

# Coordination polymer chains built from Cu<sup>II</sup> and adipate ions linked by hydrogen bonds to form a three-dimensional framework structure

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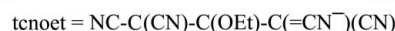
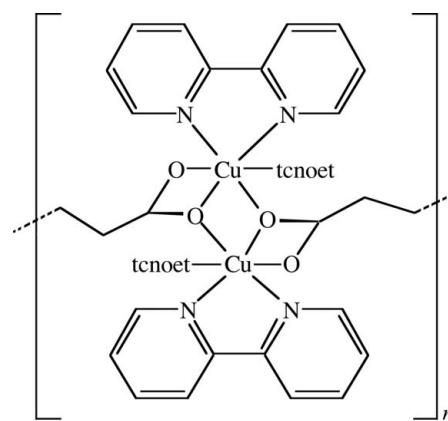
In the title compound, *catena*-poly[bis[(2,2'-bipyridine- $\kappa^2N,N'$ )-(1,1,3,3-tetracyano-2-ethoxypropenido- $\kappa N$ )copper(II)]- $\mu_4$ -hexanedioato- $\kappa^6O^1,O^1':O^6,O^6':O^6$ ], [Cu<sub>2</sub>(C<sub>9</sub>H<sub>5</sub>N<sub>4</sub>O)<sub>2</sub>(C<sub>6</sub>H<sub>8</sub>O<sub>4</sub>)(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>]<sub>n</sub>, the adipate (hexanedioate) dianion lies across a centre of inversion in the space group *P* $\bar{1}$ . The Cu<sup>II</sup> centre adopts a distorted form of axially elongated (4+2) coordination, and the Cu<sup>II</sup> and adipate components form a one-dimensional coordination polymer from which the 2,2'-bipyridine and 1,1,3,3-tetracyano-2-ethoxypropenide components are pendent, and where each adipate dianion is bonded to four different Cu<sup>II</sup> centres. The coordination polymer chains are linked into a three-dimensional framework structure by a combination of C—H...N and C—H...O hydrogen bonds, augmented by a  $\pi$ - $\pi$  stacking interaction.

**Keywords:** crystal structure; one-dimensional coordination polymer; copper(II) complex; adipate;  $\pi$ - $\pi$  stacking interactions; 2,2'-bipyridine; polynitrile anions; 1,1,3,3-tetracyano-2-ethoxypropenide.

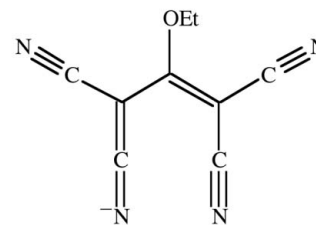
## 1. Introduction

The design and synthesis of metal coordination compounds containing carboxylate ligands is currently an active area of research due to their potential applications in the fields of molecular magnetism (Setifi *et al.*, 2006, 2007; Setifi, Setifi, Ghazzali *et al.*, 2014), catalysis (Ma *et al.*, 2009), nonlinear optics (Zang *et al.*, 2006) and luminescence (Tao *et al.*, 2000). A number of new coordination polymers containing not only carboxylate ligands but also chelating diamines as co-ligands have been reported recently (Mukherjee *et al.*, 2003; Zheng *et al.*, 2002, 2004; Zheng & Lin, 2003; Ghosh *et al.*, 2007;

Kathalikkattil *et al.*, 2010; Setifi, Setifi, Ghazzali *et al.*, 2014). In addition to a variety of coordination polymer types, finite complexes have also been observed, ranging from dinuclear (Setifi, Setifi, Ghazzali *et al.*, 2014) to octanuclear (Ghosh *et al.*, 2007). In this context, the aim of some of our recent work has been to extend the potential versatility of such complexes to include four-component systems which also incorporate polynitrile anions as ligands and/or counter-ions, as such anions are of interest in exhibiting both a high degree of electronic delocalization and a variety of coordination modes (Atmani *et al.*, 2008; Setifi, Domasevitch *et al.*, 2013; Setifi, Setifi *et al.*, 2013; Setifi, Setifi, El Ammari *et al.*, 2014). Accordingly, we report here the synthesis, molecular structure and supramolecular assembly of the title compound, [Cu<sub>2</sub>(tcnoet)<sub>2</sub>(adipate)(bipy)<sub>2</sub>]<sub>n</sub>, (I), where adipate represents hexane-1,6-dionate, bipy represents 2,2'-bipyridine and tcnoet represents 1,1,3,3-tetracyano-2-ethoxypropenide.



(I)



(A)

## 2. Experimental

### 2.1. Synthesis and crystallization

The salt K(tcnoet) was prepared following the published method of Middleton *et al.* (1958). Under aerobic conditions, an ethanolic solution (5 ml) of 2,2'-bipyridine (50.0 mg, 0.32 mmol) was added, with stirring at ambient temperature, to an ethanol solution (5 ml) of copper(II) chloride dihydrate (54.5 mg, 0.32 mmol). A pale-green precipitate appeared quickly in the green solution. An aqueous solution of disodium adipate (2 M) was then added slowly with stirring until complete dissolution of the precipitate had occurred (*ca* 15 ml). To the resulting blue solution was added an aqueous solution (10 ml) of K(tcnoet) (144 mg, 0.64 mmol). Slow

**Table 1**

Experimental details.

Crystal data	
Chemical formula	[Cu <sub>2</sub> (C <sub>9</sub> H <sub>5</sub> N <sub>4</sub> O) <sub>2</sub> (C <sub>6</sub> H <sub>8</sub> O <sub>4</sub> )(C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>2</sub> ]
<i>M<sub>r</sub></i>	476.97
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.8825 (3), 10.5610 (4), 12.2541 (5)
$\alpha$ , $\beta$ , $\gamma$ (°)	71.724 (3), 80.582 (4), 84.974 (3)
<i>V</i> (Å <sup>3</sup> )	1076.03 (7)
<i>Z</i>	2
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	1.05
Crystal size (mm)	0.20 × 0.15 × 0.10
Data collection	
Diffractometer	Agilent Xcalibur Sapphire2 diffractometer
Absorption correction	Multi-scan ( <i>SADABS</i> ; Sheldrick, 2003)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.771, 0.929
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	10761, 6143, 4850
<i>R<sub>int</sub></i>	0.021
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.703
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.032, 0.078, 0.96
No. of reflections	6143
No. of parameters	290
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$ , $\Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.46, -0.24

Computer programs: *CrysAlis PRO* (Agilent, 2013), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2014) and *PLATON* (Spek, 2009).

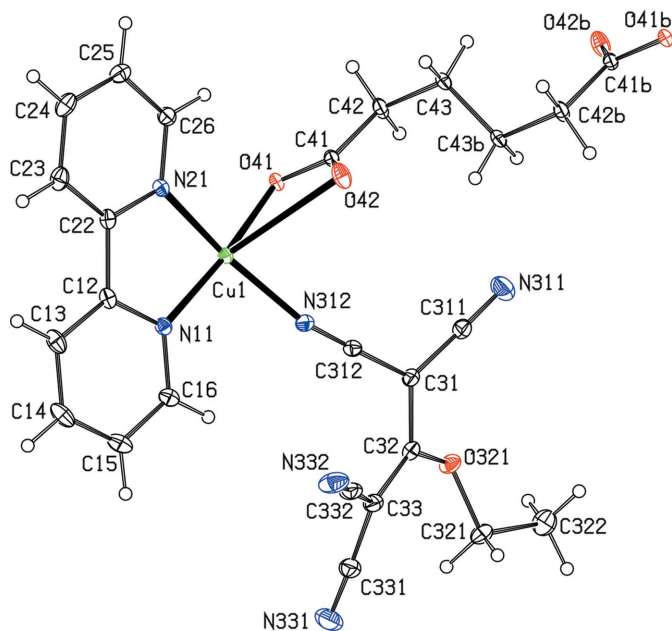
evaporation of this final solution, at ambient temperature and in air, gave blue crystals of (I) suitable for single-crystal X-ray diffraction (yield 37%).

## 2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms were located in difference maps and then treated as riding atoms in geometrically idealized positions, with C–H = 0.95 (aromatic), 0.98 (CH<sub>3</sub>) or 0.99 Å (CH<sub>2</sub>), and with *U*<sub>iso</sub>(H) = *kU*<sub>eq</sub>(C), where *k* = 1.5 for the methyl group, which was permitted to rotate but not to tilt, and 1.2 for all other H atoms. Reflection 110, which had been attenuated by the beam stop, was omitted from the refinements.

## 3. Comment

The title compound, (I) (Fig. 1), is closely related to [Cu<sub>4</sub>(adipate)<sub>3</sub>(bipy)<sub>4</sub>](tcoet)<sub>2</sub>, (II) (Setifi *et al.*, 2006). The composition of these two compounds differs only in the molecular ratio of the adipate and tcoet anionic components. Both compounds were prepared from reaction mixtures containing Cu<sup>II</sup>, bipy and tcoet in a molar ratio of 2:2:1, together with an excess of sodium adipate, but (I) was formed in an aqueous ethanol solution, whereas (II) was formed in aqueous methanol. As discussed below, the structures of (I) and (II) are markedly different, suggesting that a rich variety of structural topologies is potentially accessible with only

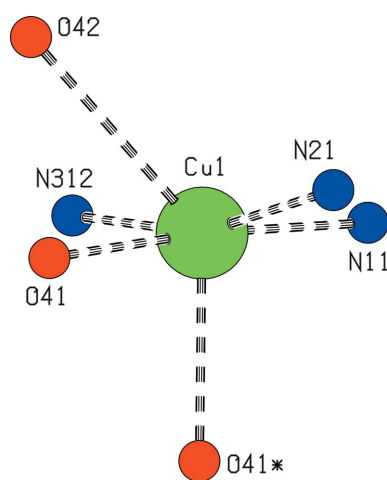


**Figure 1**

The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Atoms labelled with the suffix 'b' are at the symmetry position ( $-x + 1, -y + 1, -z + 1$ ).

minor variations in the reaction conditions used for their synthesis. Compound (I) contains [Cu(tcnoet)(bipy)] units lying in general positions and adipate units lying across centres of inversion; the reference adipate unit was selected as that lying across ( $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ) (Fig. 1).

The coordination polyhedron around the Cu<sup>II</sup> centre in (I) can be regarded as having square-pyramidal geometry, where there are three independent ligating N atoms and two symmetry-related atoms of type O41, augmented by a rather long contact to atom O42, so forming a distorted form of the normal axially elongated (4+2) coordination geometry,

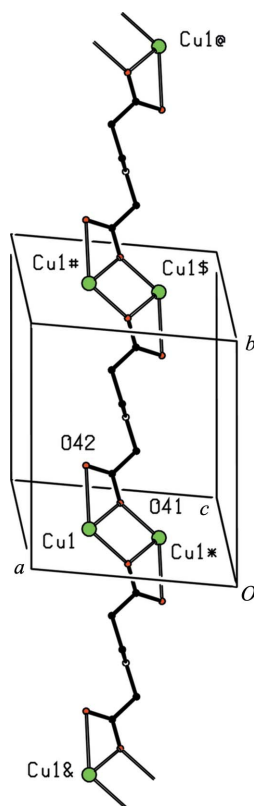


**Figure 2**

Part of the crystal structure of (I), showing the coordination around the Cu<sup>II</sup> centre, where a square-pyramidal geometry is augmented by a long contact to atom O42. The atom marked with an asterisk (\*) is at the symmetry position ( $-x + 1, -y, -z + 1$ ).

possibly better described for (I) as (4+1+1) (Fig. 2). The bipy ligand occupies a mutually *cis* pair of equatorial sites, the other two of which are occupied by one of the N atoms of the tcnocet ligand, bonded in a  $\kappa N$  mode (Batten & Murray, 2003), and by one of the carboxylate atoms, O41, of the adipate dianion. Two other sites are occupied by O atoms, *viz.* atom O42 of the reference adipate dianion centred across  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  and atom O41 at  $(-x + 1, -y, -z + 1)$ , which is part of the adipate dianion centred across  $(\frac{1}{2}, -\frac{1}{2}, \frac{1}{2})$ . While the four equatorial bonds to  $\text{Cu}^{\text{II}}$  are fairly similar in length (Table 2), the two ‘axial’ Cu—O distances are significantly different. Except for the very small angle subtended at the  $\text{Cu}^{\text{II}}$  centre by the chelating adipate dianion, the bond angles between mutually *cis* pairs of ligating sites range from 78.46 (4) to 99.15 (5)°, while the corresponding angles between mutually *trans* pairs of sites are 162.55 (6) and 173.79 (5)° for the equatorial ligands, but only 130.61 (4)° for the two axial ligands (*cf.* Fig. 2).

In the tcnocet unit of (I), the two independent  $-\text{C}(\text{CN})_2$  units are twisted, in conrotatory fashion, out of the plane of the central propenide unit. The dihedral angles between the central  $\text{C}_3$  fragment and the two  $-\text{C}(\text{CN})_2$  units containing atoms C31 and C33 are 23.0 (2) and 23.8 (2)°, entirely typical of the behaviour of this anion and its simple analogues (Setifi *et al.*, 2010; Setifi, Domasevitch *et al.*, 2013; Setifi, Setifi *et al.*,



**Figure 3**

Part of the crystal structure of (I), showing the formation of a coordination polymer chain along [010]. For the sake of clarity, the bipy and tcnocet ligands have been omitted, as have the H atoms of the adipate unit. The Cu atoms marked with an asterisk (\*), a hash (#), an ampersand (&), a dollar sign (\$) or an ‘at’ symbol (@) are at the symmetry positions  $(-x + 1, -y, -z + 1)$ ,  $(x, y + 1, z)$ ,  $(x, y - 1, z)$ ,  $(-x + 1, -y + 1, -z + 1)$  and  $(-x + 1, -y + 2, -z + 1)$ , respectively.

**Table 2**

Selected geometric parameters (Å, °).

Cu1—N11	1.9835 (13)	C31—C312	1.406 (2)
Cu1—N21	1.9914 (13)	O41—C41	1.3029 (18)
Cu1—N312	1.9943 (14)	C311—N311	1.151 (2)
Cu1—O41	1.9466 (11)	C312—N312	1.146 (2)
Cu1—O42	2.7741 (14)	C33—C331	1.425 (2)
Cu1—O41 <sup>i</sup>	2.2737 (11)	C33—C332	1.423 (3)
C31—C32	1.418 (2)	C331—N331	1.146 (2)
C32—C33	1.391 (2)	C332—N332	1.149 (2)
C31—C311	1.422 (2)	O42—C41	1.2250 (19)
N11—Cu1—N21	81.40 (5)	O42—Cu1—N21	89.09 (5)
N11—Cu1—O41	173.79 (5)	O42—Cu1—N312	79.72 (5)
N21—Cu1—O41	95.13 (5)	O41—Cu1—O41 <sup>i</sup>	78.46 (4)
N11—Cu1—N312	96.26 (6)	O42—Cu1—O41 <sup>i</sup>	130.61 (4)
N21—Cu1—N312	162.55 (6)	N11—Cu1—O41 <sup>i</sup>	96.88 (5)
O41—Cu1—N312	88.58 (5)	N21—Cu1—O41 <sup>i</sup>	98.30 (5)
O41—Cu1—O42	52.20 (4)	N312—Cu1—O41 <sup>i</sup>	99.15 (5)
O42—Cu1—N11	132.48 (5)		
C31—C32—C33—C331	154.77 (18)	C33—C32—C31—C311	165.66 (17)
C31—C32—C33—C332	-20.6 (3)	C41—C42—C43—C43 <sup>ii</sup>	70.2 (2)

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

2013; Setifi, Setifi, El Ammari *et al.*, 2014; Setifi, Lehchili *et al.*, 2014). On the other hand, the bond distances (Table 2) provide evidence for some localization of the negative charge, in contrast with the strong delocalization often observed for this anion and its analogues. Thus, the backbone C32—C33 distance is shorter than C31—C32, while the C31—C312 distance is shorter than the other C—CN distances, which are all very similar. These observations suggest significant localization of the negative charge on atom N312, which is the only N atom of this unit bonded to  $\text{Cu}^{\text{II}}$ , as in form (A) (see Scheme).

Within the carboxylate group of the adipate dianion of (I), the two C—O distances are significantly different. Indeed, the C41—O41 and C41—O42 distances are rather similar to the distances for single and double C—O bonds, respectively, in carboxylic acid esters, where single C—O bonds have a mean value of 1.336 Å with a lower quartile value of 1.328 Å, and double bonds have a mean value of 1.196 Å with an upper quartile value of 1.202 Å (Allen *et al.*, 1987). This difference in (I) is thus indicative of strong localization of the negative charge on atom O41. In fact, this atom acts as a bridging atom between the two  $\text{Cu}^{\text{II}}$  centres at  $(x, y, z)$  and  $(-x + 1, -y, -z + 1)$ , so forming a centrosymmetric motif in the form of three edge-fused four-membered rings, consisting of a central  $\text{Cu}_2\text{O}_2$  ring flanked by two inversion-related  $\text{CO}_2\text{Cu}$  rings (Fig. 3 and Scheme). Propagation of this fused-ring motif by inversion generates a coordination polymer chain built only from the  $\text{Cu}^{\text{II}}$  centres and the adipate dianions, running parallel to the [010] direction (Fig. 3), and along which  $\text{Cu}_2\text{O}_2$  rings centred at  $(\frac{1}{2}, n, \frac{1}{2})$  alternate with adipate dianions centred at  $(\frac{1}{2}, n + \frac{1}{2}, \frac{1}{2})$ , where  $n$  represents an integer in each case.

These coordination polymer chains running parallel to [010] are linked into a three-dimensional framework structure by a combination of C—H···N and C—H···O hydrogen bonds (Table 3), and it is convenient to consider the framework formation in terms of simpler substructures (Ferguson *et al.*, 1998*a,b*; Gregson *et al.*, 2000). In the simplest of these

**Table 3**

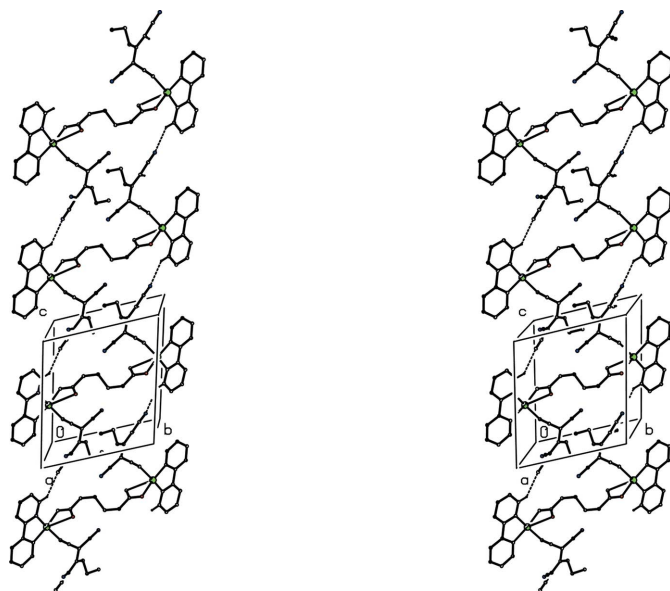
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C13—H13 $\cdots$ O42 <sup>iii</sup>	0.95	2.42	3.118 (2)	130
C15—H15 $\cdots$ N332 <sup>iv</sup>	0.95	2.55	3.322 (3)	138
C23—H23 $\cdots$ O42 <sup>iii</sup>	0.95	2.39	3.155 (2)	138
C26—H26 $\cdots$ N331 <sup>v</sup>	0.95	2.50	3.316 (3)	144

Symmetry codes: (iii)  $-x + 2, -y, -z + 1$ ; (iv)  $-x + 2, -y, -z$ ; (v)  $x, y, z + 1$ .

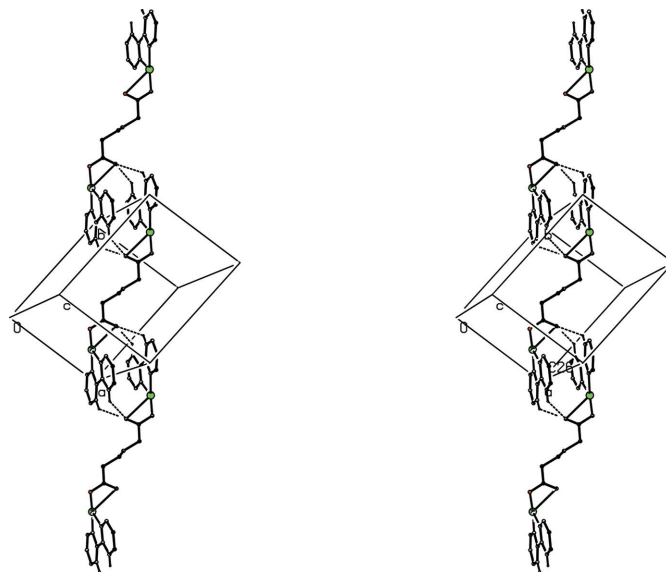
hydrogen-bonded substructures, polymer chains related by translation along [001] are linked by the C—H $\cdots$ N hydrogen bond having atom N331 as the acceptor, forming a chain of edge-fused  $R_2^2(40)$  (Bernstein *et al.*, 1995) rings running parallel to the [001] direction (Fig. 4).

A more complex substructure is generated by the combination of the two C—H $\cdots$ O hydrogen bonds, where atoms C13 and C23 of the bipyridine unit at  $(x, y, z)$ , which itself forms part of the coordination polymer chain along  $(\frac{1}{2}, y, \frac{1}{2})$ , both act as hydrogen-bond donors to atom O42 at  $(-x + 2, -y, -z + 1)$ , which lies in the coordination polymer chain along  $(\frac{3}{2}, y, \frac{1}{2})$ . These linkages are augmented by a  $\pi$ – $\pi$  stacking interaction. The planes of the pyridine rings containing atoms N11 and N21 at  $(x, y, z)$  and  $(-x + 2, -y, -z + 1)$ , respectively, make a dihedral angle of 4.83 (8)°. The ring-centroid separation is 3.7389 (10) Å and the shortest perpendicular distance from the centroid of one ring to the plane of the other is 3.409 Å, corresponding to a ring-centroid offset of *ca* 1.54 Å. Thus, while the C—H $\cdots$ O angles in the hydrogen bonds here are not large (*cf.* Wood *et al.*, 2009), the combined action of the two generates a chain running parallel to the [1 $\bar{1}$ 0] direction, in which cage-like structures contain  $R_2^1(7)$  and  $R_2^2(12)$  rings and where the hydrogen bonding is augmented by the  $\pi$ – $\pi$  stacking interaction (Fig. 5). The combination of chains along



**Figure 4**

A stereoview of part of the crystal structure of (I), showing the formation of a chain of hydrogen-bonded edge-fused  $R_2^2(40)$  rings running parallel to the [001] direction. Dashed lines indicate hydrogen bonds. For the sake of clarity, H atoms not involved in the motif shown have been omitted.



**Figure 5**

A stereoview of part of the crystal structure of (I), showing the formation of a hydrogen-bonded chain running parallel to the [1 $\bar{1}$ 0] direction, comprising cage-like aggregates containing  $R_2^1(7)$  and  $R_2^2(12)$  rings augmented by  $\pi$ – $\pi$  stacking interactions. Dashed lines indicate hydrogen bonds. For the sake of clarity, the tcnocet ligands and H atoms not involved in the motifs shown have been omitted.

the [010], [001] and [1 $\bar{1}$ 0] directions suffices to generate a single three-dimensional framework, which is modestly reinforced by the second, longer, C—H $\cdots$ N hydrogen bond.

It is of interest briefly to compare the one-dimensional coordination polymer based upon six-coordinate  $\text{Cu}^{\text{II}}$  found in (I) with the structures of some closely related  $\text{Cu}^{\text{II}}$  complexes containing both adipate and 2,2'-bipyridine ligands. In  $[\text{Cu}_4(\text{adipate})_3(\text{bipy})_4](\text{tcnoet})_2$ , (II), mentioned above (Setifi *et al.*, 2006), pairs of five-coordinate  $\text{Cu}^{\text{II}}$  centres separated by 3.154 (1) Å and having trigonal-bipyramidal geometry are triply bridged; two of the bridges are O atoms from two different adipate units, while the third bridge is a bidentate carboxylate unit. There are two independent adipate units in the structure, one bonded to three different  $\text{Cu}^{\text{II}}$  centres in a  $\mu_3$ -mode (Batten & Murray, 2003), forming a centrosymmetric  $[\text{Cu}_4(\text{adipate})_2(\text{bipy})_4]$  unit, while the other lies across a centre of inversion and binds in a  $\mu_2$ -mode, so linking the tetrameric units into a rather complex one-dimensional coordination polymer. Similar pairs of triply bridged  $\text{Cu}^{\text{II}}$  centres are found in  $[\{\text{CuCl}(\text{OH})(\text{bipy})_2(\text{adipate})\}(\text{tcnoet})_2 \cdot 2\text{H}_2\text{O}]$ , (III) (Setifi, Setifi & Glidewell, 2014), where the shortest Cu $\cdots$ Cu distance is 2.9806 (6) Å, but no polymer is formed in this case. By contrast, a very simple one-dimensional coordination polymer containing square-pyramidal  $\text{Cu}^{\text{II}}$  is present in  $[\text{Cu}(\text{adipate})(\text{bipy})(\text{H}_2\text{O})]_n$ , (IV) (Ghosh *et al.*, 2007; Kathalikkattil *et al.*, 2010). The rich variety of topologies in these systems is emphasized by the contrast between the linear coordination polymer found in (IV) and the finite centrosymmetric dimer present in its pentane-1,5-dionate analogue (Ghosh *et al.*, 2007). Finally, in the 2,2'-dipyrrilamine (dpa) complex  $[\text{Cu}(\text{adipate})(\text{dpa})_2 \cdot 2\text{H}_2\text{O}]$ , (V), the adipate unit bonds in a  $\mu_2$ -mode to two six-coordinate  $\text{Cu}^{\text{II}}$  centres, forming a finite

centrosymmetric dimer (Setifi, Setifi, Ghazzali *et al.*, 2014). Hence, it appears that, in systems of this type, small changes in the nature and ratio of the anionic co-ligands can affect both the coordination number and coordination geometry at Cu<sup>II</sup>, as well as the overall supramolecular assembly. However, structural generalizations of predictive value are, as yet, elusive.

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Supporting information for this paper is available from the IUCr electronic archives (Reference: YF3065).

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## supporting information

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## Coordination polymer chains built from Cu<sup>II</sup> and adipate ions linked by hydrogen bonds to form a three-dimensional framework structure

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### Computing details

Data collection: *CrysAlis PRO* (Agilent, 2013); cell refinement: *CrysAlis PRO* (Agilent, 2013); data reduction: *CrysAlis PRO* (Agilent, 2013); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2014); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2014) and *PLATON* (Spek, 2009).

**catena-poly[bis[(2,2'-bipyridine- $\kappa^2N,N'$ )(1,1,3,3-tetracyano-2-ethoxypropenido- $\kappa N$ )copper(II)]- $\mu_4$ -hexane-1,6-dioato- $\kappa^6O^1,O^1':O^1:O^6,O^6':O^6$ ]**

### Crystal data

[Cu<sub>2</sub>(C<sub>9</sub>H<sub>5</sub>N<sub>4</sub>O)<sub>2</sub>(C<sub>6</sub>H<sub>8</sub>O<sub>4</sub>)(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>]

$M_r = 476.97$

Triclinic,  $P\bar{1}$

$a = 8.8825$  (3) Å

$b = 10.5610$  (4) Å

$c = 12.2541$  (5) Å

$\alpha = 71.724$  (3)°

$\beta = 80.582$  (4)°

$\gamma = 84.974$  (3)°

$V = 1076.03$  (7) Å<sup>3</sup>

$Z = 2$

$F(000) = 488$

$D_x = 1.472$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 26499 reflections

$\theta = 3.0$ – $31.7$ °

$\mu = 1.05$  mm<sup>-1</sup>

$T = 150$  K

Plate, blue

$0.20 \times 0.15 \times 0.10$  mm

### Data collection

Agilent Xcalibur Sapphire2  
diffractometer

Radiation source: Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 9.091 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan  
(*SADABS*; Sheldrick, 2003)

$T_{\min} = 0.771$ ,  $T_{\max} = 0.929$

10761 measured reflections

6143 independent reflections

4850 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.021$

$\theta_{\max} = 30.0$ °,  $\theta_{\min} = 3.0$ °

$h = -12 \rightarrow 12$

$k = -14 \rightarrow 14$

$l = -17 \rightarrow 13$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.078$

$S = 0.96$

6143 reflections

290 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0442P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.46 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.67620 (2)	0.02804 (2)	0.43636 (2)	0.01549 (6)
N11	0.83199 (14)	-0.07966 (13)	0.36463 (11)	0.0171 (3)
C12	0.92158 (17)	-0.16286 (16)	0.43799 (15)	0.0183 (3)
C13	1.02475 (19)	-0.25364 (18)	0.40281 (17)	0.0271 (4)
H13	1.0856	-0.3127	0.4556	0.033*
C14	1.0379 (2)	-0.2570 (2)	0.28951 (18)	0.0314 (4)
H14	1.1082	-0.3183	0.2637	0.038*
C15	0.9480 (2)	-0.17036 (19)	0.21448 (17)	0.0284 (4)
H15	0.9563	-0.1704	0.1362	0.034*
C16	0.84563 (19)	-0.08370 (17)	0.25537 (15)	0.0223 (3)
H16	0.7827	-0.0249	0.2041	0.027*
N21	0.78358 (15)	-0.05943 (13)	0.57302 (11)	0.0168 (3)
C22	0.89765 (17)	-0.14788 (15)	0.55611 (14)	0.0176 (3)
C23	0.98343 (19)	-0.21505 (18)	0.64309 (16)	0.0254 (4)
H23	1.0631	-0.2770	0.6300	0.030*
C24	0.9517 (2)	-0.19086 (19)	0.74950 (16)	0.0275 (4)
H24	1.0092	-0.2361	0.8102	0.033*
C25	0.83545 (19)	-0.10028 (17)	0.76607 (15)	0.0238 (4)
H25	0.8122	-0.0822	0.8383	0.029*
C26	0.75326 (19)	-0.03618 (16)	0.67625 (14)	0.0205 (3)
H26	0.6731	0.0261	0.6879	0.025*
C31	0.45825 (19)	0.31347 (16)	0.14602 (14)	0.0196 (3)
C32	0.44649 (18)	0.29425 (16)	0.03834 (14)	0.0200 (3)
C33	0.5597 (2)	0.22925 (18)	-0.01953 (14)	0.0239 (4)
C311	0.3582 (2)	0.40499 (17)	0.18925 (15)	0.0235 (3)
N311	0.2789 (2)	0.47836 (18)	0.22640 (16)	0.0390 (4)
C312	0.54965 (18)	0.22554 (16)	0.22276 (14)	0.0196 (3)
N312	0.62068 (17)	0.15319 (14)	0.28773 (12)	0.0232 (3)
O321	0.31363 (13)	0.34181 (12)	0.00000 (10)	0.0251 (3)
C321	0.3025 (2)	0.38306 (19)	-0.12369 (15)	0.0292 (4)
H32A	0.2851	0.3052	-0.1481	0.035*
H32B	0.3977	0.4247	-0.1697	0.035*
C322	0.1697 (3)	0.4819 (2)	-0.14135 (19)	0.0453 (6)
H32C	0.1895	0.5591	-0.1184	0.068*
H32D	0.0769	0.4399	-0.0938	0.068*
H32E	0.1560	0.5113	-0.2234	0.068*

C331	0.5301 (2)	0.1641 (2)	-0.09915 (16)	0.0318 (4)
N331	0.5069 (2)	0.1076 (2)	-0.16029 (17)	0.0473 (5)
C332	0.7124 (2)	0.2165 (2)	0.00508 (15)	0.0290 (4)
N332	0.83659 (19)	0.2075 (2)	0.02288 (14)	0.0397 (4)
O41	0.51673 (12)	0.11565 (10)	0.51947 (9)	0.0163 (2)
O42	0.68662 (13)	0.27034 (12)	0.47807 (12)	0.0268 (3)
C41	0.55653 (18)	0.23265 (15)	0.51653 (13)	0.0166 (3)
C42	0.43386 (19)	0.31663 (16)	0.56424 (15)	0.0221 (3)
H42A	0.3959	0.2665	0.6457	0.027*
H42B	0.3474	0.3312	0.5193	0.027*
C43	0.4852 (2)	0.45202 (15)	0.56094 (14)	0.0222 (3)
H43A	0.4056	0.4922	0.6080	0.027*
H43B	0.5798	0.4387	0.5968	0.027*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cu1	0.01577 (10)	0.01501 (10)	0.01572 (10)	0.00385 (7)	-0.00233 (7)	-0.00586 (7)
N11	0.0151 (6)	0.0169 (6)	0.0192 (7)	-0.0001 (5)	-0.0002 (5)	-0.0067 (5)
C12	0.0126 (7)	0.0164 (7)	0.0265 (8)	-0.0006 (6)	-0.0022 (6)	-0.0078 (7)
C13	0.0189 (8)	0.0256 (9)	0.0410 (11)	0.0061 (7)	-0.0062 (7)	-0.0170 (8)
C14	0.0207 (8)	0.0333 (10)	0.0471 (12)	0.0045 (7)	0.0000 (8)	-0.0261 (9)
C15	0.0241 (9)	0.0357 (10)	0.0309 (10)	-0.0021 (8)	0.0026 (7)	-0.0209 (8)
C16	0.0216 (8)	0.0247 (8)	0.0218 (8)	-0.0003 (7)	-0.0004 (6)	-0.0104 (7)
N21	0.0160 (6)	0.0163 (6)	0.0190 (7)	0.0004 (5)	-0.0028 (5)	-0.0067 (5)
C22	0.0132 (7)	0.0156 (7)	0.0232 (8)	-0.0002 (6)	-0.0027 (6)	-0.0048 (6)
C23	0.0186 (8)	0.0243 (9)	0.0295 (9)	0.0041 (7)	-0.0057 (7)	-0.0029 (7)
C24	0.0226 (8)	0.0298 (9)	0.0256 (9)	-0.0011 (7)	-0.0094 (7)	0.0008 (8)
C25	0.0257 (8)	0.0261 (9)	0.0185 (8)	-0.0059 (7)	-0.0031 (7)	-0.0040 (7)
C26	0.0208 (8)	0.0200 (8)	0.0208 (8)	-0.0007 (6)	-0.0023 (6)	-0.0068 (7)
C31	0.0214 (8)	0.0190 (8)	0.0171 (8)	0.0017 (6)	-0.0036 (6)	-0.0039 (6)
C32	0.0206 (8)	0.0192 (8)	0.0174 (8)	-0.0014 (6)	-0.0028 (6)	-0.0014 (6)
C33	0.0268 (9)	0.0264 (9)	0.0182 (8)	0.0038 (7)	-0.0051 (7)	-0.0069 (7)
C311	0.0259 (8)	0.0225 (8)	0.0215 (8)	0.0004 (7)	-0.0060 (7)	-0.0047 (7)
N311	0.0415 (10)	0.0365 (10)	0.0425 (10)	0.0100 (8)	-0.0056 (8)	-0.0202 (8)
C312	0.0212 (8)	0.0207 (8)	0.0163 (8)	-0.0007 (6)	0.0006 (6)	-0.0066 (6)
N312	0.0286 (7)	0.0232 (7)	0.0167 (7)	0.0058 (6)	-0.0030 (6)	-0.0063 (6)
O321	0.0229 (6)	0.0320 (7)	0.0188 (6)	0.0045 (5)	-0.0071 (5)	-0.0049 (5)
C321	0.0343 (10)	0.0329 (10)	0.0206 (9)	0.0028 (8)	-0.0128 (8)	-0.0052 (8)
C322	0.0541 (14)	0.0448 (13)	0.0393 (12)	0.0192 (11)	-0.0265 (11)	-0.0118 (10)
C331	0.0384 (10)	0.0337 (10)	0.0241 (9)	0.0124 (8)	-0.0079 (8)	-0.0117 (8)
N331	0.0595 (12)	0.0515 (12)	0.0417 (11)	0.0196 (10)	-0.0180 (9)	-0.0301 (10)
C332	0.0323 (10)	0.0353 (10)	0.0166 (8)	0.0063 (8)	0.0008 (7)	-0.0083 (8)
N332	0.0286 (9)	0.0629 (12)	0.0246 (8)	0.0078 (8)	-0.0005 (7)	-0.0134 (8)
O41	0.0177 (5)	0.0123 (5)	0.0201 (6)	0.0013 (4)	-0.0024 (4)	-0.0070 (4)
O42	0.0172 (6)	0.0208 (6)	0.0442 (8)	-0.0005 (5)	-0.0011 (5)	-0.0140 (6)
C41	0.0191 (7)	0.0135 (7)	0.0183 (8)	0.0022 (6)	-0.0048 (6)	-0.0061 (6)
C42	0.0236 (8)	0.0134 (7)	0.0271 (9)	0.0003 (6)	0.0045 (7)	-0.0074 (7)



C43	0.0339 (9)	0.0132 (7)	0.0207 (8)	-0.0003 (7)	-0.0006 (7)	-0.0086 (6)
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*Geometric parameters (Å, °)*

Cu1—N11	1.9835 (13)	C32—C33	1.391 (2)
Cu1—N21	1.9914 (13)	C31—C311	1.422 (2)
Cu1—N312	1.9943 (14)	C31—C312	1.406 (2)
Cu1—O41	1.9466 (11)	O41—C41	1.3029 (18)
Cu1—O42	2.7741 (14)	C311—N311	1.151 (2)
Cu1—O41 <sup>i</sup>	2.2737 (11)	C312—N312	1.146 (2)
N11—C16	1.338 (2)	C32—O321	1.3400 (19)
N11—C12	1.353 (2)	C33—C331	1.425 (2)
C12—C13	1.386 (2)	C33—C332	1.423 (3)
C12—C22	1.484 (2)	O321—C321	1.458 (2)
C13—C14	1.386 (3)	C321—C322	1.501 (3)
C13—H13	0.9500	C321—H32A	0.9900
C14—C15	1.381 (3)	C321—H32B	0.9900
C14—H14	0.9500	C322—H32C	0.9800
C15—C16	1.381 (2)	C322—H32D	0.9800
C15—H15	0.9500	C322—H32E	0.9800
C16—H16	0.9500	C331—N331	1.146 (2)
N21—C26	1.343 (2)	C332—N332	1.149 (2)
N21—C22	1.3524 (19)	O41—Cu1 <sup>i</sup>	2.2737 (11)
C22—C23	1.384 (2)	O42—C41	1.2250 (19)
C23—C24	1.386 (3)	C41—C42	1.504 (2)
C23—H23	0.9500	C42—C43	1.525 (2)
C24—C25	1.379 (2)	C42—H42A	0.9900
C24—H24	0.9500	C42—H42B	0.9900
C25—C26	1.383 (2)	C43—C43 <sup>ii</sup>	1.515 (3)
C25—H25	0.9500	C43—H43A	0.9900
C26—H26	0.9500	C43—H43B	0.9900
C31—C32	1.418 (2)		
N11—Cu1—N21	81.40 (5)	N21—C26—C25	121.84 (15)
N11—Cu1—O41	173.79 (5)	N21—C26—H26	119.1
N21—Cu1—O41	95.13 (5)	C25—C26—H26	119.1
N11—Cu1—N312	96.26 (6)	C312—C31—C32	120.45 (15)
N21—Cu1—N312	162.55 (6)	C312—C31—C311	117.27 (14)
O41—Cu1—N312	88.58 (5)	C32—C31—C311	121.27 (14)
O41—Cu1—O42	52.20 (4)	O321—C32—C33	123.67 (15)
O42—Cu1—N11	132.48 (5)	O321—C32—C31	113.01 (14)
O42—Cu1—N21	89.09 (5)	C33—C32—C31	123.30 (15)
O42—Cu1—N312	79.72 (5)	C32—C33—C332	120.54 (15)
O41—Cu1—O41 <sup>i</sup>	78.46 (4)	C32—C33—C331	123.30 (16)
O42—Cu1—O41 <sup>i</sup>	130.61 (4)	C332—C33—C331	116.01 (16)
N11—Cu1—O41 <sup>i</sup>	96.88 (5)	N311—C311—C31	178.43 (19)
N21—Cu1—O41 <sup>i</sup>	98.30 (5)	N312—C312—C31	178.08 (18)
N312—Cu1—O41 <sup>i</sup>	99.15 (5)	C312—N312—Cu1	160.19 (14)

C16—N11—C12	119.14 (14)	C32—O321—C321	120.66 (13)
C16—N11—Cu1	125.59 (11)	O321—C321—C322	106.34 (16)
C12—N11—Cu1	115.03 (11)	O321—C321—H32A	110.5
N11—C12—C13	121.30 (16)	C322—C321—H32A	110.5
N11—C12—C22	114.21 (13)	O321—C321—H32B	110.5
C13—C12—C22	124.48 (15)	C322—C321—H32B	110.5
C14—C13—C12	119.07 (17)	H32A—C321—H32B	108.7
C14—C13—H13	120.5	C321—C322—H32C	109.5
C12—C13—H13	120.5	C321—C322—H32D	109.5
C15—C14—C13	119.37 (16)	H32C—C322—H32D	109.5
C15—C14—H14	120.3	C321—C322—H32E	109.5
C13—C14—H14	120.3	H32C—C322—H32E	109.5
C14—C15—C16	118.76 (17)	H32D—C322—H32E	109.5
C14—C15—H15	120.6	N331—C331—C33	177.6 (2)
C16—C15—H15	120.6	N332—C332—C33	178.7 (2)
N11—C16—C15	122.34 (16)	C41—O41—Cu1	111.58 (10)
N11—C16—H16	118.8	C41—O41—Cu1 <sup>i</sup>	146.30 (10)
C15—C16—H16	118.8	Cu1—O41—Cu1 <sup>i</sup>	101.54 (4)
C26—N21—C22	119.27 (14)	O42—C41—O41	121.48 (15)
C26—N21—Cu1	125.75 (11)	O42—C41—C42	122.62 (14)
C22—N21—Cu1	114.97 (11)	O41—C41—C42	115.90 (13)
N21—C22—C23	121.33 (15)	C41—C42—C43	114.41 (14)
N21—C22—C12	114.08 (14)	C41—C42—H42A	108.7
C23—C22—C12	124.59 (14)	C43—C42—H42A	108.7
C22—C23—C24	119.22 (16)	C41—C42—H42B	108.7
C22—C23—H23	120.4	C43—C42—H42B	108.7
C24—C23—H23	120.4	H42A—C42—H42B	107.6
C25—C24—C23	119.17 (16)	C43 <sup>ii</sup> —C43—C42	113.11 (17)
C25—C24—H24	120.4	C43 <sup>ii</sup> —C43—H43A	109.0
C23—C24—H24	120.4	C42—C43—H43A	109.0
C24—C25—C26	119.18 (16)	C43 <sup>ii</sup> —C43—H43B	109.0
C24—C25—H25	120.4	C42—C43—H43B	109.0
C26—C25—H25	120.4	H43A—C43—H43B	107.8
C16—N11—C12—C13	-1.3 (2)	C23—C24—C25—C26	0.2 (3)
Cu1—N11—C12—C13	173.42 (13)	C22—N21—C26—C25	0.0 (2)
C16—N11—C12—C22	179.19 (14)	Cu1—N21—C26—C25	-179.01 (12)
Cu1—N11—C12—C22	-6.14 (17)	C24—C25—C26—N21	-0.1 (3)
N11—C12—C13—C14	1.3 (3)	C312—C31—C32—O321	152.09 (15)
C22—C12—C13—C14	-179.24 (16)	C311—C31—C32—O321	-16.1 (2)
C12—C13—C14—C15	-0.2 (3)	C312—C31—C32—C33	-26.2 (3)
C13—C14—C15—C16	-0.8 (3)	O321—C32—C33—C332	161.28 (16)
C12—N11—C16—C15	0.2 (2)	O321—C32—C33—C331	-23.3 (3)
Cu1—N11—C16—C15	-173.86 (13)	C31—C32—C33—C331	154.77 (18)
C14—C15—C16—N11	0.8 (3)	C31—C32—C33—C332	-20.6 (3)
C26—N21—C22—C23	0.1 (2)	C33—C32—C31—C311	165.66 (17)
Cu1—N21—C22—C23	179.22 (12)	C33—C32—O321—C321	-27.7 (2)
C26—N21—C22—C12	-178.94 (14)	C31—C32—O321—C321	154.06 (15)

Cu1—N21—C22—C12	0.14 (17)	C32—O321—C321—C322	-155.75 (16)
N11—C12—C22—N21	3.9 (2)	Cu1—O41—C41—O42	-8.53 (19)
C13—C12—C22—N21	-175.61 (15)	Cu1 <sup>i</sup> —O41—C41—O42	-177.28 (12)
N11—C12—C22—C23	-175.12 (15)	Cu1—O41—C41—C42	172.13 (11)
C13—C12—C22—C23	5.3 (3)	Cu1 <sup>i</sup> —O41—C41—C42	3.4 (3)
N21—C22—C23—C24	-0.1 (3)	O42—C41—C42—C43	-0.2 (2)
C12—C22—C23—C24	178.90 (16)	O41—C41—C42—C43	179.18 (14)
C22—C23—C24—C25	-0.1 (3)	C41—C42—C43—C43 <sup>ii</sup>	70.2 (2)

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

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
C13—H13 $\cdots$ O42 <sup>iii</sup>	0.95	2.42	3.118 (2)	130
C15—H15 $\cdots$ N332 <sup>iv</sup>	0.95	2.55	3.322 (3)	138
C23—H23 $\cdots$ O42 <sup>iii</sup>	0.95	2.39	3.155 (2)	138
C26—H26 $\cdots$ N331 <sup>v</sup>	0.95	2.50	3.316 (3)	144

Symmetry codes: (iii)  $-x+2, -y, -z+1$ ; (iv)  $-x+2, -y, -z$ ; (v)  $x, y, z+1$ .

## supporting information

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## Coordination polymer chains built from Cu<sup>II</sup> and adipate ions linked by hydrogen bonds to form a three-dimensional framework structure

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### Computing details

Data collection: *CrysAlis PRO* (Agilent, 2013); cell refinement: *CrysAlis PRO* (Agilent, 2013); data reduction: *CrysAlis PRO* (Agilent, 2013); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2014); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2014) and *PLATON* (Spek, 2009).

**catena-poly[bis[(2,2'-bipyridine- $\kappa^2N,N'$ )(1,1,3,3-tetracyano-2-ethoxypropenido- $\kappa N$ )copper(II)]- $\mu_4$ -hexane-1,6-dioato- $\kappa^6O^1,O^1':O^1:O^6,O^6':O^6$ ]**

### Crystal data

[Cu<sub>2</sub>(C<sub>9</sub>H<sub>5</sub>N<sub>4</sub>O)<sub>2</sub>(C<sub>6</sub>H<sub>8</sub>O<sub>4</sub>)(C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>]

$M_r = 476.97$

Triclinic,  $P\bar{1}$

$a = 8.8825$  (3) Å

$b = 10.5610$  (4) Å

$c = 12.2541$  (5) Å

$\alpha = 71.724$  (3)°

$\beta = 80.582$  (4)°

$\gamma = 84.974$  (3)°

$V = 1076.03$  (7) Å<sup>3</sup>

$Z = 2$

$F(000) = 488$

$D_x = 1.472$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 26499 reflections

$\theta = 3.0$ – $31.7$ °

$\mu = 1.05$  mm<sup>-1</sup>

$T = 150$  K

Plate, blue

$0.20 \times 0.15 \times 0.10$  mm

### Data collection

Agilent Xcalibur Sapphire2  
diffractometer

Radiation source: Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 9.091 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan  
(*SADABS*; Sheldrick, 2003)

$T_{\min} = 0.771$ ,  $T_{\max} = 0.929$

10761 measured reflections

6143 independent reflections

4850 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.021$

$\theta_{\max} = 30.0$ °,  $\theta_{\min} = 3.0$ °

$h = -12 \rightarrow 12$

$k = -14 \rightarrow 14$

$l = -17 \rightarrow 13$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.078$

$S = 0.96$

6143 reflections

290 parameters

0 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0442P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.46 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.24 \text{ e } \text{Å}^{-3}$

### Special details

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{Å}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.67620 (2)	0.02804 (2)	0.43636 (2)	0.01549 (6)
N11	0.83199 (14)	-0.07966 (13)	0.36463 (11)	0.0171 (3)
C12	0.92158 (17)	-0.16286 (16)	0.43799 (15)	0.0183 (3)
C13	1.02475 (19)	-0.25364 (18)	0.40281 (17)	0.0271 (4)
H13	1.0856	-0.3127	0.4556	0.033*
C14	1.0379 (2)	-0.2570 (2)	0.28951 (18)	0.0314 (4)
H14	1.1082	-0.3183	0.2637	0.038*
C15	0.9480 (2)	-0.17036 (19)	0.21448 (17)	0.0284 (4)
H15	0.9563	-0.1704	0.1362	0.034*
C16	0.84563 (19)	-0.08370 (17)	0.25537 (15)	0.0223 (3)
H16	0.7827	-0.0249	0.2041	0.027*
N21	0.78358 (15)	-0.05943 (13)	0.57302 (11)	0.0168 (3)
C22	0.89765 (17)	-0.14788 (15)	0.55611 (14)	0.0176 (3)
C23	0.98343 (19)	-0.21505 (18)	0.64309 (16)	0.0254 (4)
H23	1.0631	-0.2770	0.6300	0.030*
C24	0.9517 (2)	-0.19086 (19)	0.74950 (16)	0.0275 (4)
H24	1.0092	-0.2361	0.8102	0.033*
C25	0.83545 (19)	-0.10028 (17)	0.76607 (15)	0.0238 (4)
H25	0.8122	-0.0822	0.8383	0.029*
C26	0.75326 (19)	-0.03618 (16)	0.67625 (14)	0.0205 (3)
H26	0.6731	0.0261	0.6879	0.025*
C31	0.45825 (19)	0.31347 (16)	0.14602 (14)	0.0196 (3)
C32	0.44649 (18)	0.29425 (16)	0.03834 (14)	0.0200 (3)
C33	0.5597 (2)	0.22925 (18)	-0.01953 (14)	0.0239 (4)
C311	0.3582 (2)	0.40499 (17)	0.18925 (15)	0.0235 (3)
N311	0.2789 (2)	0.47836 (18)	0.22640 (16)	0.0390 (4)
C312	0.54965 (18)	0.22554 (16)	0.22276 (14)	0.0196 (3)
N312	0.62068 (17)	0.15319 (14)	0.28773 (12)	0.0232 (3)
O321	0.31363 (13)	0.34181 (12)	0.00000 (10)	0.0251 (3)
C321	0.3025 (2)	0.38306 (19)	-0.12369 (15)	0.0292 (4)
H32A	0.2851	0.3052	-0.1481	0.035*
H32B	0.3977	0.4247	-0.1697	0.035*
C322	0.1697 (3)	0.4819 (2)	-0.14135 (19)	0.0453 (6)
H32C	0.1895	0.5591	-0.1184	0.068*
H32D	0.0769	0.4399	-0.0938	0.068*
H32E	0.1560	0.5113	-0.2234	0.068*

C331	0.5301 (2)	0.1641 (2)	-0.09915 (16)	0.0318 (4)
N331	0.5069 (2)	0.1076 (2)	-0.16029 (17)	0.0473 (5)
C332	0.7124 (2)	0.2165 (2)	0.00508 (15)	0.0290 (4)
N332	0.83659 (19)	0.2075 (2)	0.02288 (14)	0.0397 (4)
O41	0.51673 (12)	0.11565 (10)	0.51947 (9)	0.0163 (2)
O42	0.68662 (13)	0.27034 (12)	0.47807 (12)	0.0268 (3)
C41	0.55653 (18)	0.23265 (15)	0.51653 (13)	0.0166 (3)
C42	0.43386 (19)	0.31663 (16)	0.56424 (15)	0.0221 (3)
H42A	0.3959	0.2665	0.6457	0.027*
H42B	0.3474	0.3312	0.5193	0.027*
C43	0.4852 (2)	0.45202 (15)	0.56094 (14)	0.0222 (3)
H43A	0.4056	0.4922	0.6080	0.027*
H43B	0.5798	0.4387	0.5968	0.027*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cu1	0.01577 (10)	0.01501 (10)	0.01572 (10)	0.00385 (7)	-0.00233 (7)	-0.00586 (7)
N11	0.0151 (6)	0.0169 (6)	0.0192 (7)	-0.0001 (5)	-0.0002 (5)	-0.0067 (5)
C12	0.0126 (7)	0.0164 (7)	0.0265 (8)	-0.0006 (6)	-0.0022 (6)	-0.0078 (7)
C13	0.0189 (8)	0.0256 (9)	0.0410 (11)	0.0061 (7)	-0.0062 (7)	-0.0170 (8)
C14	0.0207 (8)	0.0333 (10)	0.0471 (12)	0.0045 (7)	0.0000 (8)	-0.0261 (9)
C15	0.0241 (9)	0.0357 (10)	0.0309 (10)	-0.0021 (8)	0.0026 (7)	-0.0209 (8)
C16	0.0216 (8)	0.0247 (8)	0.0218 (8)	-0.0003 (7)	-0.0004 (6)	-0.0104 (7)
N21	0.0160 (6)	0.0163 (6)	0.0190 (7)	0.0004 (5)	-0.0028 (5)	-0.0067 (5)
C22	0.0132 (7)	0.0156 (7)	0.0232 (8)	-0.0002 (6)	-0.0027 (6)	-0.0048 (6)
C23	0.0186 (8)	0.0243 (9)	0.0295 (9)	0.0041 (7)	-0.0057 (7)	-0.0029 (7)
C24	0.0226 (8)	0.0298 (9)	0.0256 (9)	-0.0011 (7)	-0.0094 (7)	0.0008 (8)
C25	0.0257 (8)	0.0261 (9)	0.0185 (8)	-0.0059 (7)	-0.0031 (7)	-0.0040 (7)
C26	0.0208 (8)	0.0200 (8)	0.0208 (8)	-0.0007 (6)	-0.0023 (6)	-0.0068 (7)
C31	0.0214 (8)	0.0190 (8)	0.0171 (8)	0.0017 (6)	-0.0036 (6)	-0.0039 (6)
C32	0.0206 (8)	0.0192 (8)	0.0174 (8)	-0.0014 (6)	-0.0028 (6)	-0.0014 (6)
C33	0.0268 (9)	0.0264 (9)	0.0182 (8)	0.0038 (7)	-0.0051 (7)	-0.0069 (7)
C311	0.0259 (8)	0.0225 (8)	0.0215 (8)	0.0004 (7)	-0.0060 (7)	-0.0047 (7)
N311	0.0415 (10)	0.0365 (10)	0.0425 (10)	0.0100 (8)	-0.0056 (8)	-0.0202 (8)
C312	0.0212 (8)	0.0207 (8)	0.0163 (8)	-0.0007 (6)	0.0006 (6)	-0.0066 (6)
N312	0.0286 (7)	0.0232 (7)	0.0167 (7)	0.0058 (6)	-0.0030 (6)	-0.0063 (6)
O321	0.0229 (6)	0.0320 (7)	0.0188 (6)	0.0045 (5)	-0.0071 (5)	-0.0049 (5)
C321	0.0343 (10)	0.0329 (10)	0.0206 (9)	0.0028 (8)	-0.0128 (8)	-0.0052 (8)
C322	0.0541 (14)	0.0448 (13)	0.0393 (12)	0.0192 (11)	-0.0265 (11)	-0.0118 (10)
C331	0.0384 (10)	0.0337 (10)	0.0241 (9)	0.0124 (8)	-0.0079 (8)	-0.0117 (8)
N331	0.0595 (12)	0.0515 (12)	0.0417 (11)	0.0196 (10)	-0.0180 (9)	-0.0301 (10)
C332	0.0323 (10)	0.0353 (10)	0.0166 (8)	0.0063 (8)	0.0008 (7)	-0.0083 (8)
N332	0.0286 (9)	0.0629 (12)	0.0246 (8)	0.0078 (8)	-0.0005 (7)	-0.0134 (8)
O41	0.0177 (5)	0.0123 (5)	0.0201 (6)	0.0013 (4)	-0.0024 (4)	-0.0070 (4)
O42	0.0172 (6)	0.0208 (6)	0.0442 (8)	-0.0005 (5)	-0.0011 (5)	-0.0140 (6)
C41	0.0191 (7)	0.0135 (7)	0.0183 (8)	0.0022 (6)	-0.0048 (6)	-0.0061 (6)
C42	0.0236 (8)	0.0134 (7)	0.0271 (9)	0.0003 (6)	0.0045 (7)	-0.0074 (7)

C43	0.0339 (9)	0.0132 (7)	0.0207 (8)	-0.0003 (7)	-0.0006 (7)	-0.0086 (6)
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*Geometric parameters (Å, °)*

Cu1—N11	1.9835 (13)	C32—C33	1.391 (2)
Cu1—N21	1.9914 (13)	C31—C311	1.422 (2)
Cu1—N312	1.9943 (14)	C31—C312	1.406 (2)
Cu1—O41	1.9466 (11)	O41—C41	1.3029 (18)
Cu1—O42	2.7741 (14)	C311—N311	1.151 (2)
Cu1—O41 <sup>i</sup>	2.2737 (11)	C312—N312	1.146 (2)
N11—C16	1.338 (2)	C32—O321	1.3400 (19)
N11—C12	1.353 (2)	C33—C331	1.425 (2)
C12—C13	1.386 (2)	C33—C332	1.423 (3)
C12—C22	1.484 (2)	O321—C321	1.458 (2)
C13—C14	1.386 (3)	C321—C322	1.501 (3)
C13—H13	0.9500	C321—H32A	0.9900
C14—C15	1.381 (3)	C321—H32B	0.9900
C14—H14	0.9500	C322—H32C	0.9800
C15—C16	1.381 (2)	C322—H32D	0.9800
C15—H15	0.9500	C322—H32E	0.9800
C16—H16	0.9500	C331—N331	1.146 (2)
N21—C26	1.343 (2)	C332—N332	1.149 (2)
N21—C22	1.3524 (19)	O41—Cu1 <sup>i</sup>	2.2737 (11)
C22—C23	1.384 (2)	O42—C41	1.2250 (19)
C23—C24	1.386 (3)	C41—C42	1.504 (2)
C23—H23	0.9500	C42—C43	1.525 (2)
C24—C25	1.379 (2)	C42—H42A	0.9900
C24—H24	0.9500	C42—H42B	0.9900
C25—C26	1.383 (2)	C43—C43 <sup>ii</sup>	1.515 (3)
C25—H25	0.9500	C43—H43A	0.9900
C26—H26	0.9500	C43—H43B	0.9900
C31—C32	1.418 (2)		
N11—Cu1—N21	81.40 (5)	N21—C26—C25	121.84 (15)
N11—Cu1—O41	173.79 (5)	N21—C26—H26	119.1
N21—Cu1—O41	95.13 (5)	C25—C26—H26	119.1
N11—Cu1—N312	96.26 (6)	C312—C31—C32	120.45 (15)
N21—Cu1—N312	162.55 (6)	C312—C31—C311	117.27 (14)
O41—Cu1—N312	88.58 (5)	C32—C31—C311	121.27 (14)
O41—Cu1—O42	52.20 (4)	O321—C32—C33	123.67 (15)
O42—Cu1—N11	132.48 (5)	O321—C32—C31	113.01 (14)
O42—Cu1—N21	89.09 (5)	C33—C32—C31	123.30 (15)
O42—Cu1—N312	79.72 (5)	C32—C33—C332	120.54 (15)
O41—Cu1—O41 <sup>i</sup>	78.46 (4)	C32—C33—C331	123.30 (16)
O42—Cu1—O41 <sup>i</sup>	130.61 (4)	C332—C33—C331	116.01 (16)
N11—Cu1—O41 <sup>i</sup>	96.88 (5)	N311—C311—C31	178.43 (19)
N21—Cu1—O41 <sup>i</sup>	98.30 (5)	N312—C312—C31	178.08 (18)
N312—Cu1—O41 <sup>i</sup>	99.15 (5)	C312—N312—Cu1	160.19 (14)



C16—N11—C12	119.14 (14)	C32—O321—C321	120.66 (13)
C16—N11—Cu1	125.59 (11)	O321—C321—C322	106.34 (16)
C12—N11—Cu1	115.03 (11)	O321—C321—H32A	110.5
N11—C12—C13	121.30 (16)	C322—C321—H32A	110.5
N11—C12—C22	114.21 (13)	O321—C321—H32B	110.5
C13—C12—C22	124.48 (15)	C322—C321—H32B	110.5
C14—C13—C12	119.07 (17)	H32A—C321—H32B	108.7
C14—C13—H13	120.5	C321—C322—H32C	109.5
C12—C13—H13	120.5	C321—C322—H32D	109.5
C15—C14—C13	119.37 (16)	H32C—C322—H32D	109.5
C15—C14—H14	120.3	C321—C322—H32E	109.5
C13—C14—H14	120.3	H32C—C322—H32E	109.5
C14—C15—C16	118.76 (17)	H32D—C322—H32E	109.5
C14—C15—H15	120.6	N331—C331—C33	177.6 (2)
C16—C15—H15	120.6	N332—C332—C33	178.7 (2)
N11—C16—C15	122.34 (16)	C41—O41—Cu1	111.58 (10)
N11—C16—H16	118.8	C41—O41—Cu1 <sup>i</sup>	146.30 (10)
C15—C16—H16	118.8	Cu1—O41—Cu1 <sup>i</sup>	101.54 (4)
C26—N21—C22	119.27 (14)	O42—C41—O41	121.48 (15)
C26—N21—Cu1	125.75 (11)	O42—C41—C42	122.62 (14)
C22—N21—Cu1	114.97 (11)	O41—C41—C42	115.90 (13)
N21—C22—C23	121.33 (15)	C41—C42—C43	114.41 (14)
N21—C22—C12	114.08 (14)	C41—C42—H42A	108.7
C23—C22—C12	124.59 (14)	C43—C42—H42A	108.7
C22—C23—C24	119.22 (16)	C41—C42—H42B	108.7
C22—C23—H23	120.4	C43—C42—H42B	108.7
C24—C23—H23	120.4	H42A—C42—H42B	107.6
C25—C24—C23	119.17 (16)	C43 <sup>ii</sup> —C43—C42	113.11 (17)
C25—C24—H24	120.4	C43 <sup>ii</sup> —C43—H43A	109.0
C23—C24—H24	120.4	C42—C43—H43A	109.0
C24—C25—C26	119.18 (16)	C43 <sup>ii</sup> —C43—H43B	109.0
C24—C25—H25	120.4	C42—C43—H43B	109.0
C26—C25—H25	120.4	H43A—C43—H43B	107.8
C16—N11—C12—C13	-1.3 (2)	C23—C24—C25—C26	0.2 (3)
Cu1—N11—C12—C13	173.42 (13)	C22—N21—C26—C25	0.0 (2)
C16—N11—C12—C22	179.19 (14)	Cu1—N21—C26—C25	-179.01 (12)
Cu1—N11—C12—C22	-6.14 (17)	C24—C25—C26—N21	-0.1 (3)
N11—C12—C13—C14	1.3 (3)	C312—C31—C32—O321	152.09 (15)
C22—C12—C13—C14	-179.24 (16)	C311—C31—C32—O321	-16.1 (2)
C12—C13—C14—C15	-0.2 (3)	C312—C31—C32—C33	-26.2 (3)
C13—C14—C15—C16	-0.8 (3)	O321—C32—C33—C332	161.28 (16)
C12—N11—C16—C15	0.2 (2)	O321—C32—C33—C331	-23.3 (3)
Cu1—N11—C16—C15	-173.86 (13)	C31—C32—C33—C331	154.77 (18)
C14—C15—C16—N11	0.8 (3)	C31—C32—C33—C332	-20.6 (3)
C26—N21—C22—C23	0.1 (2)	C33—C32—C31—C311	165.66 (17)
Cu1—N21—C22—C23	179.22 (12)	C33—C32—O321—C321	-27.7 (2)
C26—N21—C22—C12	-178.94 (14)	C31—C32—O321—C321	154.06 (15)

Cu1—N21—C22—C12	0.14 (17)	C32—O321—C321—C322	-155.75 (16)
N11—C12—C22—N21	3.9 (2)	Cu1—O41—C41—O42	-8.53 (19)
C13—C12—C22—N21	-175.61 (15)	Cu1 <sup>i</sup> —O41—C41—O42	-177.28 (12)
N11—C12—C22—C23	-175.12 (15)	Cu1—O41—C41—C42	172.13 (11)
C13—C12—C22—C23	5.3 (3)	Cu1 <sup>i</sup> —O41—C41—C42	3.4 (3)
N21—C22—C23—C24	-0.1 (3)	O42—C41—C42—C43	-0.2 (2)
C12—C22—C23—C24	178.90 (16)	O41—C41—C42—C43	179.18 (14)
C22—C23—C24—C25	-0.1 (3)	C41—C42—C43—C43 <sup>ii</sup>	70.2 (2)

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

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
C13—H13 $\cdots$ O42 <sup>iii</sup>	0.95	2.42	3.118 (2)	130
C15—H15 $\cdots$ N332 <sup>iv</sup>	0.95	2.55	3.322 (3)	138
C23—H23 $\cdots$ O42 <sup>iii</sup>	0.95	2.39	3.155 (2)	138
C26—H26 $\cdots$ N331 <sup>v</sup>	0.95	2.50	3.316 (3)	144

Symmetry codes: (iii)  $-x+2, -y, -z+1$ ; (iv)  $-x+2, -y, -z$ ; (v)  $x, y, z+1$ .