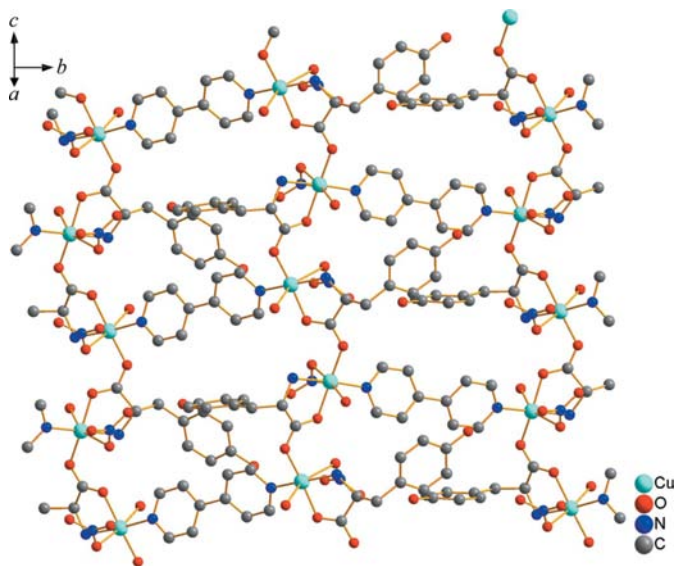


Figure 1

The asymmetric unit of (I), together with symmetry-related atoms to complete the coordination unit. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i)  $x, y, z - 1$ ; (ii)  $2 - x, y - \frac{1}{2}, 1 - z$ ; (vi)  $2 - x, y + \frac{1}{2}, 1 - z$ .]

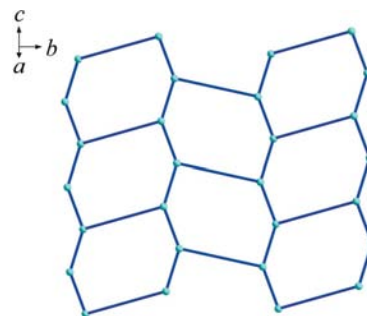


**Figure 2**  
Ball-and-stick representation of the two-dimensional sheet in (I). H atoms have been omitted for clarity.

direction. The separations between the Cu atoms in the chain are 5.180 (1) and 5.193 (1) Å. As shown in Fig. 2, these chains are further connected by the 4,4'-bipy linkers into a two-dimensional undulating sheet. Fig. 3 shows a schematic depiction of the sheet, which has a (6,3) topology (Batten & Robson, 1998), with Cu atoms as the three-connected nodes and with meshes of dimensions  $9.82 \times 11.06$  Å. Moreover, these sheets are arranged parallel to the (100) plane and connected by three types of hydrogen bonds (Table 2). One is formed between a hydroxyl group and a water O atom [O6—H6A...O2W<sup>iii</sup>; symmetry code: (iii)  $1 - x, \frac{1}{2} + y, 1 - z$ ], the second involves the coordinated water molecules and nitrate ions, and the third involves the amino groups and nitrate ions.

It has been observed in the structures of [Cu(L-tyr)(1,10-phenanthroline)(H<sub>2</sub>O)](ClO<sub>4</sub>)·H<sub>2</sub>O (Sugimori *et al.*, 1997) and [Cu(L-I<sub>2</sub>tyr)(NO<sub>3</sub>)(2,2'-bipyridine)]·CH<sub>3</sub>OH (Zhang *et al.*, 1996) that the phenol ring of the L-tyr ligand folds back to be located over the Cu atom with an intramolecular phenol ring...Cu coordination plane interaction, whereas the two phenol rings in (I) each extend away from the Cu atoms. The phenol ring with hydroxyl atom O3 inserts itself into the mesh of the sheet to form a hydrogen bond between atom O3 and nitrate atom O11( $2 - x, y - \frac{1}{2}, 1 - z$ ) of the opposite chain, while the phenol ring with hydroxyl atom O6 lies between two sheets, stabilized by a  $\pi$ - $\pi$  interaction with a pyridyl ring of a neighbouring sheet [centroid-to-centroid distance = 3.56 (1) Å]. As a result, the channels along the [100] direction formed by the aligned meshes of the sheets are blocked by the side chains of the L-tyr ligands.

The rational design and controlled synthesis of coordination frameworks have been a challenging subject in crystal engineering. Small changes in the variables of reaction, such as stoichiometry, pH value, temperature, solvent and metal source, can have a profound influence on the structures of the



**Figure 3**  
Schematic view of the (6,3) net in (I). Short and long lines represent the L-tyr and 4,4'-bipy ligands, respectively.

products. For the Cu<sup>II</sup>-amino acid-4,4'-bipy system, it seems that the ratio of Cu<sup>II</sup> to amino acid to 4,4'-bipy is related to structural architecture. We note that a zero-dimensional dinuclear complex is formed for an L-valinate complex when the ratio is 2:2:3 (Lou & Hong, 2008), while one-dimensional helical chains have been found in L-threoninate and L-alaninate complexes with a ratio of 1:1:1, regardless of a polar or nonpolar side chain (Lou *et al.*, 2005). Two-dimensional frameworks are observed in (I), with the polar L-tyr ligand, and in a nonpolar L-valinate complex (Lou *et al.*, 2007), both of which have a ratio of 2:2:1. Clearly, despite the observed structural relevance to component ratios, further work is needed for understanding the factors affecting these structural architectures.

In conclusion, we have synthesized a two-dimensional chiral coordination polymer based on a mixed-ligand system, in which the L-tyr ligand provides a chiral source and the 4,4'-bipy ligand is used to extend the framework. This study offers helpful information for engineering this type of chiral coordination polymer by considering the ratios of metal ion and organic components.

## Experimental

Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (0.096 g, 0.4 mmol) and L-tyrosine (0.072 g, 0.4 mmol) were dissolved in hot water (20 ml) with stirring. To this solution was added a solution of 4,4'-bipyridine (0.031 g, 0.2 mmol) in methanol (10 ml). The resulting solution was allowed to stand at room temperature and blue crystals of (I) suitable for X-ray diffraction analysis were obtained after two weeks.

### Crystal data

[Cu <sub>2</sub> (C <sub>9</sub> H <sub>10</sub> NO <sub>3</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> (C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> )·(H <sub>2</sub> O) <sub>2</sub> ]	$\beta = 108.150$ (2)°
$M_r = 803.68$	$V = 1581.8$ (5) Å <sup>3</sup>
Monoclinic, $P2_1$	$Z = 2$
$a = 7.6075$ (13) Å	Mo $K\alpha$ radiation
$b = 22.281$ (4) Å	$\mu = 1.43$ mm <sup>-1</sup>
$c = 9.8205$ (16) Å	$T = 293$ (2) K
	$0.33 \times 0.19 \times 0.17$ mm

### Data collection

Bruker SMART APEX CCD area-detector diffractometer	8422 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	5584 independent reflections
$T_{\min} = 0.652$ , $T_{\max} = 0.791$	5003 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.032$

**Table 1**

Selected bond lengths (Å).

Cu1—O5 <sup>i</sup>	1.968 (4)	Cu2—N4	1.964 (5)
Cu1—O1	1.993 (4)	Cu2—O4	1.964 (4)
Cu1—N3	2.002 (5)	Cu2—O2	1.968 (4)
Cu1—N1	2.004 (4)	Cu2—N2 <sup>ii</sup>	1.989 (5)
Cu1—O1W	2.461 (4)	Cu2—O2W	2.627 (5)
Cu1—O7	2.565 (5)	Cu2—O10	2.808 (7)

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

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3 $\cdots$ O11 <sup>ii</sup>	0.87	1.90	2.761 (9)	169
O6—H6A $\cdots$ O2W <sup>iii</sup>	0.86	1.91	2.768 (7)	175
O1W—H1W $\cdots$ O9 <sup>iv</sup>	0.93	1.95	2.876 (7)	171
O1W—H2W $\cdots$ O11 <sup>v</sup>	0.86	2.00	2.849 (8)	172
O2W—H4W $\cdots$ O8 <sup>iv</sup>	0.87	1.90	2.772 (8)	173
O2W—H3W $\cdots$ O12 <sup>iv</sup>	0.86	1.97	2.779 (8)	157
N3—H3A $\cdots$ O12 <sup>v</sup>	0.90	2.20	3.063 (7)	159
N4—H4A $\cdots$ O1	0.90	2.36	2.974 (6)	126
N4—H4B $\cdots$ O9 <sup>iv</sup>	0.90	2.18	3.018 (7)	155

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

### Refinement

$$R[F^2 > 2\sigma(F^2)] = 0.052$$

$$wR(F^2) = 0.137$$

$$S = 1.08$$

5584 reflections

439 parameters

1 restraint

H-atom parameters constrained

$$\Delta\rho_{\max} = 1.23 \text{ e \AA}^{-3}$$

$$\Delta\rho_{\min} = -0.87 \text{ e \AA}^{-3}$$

Absolute structure: Flack (1983),

with 2506 Friedel pairs

Flack parameter: 0.010 (18)

H atoms bonded to O atoms were located in a difference Fourier map and fixed in the refinement, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$ . Other H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 (aromatic), 0.97 (CH<sub>2</sub>) or 0.98 Å (CH) and N—H = 0.90 Å, and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ . The highest residual electron density is 0.94 Å<sup>-3</sup> from atom Cu2 and the deepest hole is 0.93 Å<sup>-3</sup> from atom Cu1.

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3088). Services for accessing these data are described at the back of the journal.

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