

# *catena*-Poly[[[(oxamide dioxime- $\kappa^2N,N'$ )copper(II)]- $\mu$ -L-tartrato- $\kappa^4O^1,O^2:O^3,O^4$ ] tetrahydrate]: a chiral nanochannel framework hosting solvent water molecules

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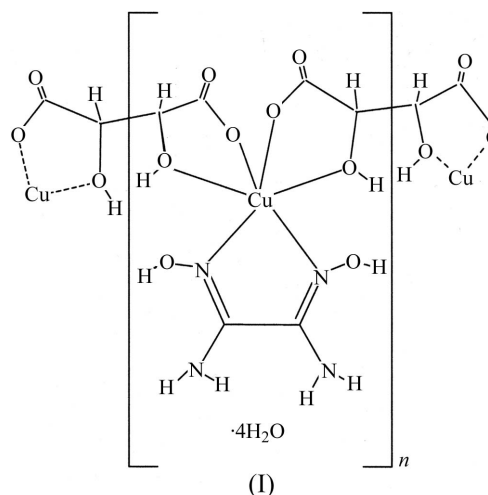
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The crystal structure of the title compound,  $\{[\text{Cu}(\text{C}_4\text{H}_4\text{O}_6)(\text{C}_2\text{H}_6\text{N}_4\text{O}_2)] \cdot 4\text{H}_2\text{O}\}_n$ , contains the central  $\text{Cu}^{\text{II}}$  cation in a distorted octahedral coordination, symmetrically chelated by the two imine N atoms of a neutral oxamide dioxime ( $\text{H}_2\text{oxado}$ ) ligand [ $\text{Cu}-\text{N} = 1.9829(16) \text{ \AA}$ ] and unsymmetrically bis-chelated by two halves of the L-(+)-tartrate(2-) (*tart*) ligands, each half being linked to the  $\text{Cu}^{\text{II}}$  cation *via* the deprotonated carboxylate group and protonated hydroxy group [ $\text{Cu}-\text{O} = 1.9356(14)$  and  $2.4674(13) \text{ \AA}$ , respectively]. The extended asymmetric unit is defined by twofold axes, one passing through the  $\text{Cu}^{\text{II}}$  cation and the centre of the oxamide dioxime ( $\text{H}_2\text{oxado}$ ) ligand and the another two (symmetry related) bisecting the central C—C bonds of the tartrate ions. The structure is chiral, consisting of enantiomeric linear-chain polymers oriented along [001], with virtual monomeric  $\{\text{Cu}(\text{tart}_{0.5})_2(\text{H}_2\text{oxado})\}$  repeat units and with the chains interleaved face-to-face into 'twin pillars'. Nanochannels exist, running parallel to the *c* axis and bisecting *a* and *b*, which host 'double strings' of solvent water molecules. Extensive hydrogen bonding ( $\text{O}-\text{H} \cdots \text{O}$  and  $\text{N}-\text{H} \cdots \text{O}$ ) between the chains and solvent water molecules, together with extended  $\pi-\sigma$  interactions, consolidate the bulk crystal structure.

## Comment

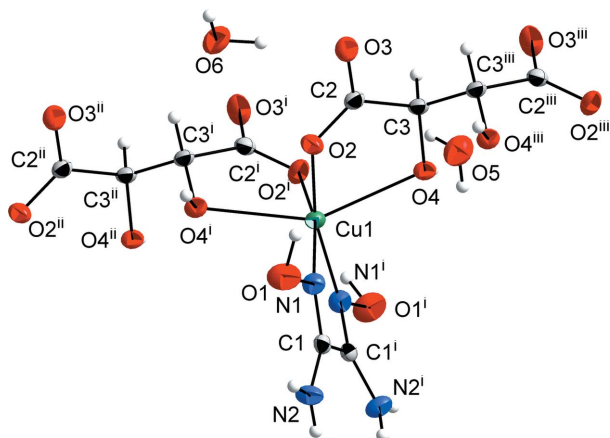
A considerable number of crystal structures have been reported which deal with a wide range of metal(II) complexes based mainly on the tartrate(2-) ligand system (Adama *et al.*, 2007; Bélombé, Nenwa, Fokwa & Dronskowski, 2009; Ge *et al.*, 2008; González-Silgo *et al.*, 1999; Liu *et al.*, 2010; McCann *et al.*, 1997; Ruiz-Pérez *et al.*, 1996; Scherb *et al.*, 2002; Soylyu, 1985;

Zhang *et al.*, 2003; Zhao *et al.*, 2009). Most of these studies utilized the tartrate(2-) anion (predominantly in the form of its pure enantiomers) and water molecules as the ligands linked directly to the central metal. Only a few examples have been reported where the tartrate(2-) ligand shares coordination to the central metal with another type of neutral ligand system, *e.g.* with two imidazole molecules to coordinate to  $\text{Zn}^{\text{II}}$  (Adama *et al.*, 2007), and with a phenanthroline molecule to coordinate to  $\text{Mn}^{\text{II}}$  (Zhang *et al.*, 2003) or  $\text{Cu}^{\text{II}}$  (McCann *et al.*, 1997). Therefore, the title compound, (I), represents only the second example of a chiral heteroleptic  $\text{Cu}^{\text{II}}$  complex polymer to be elucidated hitherto, involving the neutral chelating oxamide dioxime in lieu of the phenanthroline ligand.



The intrinsic nature of the tartrate(2-) anion (*tart*) as a polydentate ligand system offering various coordination modes to central metal ions, hence yielding a wide range of magnetic and optically active materials (applicable in advanced technologies), has been underscored in previous studies (Liu *et al.*, 2010; Scherb *et al.*, 2002; Soylyu, 1985). Our current research aims to design, synthesize and study crystallized multifunctional materials that may combine, within a single system, a whole set of interesting physico-chemical properties, such as magnetic, optoelectronic, nanoporous, electrical or hydrogen-bonding properties, among others (Bélombé, Nenwa, Mbiangué, Bebga *et al.*, 2009; Bélombé, Nenwa, Mbiangué, Majoumo-Mbé *et al.*, 2009). Along these lines, we have recently prepared the chiral and paramagnetic metal-organic  $\text{Ni}^{\text{II}}$  salt,  $[\text{Ni}(\text{H}_2\text{oxado})_3][\text{L-(+)}\text{tart}] \cdot 4\text{H}_2\text{O}$  ( $\text{H}_2\text{oxado}$  is oxamide dioxime), which shows good promise of ferromagnetic ordering at about 10 K, and the report of which is currently in progress. An attempt to synthesize the  $\text{Cu}^{\text{II}}$  homologue led to the isolation of the unexpected title complex polymer, (I), which crystallizes in a new type of chiral channel lattice framework, hosting interesting 'double strings' or 'double filaments' of hydrogen-bonded solvent water molecules. We report herein the synthesis and crystal structure of  $\{[\text{Cu}(\text{tart})(\text{H}_2\text{oxado})] \cdot 4\text{H}_2\text{O}\}_n$ , (I).

The crystal structure of (I) consists of the chiral building blocks depicted in Fig. 1, highlighting the asymmetric unit. The crystal topology of (I) closely resembles that of the homo-


**Figure 1**

The extended asymmetric unit of (I), showing the coordination environment of the  $\text{Cu}^{\text{II}}$  cation and the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i)  $y, x, -z$ ; (ii)  $y, x, -z + 1$ ; (iii)  $x, y, z - 1$ .]

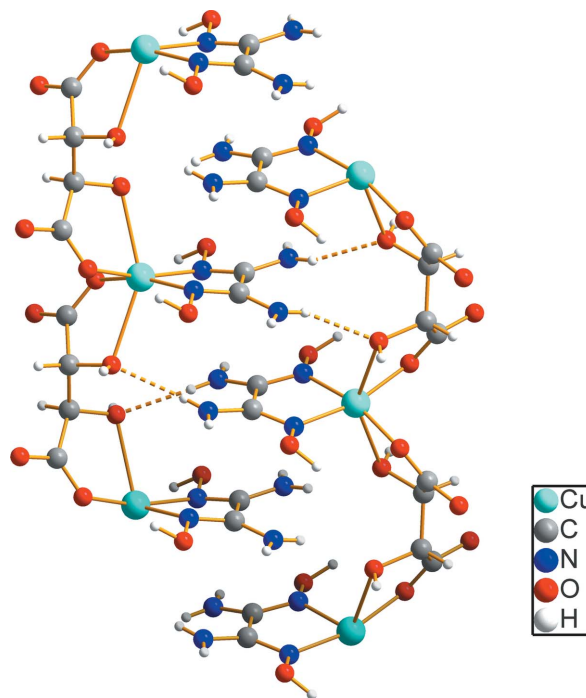
logous  $[\text{Cu}(\text{tart})(\text{phen})]\cdot 6\text{H}_2\text{O}$  compound, (II), published earlier (McCann *et al.*, 1997), with phenanthroline (phen) in lieu of the present oxamide dioxime as the neutral ligand. Thus, the two homologues appear to represent the only examples of such mixed-ligand  $\text{Cu}^{\text{II}}$ -tartrate complexes elucidated to date. It is worth noting that (II) crystallizes with orthorhombic symmetry, whereas (I) crystallizes in the tetragonal system.

In (I), the  $\text{Cu}^{\text{II}}$  cation lies on a twofold axis which also relates the two halves of the chelating oxamide dioxime ligand. The coordination geometry at the  $\text{Cu}^{\text{II}}$  cation in (I) is a distorted prolate octahedron, similar to that in (II), despite the higher symmetry in (I). In (I), the  $\text{Cu}-\text{O}_{\text{COO}}$  bond to O2 [1.9356 (14) Å] is significantly shorter than the  $\text{Cu}-\text{O}_{\text{OH}}$  bond to O4 [2.4674 (13) Å]. In (II), by contrast, the two  $\text{Cu}-\text{O}_{\text{OH}}$  bond lengths of 2.308 (4) and 2.328 (3) Å are unequal and shorter than those in (I). In (I), these bonds form an  $\text{O4}-\text{Cu1}-\text{O4}^i$  angle of 149.31 (4)°, and while they are longer than in (II), they do compare fairly well with corresponding values observed earlier in related metal(II) tartrates, *e.g.* in  $\text{Mn}^{\text{II}}-\text{O}_{\text{OH}}$  (2.433 and 2.621 Å; Soyulu, 1985) and in  $\text{Cd}^{\text{II}}-\text{O}_{\text{OH}}$  [2.470 (3) and 2.449 (3) Å; Zhao *et al.*, 2009].

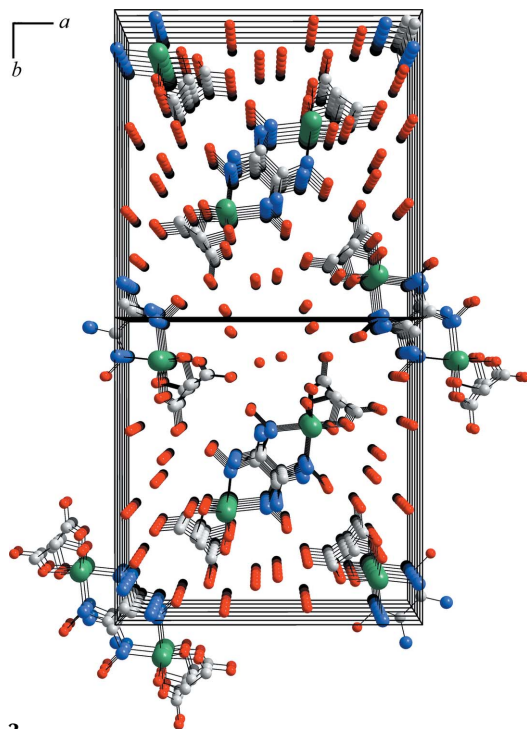
The two materials adopt the same polymerization pattern, by which the tartrate(2-) ions act as bis-bidentate ligands to bridge neighbouring  $\text{Cu}^{\text{II}}$  sites, offering at each ligand end the deprotonated  $\text{O}_{\text{COO}^-}$  and protonated  $\text{O}_{\text{OH}}$  atoms as O-atom donors. In (I), the tartrate anion is located so that a twofold axis bisects the central bond. The ends lie within two planes that are rotated relative to each other about the  $\text{C3}-\text{C3}^{\text{iii}}$  line by a dihedral angle of 78.90 (8)° (see Fig. 1 for symmetry code). Thus, the polymerization pattern ultimately gives rise to linear chain coordination motifs, with the chains oriented parallel to [100] in (II) but parallel to [001] in (I). The planes of the neutral ligands (phen or  $\text{H}_2\text{oxado}$ ) lie virtually perpendicular to the respective polymeric chains, with an intrachain  $\text{Cu}\cdots\text{Cu}$  spacing of 6.6239 (4) Å ( $= c$ ) in (I) and 6.6640 (14) Å in (II). Note that in Fig. 1 the virtual repeat unit

of a polymeric chain consists of two symmetry-related halves of tartrate(2-) ligands, involving atoms  $\text{O2}/\text{C2}/\text{O3}/\text{C3}/\text{O4}$  and  $\text{O2}^i/\text{C2}^i/\text{O3}^i/\text{C3}^i/\text{O4}^i$  (symmetry code as in Fig. 1), and one oxamide dioxime ligand. The three ligands each chelate the central  $\text{Cu}^{\text{II}}$  cation in a pentacyclic coordination, the coordination polyhedron being defined by rotational symmetry about a  $C_2$  axis through the  $\text{Cu}^{\text{II}}$  center and the mid-point of the  $\text{C1}-\text{C1}^i$  segment in the  $\text{H}_2\text{oxado}$  ligand. It is quite obvious that the  $\text{H}_2\text{oxado}$  ligand, with its hydroximinic and aminic functional groups, will promote hydrogen bonding more efficiently than the phenanthroline ligand, which lacks such functional groups. Selected geometric parameters for (I) are reported in Table 1 and hydrogen-bond parameters are in Table 2.

The individual polymeric chains of (I) pair up face-to-face in a zip-type packing mode *via* mutual interleaving of their  $\text{H}_2\text{oxado}$  ligands to form 'twin pillars', as shown in Fig. 2.  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonding occurs between these pillars. The roughly planar  $\text{H}_2\text{oxado}$  ligands are superimposed on top of each other such that the  $\text{C}=\text{N}$  iminic double bonds of one ligand interact with the  $\text{C}-\text{N}$  aminic single bonds of neighbouring ligands, resulting in  $\pi-\sigma$  interactions at a centroid-centroid spacing of *ca* 3.312 Å ( $= c/2$ ). This spacing compares fairly well with the average value of 3.300 Å reported for the phenanthroline ligand in (II), where pure  $\pi-\pi$  interactions are operative. The shortest interchain separation of the metal centers is  $\text{Cu}\cdots\text{Cu} = 6.7024(2)$  Å in (I). Additionally,  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonding is observed between the  $\text{O}-\text{H}$  groups of the tartrate anions and the solvent water molecules.


**Figure 2**

Interleaving of the  $\text{H}_2\text{oxado}$  ligand of (I) *via*  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds (dashed lines), yielding a zip-like pattern. Not all hydrogen bonds are shown.



**Figure 3**  
The structure of (I) in a central projection along *c*. H atoms have been omitted.

A juxtaposition of two unit cells of (I), projected down the *c* axis, is depicted in Fig. 3, highlighting the disposition of the individual twin pillars. Any neighbouring four such pillars are oriented relative to one another so that they delineate a hose-like nanochannel, inside which the solvent water molecules line up to form four 'double strings', reminiscent of the hydrogen-bonded solvent water molecules recently observed by Vallejo *et al.* (2010) in oxalate-bridged trinuclear Cr<sup>III</sup>–Co<sup>II</sup> complexes with aromatic diimine ligands.

The structure of (I), we believe, ought to be welcomed as another promising template system within the narrow class of materials (Akutsu-Sato *et al.*, 2005; Rashid *et al.*, 2001; Infantes & Motherwell, 2002; Mascal *et al.*, 2006; Martin *et al.*, 2007) that are needed to probe the feasibility of the challenging prospect of one-dimensional proton conduction in solids (one-dimensional PCS) (Belombe *et al.*, 2007, 2008; B elomb e, Nenwa, Mbiang e, Bebiga *et al.*, 2009), a prospect that may be likened somewhat to the novel ionic high proton conduction as a function of surrounding humidity level newly documented in a metal–organic framework which hosts ammonium cations and water molecules within functionalized lattice channels (Pardo *et al.*, 2011).

## Experimental

We have now rationalized a procedure by which compound (I) can be prepared systematically in stoichiometric proportions. Thus, pure oxamide dioxime (0.12 g, 1 mmol; Ephraim, 1889; Ali *et al.*, 2004) and pure L-(+)-tartaric acid [0.17 g, 1.13 mmol (in slight excess to maintain the medium acidic pH ≤ 3), LABOSI] were dissolved in luke-warm (~318 K) water (100 ml) and stirred magnetically. CuCO<sub>3</sub>–

**Table 1**  
Selected geometric parameters ( ,  ).

Cu1–O2	1.9356 (14)	Cu1–N1	1.9829 (16)
O2 <sup>i</sup> –Cu1–O2	94.85 (9)	O2–Cu1–N1	94.61 (6)
O2–Cu1–N1 <sup>i</sup>	165.16 (6)	N1 <sup>i</sup> –Cu1–N1	78.62 (9)

Symmetry code: (i) *y*, *x*, *–z*.

**Table 2**  
Hydrogen-bond geometry ( ,  ).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N2–H2A...O3 <sup>i</sup>	0.82	2.44	3.164 (2)	148
N2–H2B...O4 <sup>ii</sup>	0.81	2.13	2.878 (2)	152
O1–H1...O6 <sup>iii</sup>	0.92	1.82	2.696 (2)	157
O4–H4...O5	0.79	1.87	2.651 (2)	168
O5–H5A...O3 <sup>iv</sup>	0.87	2.27	2.869 (2)	126
O5–H5A...O5 <sup>v</sup>	0.87	2.53	3.236 (2)	138
O5–H5B...O6 <sup>vi</sup>	0.73	2.05	2.762 (2)	164
O6–H6A...O2 <sup>vii</sup>	0.75	2.51	2.956 (2)	121
O6–H6A...O3 <sup>viii</sup>	0.75	2.62	3.362 (2)	171

Symmetry codes: (i)  $x - \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{1}{4}$ ; (ii)  $-x, -y, z - \frac{1}{2}$ ; (iii)  $y - \frac{1}{2}, -x + \frac{1}{2}, z + \frac{1}{4}$ ; (iv)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{4}$ ; (v)  $-y + \frac{1}{2}, x - \frac{1}{2}, z - \frac{1}{4}$ ; (vi)  $y, x, -z$ ; (vii)  $-y + \frac{1}{2}, x + \frac{1}{2}, z - \frac{1}{4}$ .

Cu(OH)<sub>2</sub> (0.11 g, 0.5 mmol; Riedel de Ha en, chemically pure) was added progressively. The solution mixture turned green immediately and green fibers precipitated instantaneously. The green fibers were separated by filtration, washed twice with cold water (5 ml each) and dried in air to a constant weight, yielding 0.32 g of (I) [80%, m.p. ≈ 508 K (decomposition)]. IR (KBr,  $\nu$ , cm<sup>–1</sup>): 3556 (O–H), 3392–3342 (N–H), 1715 (C=O), 1676–1497 (oxime). Single crystals of (I) suitable for X-ray diffraction were grown by slow evaporation at room temperature of a supersaturated aqueous solution over the course of a few weeks.

### Crystal data

[Cu(C <sub>4</sub> H <sub>4</sub> O <sub>6</sub> )(C <sub>2</sub> H <sub>6</sub> N <sub>4</sub> O <sub>2</sub> )]·4H <sub>2</sub> O	<i>Z</i> = 4
<i>M<sub>r</sub></i> = 401.77	Mo <i>K</i> � radiation
Tetragonal, <i>P</i> 4 <sub>3</sub> 2 <sub>1</sub> 2	$\mu$ = 1.62 mm <sup>–1</sup>
<i>a</i> = 14.6316 (9) �	<i>T</i> = 299 K
<i>c</i> = 6.6239 (4) �	0.37 × 0.18 × 0.14 mm
<i>V</i> = 1418.1 (2) � <sup>3</sup>	

### Data collection

Bruker–Nonius KappaCCD area-detector diffractometer	10357 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	1624 independent reflections
<i>T</i> <sub>min</sub> = 0.629, <i>T</i> <sub>max</sub> = 0.798	1426 reflections with <i>I</i> > 2σ( <i>I</i> )
	<i>R</i> <sub>int</sub> = 0.039

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$	$\Delta\rho_{\max} = 0.21 \text{ e �}^{-3}$
$wR(F^2) = 0.053$	$\Delta\rho_{\min} = -0.20 \text{ e �}^{-3}$
<i>S</i> = 1.02	Absolute structure: Flack (1983),
1624 reflections	644 Friedel pairs
103 parameters	Flack parameter: 0.021 (13)
H-atom parameters constrained	

H-atom positions were derived from a difference Fourier map and they were constrained to ride on their parent atoms with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(parent).

Data collection: COLLECT (Nonius, 1999); cell refinement: DIRAX (Duisenberg, 1992); data reduction: EVALCCD (Duisen-

berg *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3165). Services for accessing these data are described at the back of the journal.

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