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catena-Poly[[μ-hexanedioato-1κO^1:2κO^6-bis[aqua(5-carboxypentanoato-κO)copper(II)]]-di-μ-4,4′-bipyridine-1κN:1′$\kappa N'$;2κN:2′$\kappa N'$]

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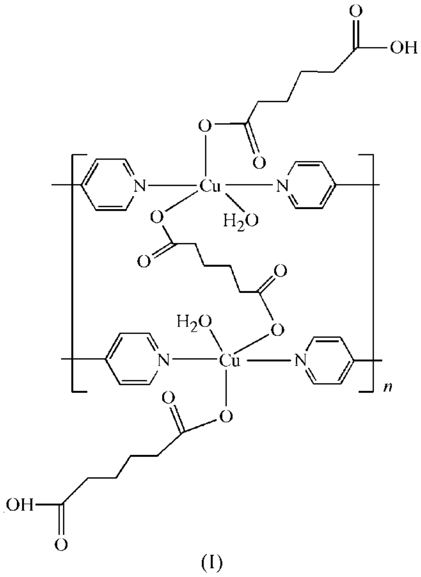
In the title compound, $[Cu_2(C_6H_8O_4)(C_6H_9O_4)_2(C_{10}H_8N_2)_2(H_2O)_2]_n$, the square-pyramidally coordinated Cu atoms are bridged by both 4,4-bipyridine and adipate ligands into ladder-like chains, with *exo*-orientated 5-carboxypentanoate ligands pendant from both side rails. Half of the adipate ligand is related to the other half by inversion symmetry. Interchain O—H···O hydrogen bonds from the aqua ligands to the carbonyl O atoms of the 5-carboxypentanoate ligands are responsible for the formation of two-dimensional grid-like (4,4)-networks, which complete a twofold interpenetration.

Comment

In recent years, interest in the utilization of aliphatic dicarboxylic acids for the rational design and synthesis of coordination polymers has grown rapidly, due to their fascinating network topologies and specific properties (Rao *et al.*, 2004; Kitagawa *et al.*, 2004). Aliphatic α,ω-dicarboxylate ligands have been recognized as important flexible spacers due to their conformational and coordination versatility, and they tend to bridge transition metal cations to form coordination polymers with low dimensionality (Zheng & Xie, 2004; Zheng & Sun, 2003; Zheng & Kong, 2002). However, even high-dimensional α,ω-dicarboxylate coordination polymers normally exhibit little porosity (Rao *et al.*, 2004). To avoid such drawbacks, our recent research has been intensively focused on the construction of porous α,ω-dicarboxylate coordination polymers by the introduction of the rigid 4,4′-bipyridine molecule as an ancillary ligand to co-bridge metal atoms into supramolecular architectures (Zheng & Ying, 2005; Zheng *et al.*, 2004; Zheng & Kong, 2003). Among these coordination polymers, the transition metal atoms are bridged by α,ω-dicarboxylate anions to generate square clusters (Li *et al.*, 1997, 2000), polymeric chains (Zheng & Kong, 2003; Rather & Zaworotko, 2003), ribbon-like chains (Zheng & Ying, 2005; Zheng *et al.*, 2004) and layers (Zheng & Ying, 2005; Zheng *et al.*, 2004; Mukherjee *et al.*, 2003), and these structural motifs are further linked by 4,4′-bipyridine ligands into layers and three-dimensional frameworks with aperture sizes dependent on the length of the dicarboxylate ligand used. In the case of the adipate compounds, the three-dimensional frameworks have such large apertures that they form a twofold interpenetration with a topology identical to that of the well known cluster compound Nb_6F_{15} (Batten & Robson, 1998). In this paper, we present the title novel coordination polymer, (I), where the Cu atoms are bridged by both diadipate dianions and 4,4′-bipyridine ligands into one-dimensional ladder-like chains.



(I)

The asymmetric unit of (I) consists of one Cu^{II} cation, one 4,4′-bipyridine molecule (bpy), one aqua ligand, one 5-car-

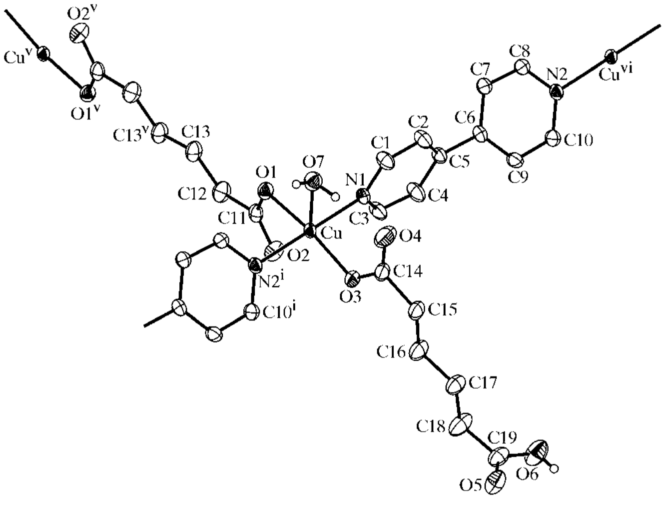


Figure 1
A view of the coordination environment around the Cu atoms in (I). Displacement ellipsoids are drawn at the 45% probability level. H atoms bonded to C atoms have been omitted for clarity. [Symmetry codes: (i) $x, y, 1 + z$; (v) $1 - x, 2 + y, 1 - z$; (vi) $x, y, z - 1$.]

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boxypentanoate anion and one half of an adipate dianion residing on a crystallographic inversion centre. As depicted in Fig. 1, the Cu atoms are each square-pyramidally coordinated by two pyridyl N atoms, *viz*. N1 and N2^{i} [symmetry code: (i) *x*, *y*, *z* + 1], of different bpy ligands and by three O atoms (O7, O3 and O1) belonging to one aqua ligand, one 5-carboxypentanoate anion and an adipate dianion, with the aqua ligand at the apical site. The Cu atom is shifted by 0.151 (1) Å toward the apical O7 atom from the equatorial plane defined by atoms O1, N1, O3 and N2^{i}. The two *trans* Cu—N bond lengths have the same value of 2.030 (2) Å (" 1), slightly longer than either of the two *trans* Cu—O bonds, of 1.954 (2) and 1.987 (1) Å. The apical Cu—O bond length is 2.365 (2) Å.

Fig. 2 demonstrates that the pentacoordinated Cu atoms are bridged by the adipate dianions into dimers, which are further linked by bpy ligands to generate ladder-like polymeric chains with the *exo*-orientated 5-carboxypentanoate ligands perpendicularly pendant from both side rails. These polymeric chains extend infinitely along the [001] direction. They approach one another and the aqua ligands of one chain form interchain hydrogen bonds, with an $R_2^2(22)$ graph set (Etter, 1991; Etter *et al.*, 1990), to the carbonyl O atoms of neighbouring adipate dianions, with O7$\cdots$O5^{ii} = 2.797 (2) Å and O7—H$\cdots$O5^{ii} = 171 (3)° [symmetry code: (ii) $-x$, $-y+1$, $-z+1$; Fig. 2 and Table 2], resulting in two-dimensional grid-like (4,4)-layers (Hagrman *et al.*, 1999). The layers are orientated parallel to (110) and (1$\overline{1}$0), and complete a twofold interpenetration, as illustrated in Fig. 3 (Batten & Robson, 1998), in such a way that the $R_2^2(22)$ hydrogen-bonded rings of one layer are clamped between the adipate rungs of the interpenetrating layers. The interpenetrating layers are held together by relatively strong interlayer hydrogen bonds from the carboxyl O6 groups to the uncoordinating carboxylate O2 atoms, with O6$\cdots$O2^{iii} = 2.593 (3) Å and O6—H$\cdots$O2^{iii} = 168 (3)° [symmetry code: (iii) $-x-\frac{1}{2}$, $y-\frac{1}{2}$, $-z+\frac{1}{2}$]. Additionally, the aqua ligand forms a relatively strong intrachain hydrogen bond to the uncoordinated carboxylate O4 atom of the pendant 5-carboxypentanoate anion [O7$\cdots$O4 = 2.647 (2) Å and O7—H$\cdots$O4 = 164 (3)°].

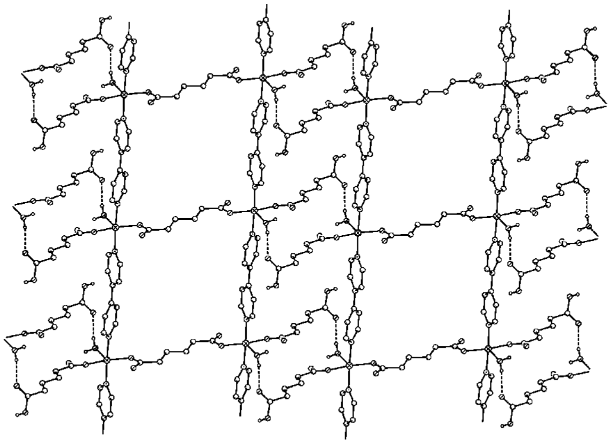

Figure 2

The grid-like (4,4)-layer generated from Cu^{II} ions bridged by 4,4-bipyridine ligands, adipate dianions and 5-carboxypentanoate anions in (I). Dashed lines indicate hydrogen bonds. H atoms bonded to C atoms have been omitted for clarity.

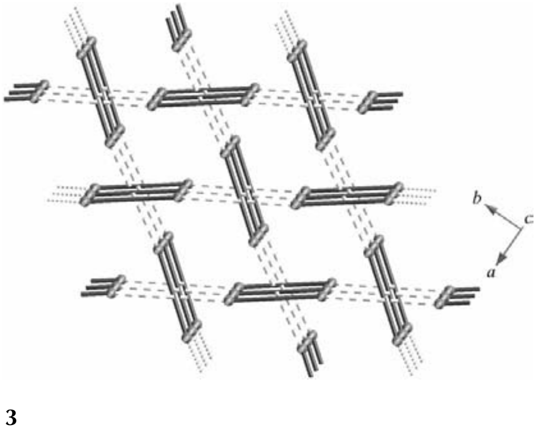

Figure 3

The topology of the twofold interpenetration of the grid-like (4,4)-layers in (I). Dark- and light-grey rods represent adipate dianions and 4,4-bipyridine ligands, respectively, and dashed grey rods represent the 5-carboxypentanoate pairs.

Both adipate and 5-carboxypenanoate anions exhibit normal geometry (Zheng & Ying, 2005; Zheng *et al.*, 2004; Mukherjee *et al.*, 2003; Ying *et al.*, 2004) and, as expected, the C—O bond distances to the coordinated O atoms are significantly longer than those to the uncoordinated O atoms. The C19—O5 distance of 1.211 (3) Å is considerabley shorter than the C19—O6 distance of 1.305 (3) Å, indicating double-bond character. The bpy ligands are found to be twisted around the central C5—C6 bond, with a dihedral angle of 45.0 (1)° between the two pyridyl components. The N1-containing pyridyl rings are oriented so as to favour formation of weak C—H$\cdots$O hydrogen bonds (Table 2) and the orientation of the N2-containing pyridyl plane may be due to steric effects from the aqua ligand (Fig. 1).

Experimental

Dropwise addition of Na_2CO_3 (1.0 *M*, 0.50 ml) to an aqueous solution (5.0 ml) of $CuSO_4{\cdot}5H_2O$ (0.075 g, 0.30 mmol) yielded a pale-blue precipitate, which was centrifuged and washed several times with doubly distilled water until there were no sulfate anions in the supernatant. The fresh precipitate was then added to a solution of 4,4′-bipyridine dihydrate (0.058 g, 0.30 mmol) and adipic acid (0.044 g, 0.30 mol) in a water–methanol mixture (20 ml, 1:1 *v*/*v*) and stirred vigorously for 30 min. The suspension which formed was filtered off and slow evaporation afforded a small number of blue crystals of (I) in the nearly colourless filtrate (pH 4.56).

Crystal data

$[Cu_2(C_6H_8O_4)(C_6H_9O_4)_2$-
$(C_{10}H_8N_2)_2(H_2O)_2]$
$M_r = 454.94$
Monoclinic, $P2_1/n$
$a = 10.885$ (2) Å
$b = 16.216$ (3) Å
$c = 11.108$ (2) Å
$\beta = 96.04$ (3)°
$V = 1949.8$ (6) Å^3
$Z = 4$

$D_x = 1.550$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 5.0$–12.5°
$\mu = 1.17$ mm^{-1}
$T = 296$ (2) K
Block, blue
0.49 × 0.31 × 0.22 mm

Data collection

Bruker *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical (using intensity measurements) (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.651$, $T_{max} = 0.776$
6298 measured reflections
4483 independent reflections
3906 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 27.5°$
$h = -1 \rightarrow 14$
$k = -21 \rightarrow 1$
$l = -14 \rightarrow 14$
3 standard reflections every 97 reflections intensity decay: no

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.101$
$S = 1.15$
4483 reflections
296 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0547P)^2 + 0.5023P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.73$ e Å^{-3}
$\Delta\rho_{min} = -0.49$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0132 (9)

Table 1
Selected geometric parameters (Å, °).

Cu—O3	1.9541 (15)	Cu—O7	2.3653 (17)
Cu—O1	1.9865 (14)	C19—O5	1.211 (3)
Cu—N1	2.0300 (17)	C19—O6	1.305 (3)
Cu—N2^{i}	2.0300 (17)		
O3—Cu—O1	165.83 (7)	N1—Cu—N2^{i}	176.23 (6)
O3—Cu—N1	90.49 (7)	O3—Cu—O7	99.57 (7)
O1—Cu—N1	89.51 (6)	O1—Cu—O7	94.59 (6)
O3—Cu—N2^{i}	90.87 (7)	N1—Cu—O7	91.64 (7)
O1—Cu—N2^{i}	88.31 (6)	N2^{i}—Cu—O7	91.59 (7)

Symmetry code: (i) $x, y, z + 1$.

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

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O6—H6⋯O2^{ii}	0.72 (3)	1.88 (3)	2.593 (3)	168 (3)
O7—H7*A*⋯O4	0.82 (3)	1.85 (3)	2.647 (2)	164 (3)
O7—H7*B*⋯O5^{iii}	0.78 (3)	2.03 (3)	2.797 (2)	171 (3)
C1—H1⋯O7	0.93	2.44	3.100 (3)	127
C3—H3⋯O2	0.93	2.59	3.233 (3)	127
C3—H3⋯O5^{iv}	0.93	2.50	3.259 (3)	139

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

All H atoms associated with C atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 and 0.97 Å, while the H atoms of the aqua ligands and the O6 carboxyl group were located in a difference Fourier synthesis, and the O—H distances were refined (see Table 2). All U_{iso}(H) values were refined freely.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); 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: HJ1068). Services for accessing these data are described at the back of the journal.

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