

Tetrakis(2,2'-bipyridine)-1 κ^4 N,N';-4 κ^4 N,N'-{ μ_4 -N,N'-bis[3-(2-oxidoethyl-amino)propyl]oxamidato(4-)-1:2:3:4 κ O: κ^3 N,N',O': κ^3 O'',N'',N''':- κ O'''}tetracopper(II) tetrakis-(perchlorate)

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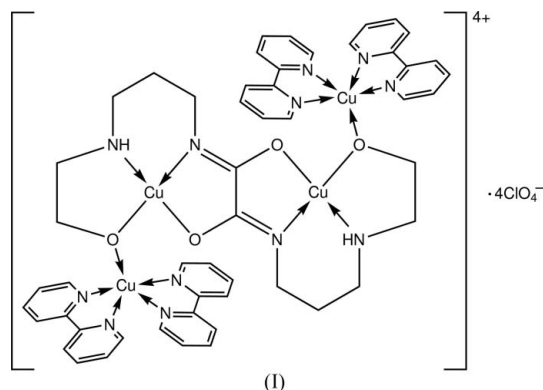
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The title complex, [Cu₄(C₁₂H₂₂N₄O₄)(C₁₀H₈N₂)₄](ClO₄)₄, has a novel tetranuclear copper(II) cation with the oxamidate and ethanolate groups of a *trans* tetraanion of *N,N'*-bis[3-(hydroxyethylamino)propyl]oxamide (H₄heap) as bridges. The Cu...Cu separation through the oxamide group is 5.1592 (15) Å, while those through the two ethanolate bridges are 3.3845 (13) and 3.3392 (13) Å. The two central copper(II) ions are in square-planar N₂O₂ environments, while the two terminal copper(II) ions have distorted N₄O square-pyramidal geometries. The heap⁴⁻ ligand, with an iminoalcohol form, has both an oxamide and two ethanolate bridges. Two of the four perchlorate anions are disordered and have long contacts with the square-planar Cu^{II} ions. The three-dimensional structure features arene-perchlorate C—H...O hydrogen bonds and π - π stacking.

Comment

Polynuclear copper(II) complexes are of interest due to their ability to bind DNA and to function as a chemical nuclease by performing strand scission (Oliveira *et al.*, 2005; Peralta *et al.*, 2006; Qian *et al.*, 2007; Sigman *et al.*, 1993). It is well known that *N,N'*-disubstituted oxamides are good candidates as bridging ligands to form polynuclear complexes because their coordinating ability towards transition metal ions can be modified and tuned by changing the nature of the amide substituents (Ojima & Nonoyama, 1988). To date, many polynuclear complexes with interesting structures based on bridging *N,N'*-disubstituted oxamides have been synthesized and their properties have been studied extensively (Messori *et al.*, 2003; Wang *et al.*, 2004). However, few complexes with

coordinating hydroxy groups in the *N,N'*-disubstituted oxamide bridging ligand have been reported (Li *et al.*, 2009; Zhu *et al.*, 2007). To the best of our knowledge, no complex with alkoxy bridges in this family of ligands has hitherto been reported [Cambridge Structural Database (CSD), Version 5.30; Allen, 2002]. In our previous studies, we chose the dianion of *N,N'*-bis(*N*-hydroxyethylaminopropyl)oxamide (H₂heap²⁻) as the bridging ligand to synthesize two binuclear copper(II) complexes (Li *et al.*, 2009; Zhu *et al.*, 2007). In both of those complexes, the hydroxy groups of the ligand coordinate to individual Cu^{II} ions but do not bridge another Cu^{II} ion. In order to explore further the coordination behaviour of the ligand under different experimental conditions, we removed the H atoms on the hydroxyl groups and chose 2,2'-bipyridine (bpy) as the terminal ligand to synthesize the title complex, [Cu₄(heap⁴⁻)(bpy)₄](ClO₄)₄ (bpy is 2,2'-bipyridine), (I), in which the heap⁴⁻ ligand, with an iminoalcohol form, has one oxamide and two ethanolate bridges simultaneously. Such an alkoxy coordination mode is thus observed for the first time in *N,N'*-disubstituted oxamides.



Compound (I) features a tetranuclear copper(II) complex cation, *viz.* [Cu₄(heap⁴⁻)(bpy)₄]⁴⁺ (Fig. 1). Two [Cu(bpy)₂]²⁺ fragments coordinate to a binuclear *trans*-oxamide copper(II) complex, [Cu₂(heap⁴⁻)], in which the oxamide and the hydroxy groups of H₄heap have lost their H atoms so as to

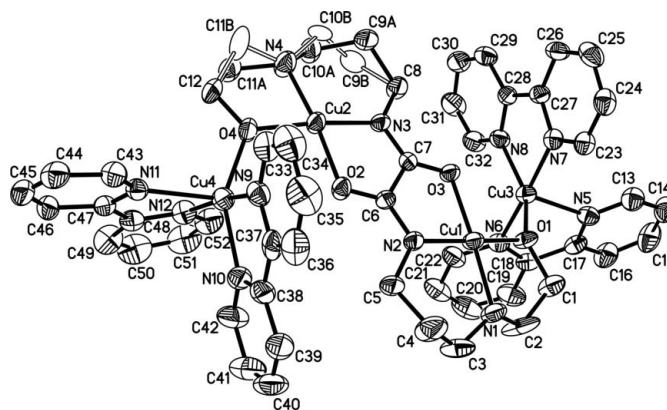
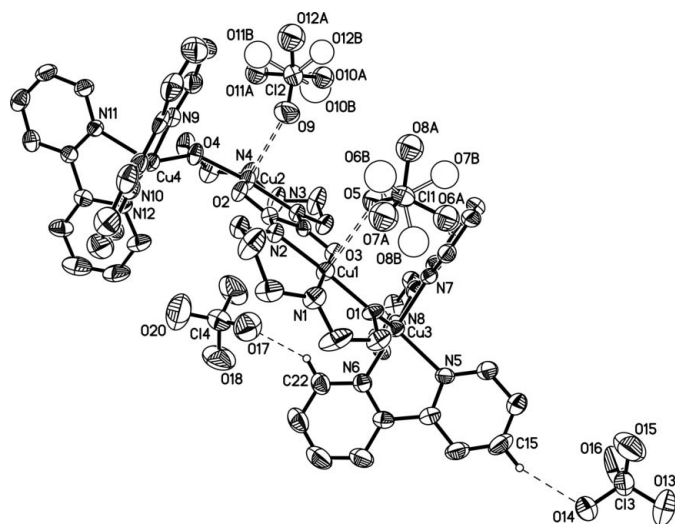


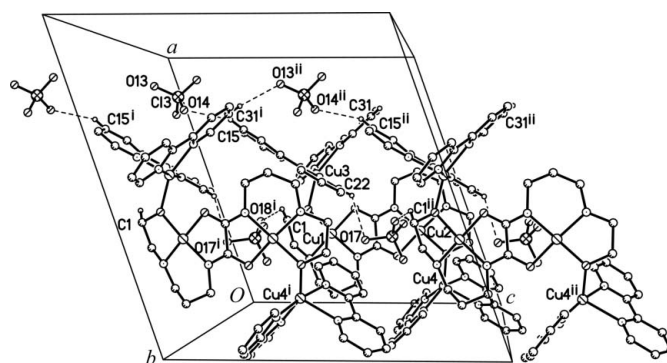
Figure 1
The structure of the tetranuclear copper(II) complex cation [Cu₄(heap⁴⁻)(bpy)₄]⁴⁺ in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Disordered atoms are drawn with open bonds and unshaded atoms, and H atoms have been omitted for clarity.


Figure 2

The asymmetric unit of (I), with displacement ellipsoids drawn at the 30% probability level. For clarity, only the coordination environments of copper(II) ions and perchlorate anions are labelled, and all H atoms (except those that participate in hydrogen bonds) have been omitted. Dashed and double-dashed lines indicate hydrogen bonds and weak coordination interactions, respectively.

bridge the copper(II) ions. The Cu...Cu distances through the two ethanolate bridges are 3.3845 (13) (Cu1...Cu3) and 3.3392 (13) Å (Cu2...Cu4), while the separation through the oxamide bridge is 5.1592 (15) Å (Cu1...Cu2). The Cu...Cu distance through the oxamide bridge is similar to those previously reported in tetracopper(II) complexes with analogous ligands (Abbati *et al.*, 1999; Albano *et al.*, 1992; van Koningsbruggen *et al.*, 1993; Li *et al.*, 2008; Gu *et al.*, 2009; Li *et al.*, 2010; Tang *et al.*, 2005). Previous structural and magnetic investigations have shown that magnetic coupling can occur between copper(II) ions bridged by an oxamide bridge, even if the Cu...Cu separation in the bridge is greater than 5 Å (Tang *et al.*, 2005), due to the remarkably efficient electron-transfer ability of this kind of ligand. The oxamide group has thus been proved to be an appropriate bridging unit to design magnetic systems (Ruiz *et al.*, 1999; Tercero *et al.*, 2002). Therefore, from the viewpoint of magnetism there should be a magnetic exchange interaction between the copper(II) ions bridged by the oxamide bridge in (I). Verification of the magnetic properties will require measurements of variable-temperature magnetic susceptibilities and electron spin resonance spectra. These are, however, beyond our present purpose.

The central copper(II) ions, Cu1 and Cu2, are in square N₂O₂ coordination environments (Fig. 1 and Table 1), with the metal centres displaced only 0.081 (3) and 0.105 (3) Å from their coordination planes, respectively. A perchlorate anion lies above the coordination plane of each Cu ion (Fig. 2), so that elongated Cu...O distances of 2.734 (6) (Cu1—O5) and 2.595 (7) Å (Cu2—O9) are formed. Each of these perchlorate groups has the remaining three O atoms disordered over two positions. The open space on the other side of the N₂O₂ planes is occupied by one perchlorate anion (Cl4), but the O atoms are too far away for significant interaction with the Cu^{II} centres. The sp²-hybridized atoms N2 and N3 have shorter


Figure 3

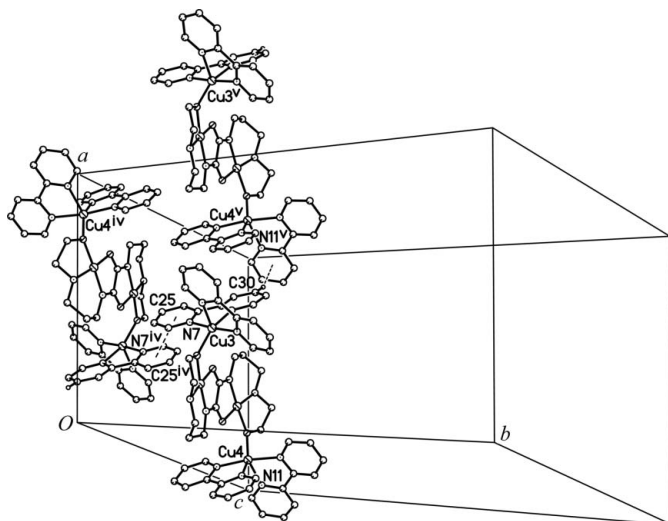
The zigzag hydrogen-bonded chain extending along the [001] direction. Hydrogen bonds are shown as dashed lines. [Symmetry codes: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $x, \frac{1}{2} - y, z + \frac{1}{2}$.]

Cu—N bonds than do the sp³-hybridized atoms N1 and N4, which is in accordance with their donor abilities (Tang *et al.*, 2005). The two terminal copper(II) ions (Cu3 and Cu4) coordinated by bpy ligands have markedly distorted N₄O square-pyramidal geometries. The τ values (Addison *et al.*, 1984) are 0.37 for Cu3 and 0.39 for Cu4. The axial Cu3—N5 and Cu4—N11 bonds are longer than those in the basal planes, as expected.

The heap⁴⁻ ligand chelates in a tetradentate manner atoms Cu1 and Cu2 with each arm. The six-membered rings formed with the propylenediamine fragments and the five-membered rings formed with the oxidoethylamine groups adopt half-chair and envelope conformations, respectively. Their puckering parameters (Cremer & Pople, 1975) are listed in Table 3. The oxamide C6—N2 and C7—N3 distances are typical C=N bond lengths, while C6—C7 is consistent with a Csp²—Csp² bond (Table 1) (Ladd & Palmer, 1985; Sun *et al.*, 2007), which implies that the ligand is in the iminoalcohol form and deprotonated at the O atoms (O2 and O3). In addition, due to the coordination with the copper(II) ions, the terminal hydroxy groups (O1 and O4) are activated and deprotonated to bridge with another copper(II) ion. Atoms O1 and O4 are sp² hybridized and almost in the plane of their three bonded atoms [offsets = 0.189 (6) Å for O1 and 0.224 (7) Å for O4]. This is the first example of such an oxide coordination mode in N,N'-disubstituted oxamides.

We also compared (I) with related oxamidate-bridged tetracopper(II) complexes, and found that most of the reported oxamidate-bridged tetracopper(II) complexes can be considered as two dinuclear copper(II) units assembled through another bridge, such as a carboxyl or azido group, to form either a circular tetranuclear system (Abbati *et al.*, 1999; van Koningsbruggen *et al.*, 1993; Li *et al.*, 2008; Gu *et al.*, 2009; Li *et al.*, 2010) or a 'dimer-of-dimers' (Tang *et al.*, 2005). By contrast, in (I), one oxamide and two ethanolate groups of the heap⁴⁻ ligand bridge copper(II) ions simultaneously to form an extended tetracopper(II) system.

In the crystal structure of (I), the cations and anions interact *via* the longer Cu—O coordination mentioned earlier, and additionally through arene—perchlorate C—H...O hydrogen bonds (Table 2 and Fig. 2) that link the tetranuclear complex


Figure 4

A view of the two kinds of π -system interactions (dashed lines), which combine the chains shown in Fig. 3 into a three-dimensional structure. [Symmetry codes: (iv) $1 - x, -y, 1 - z$; (v) $x + 1, y, z$.]

cation and two perchlorate ions (Cl3 and Cl4) into a zigzag chain extending along the c axis (Fig. 3). The chains are linked to complete the three-dimensional structure by two kinds of π -system interactions. One is a T-shaped $C-H \cdots \pi$ interaction between adjacent $[Cu_4(\text{heap}^{4-})(\text{bpy})_4]^{4+}$ cations along the a axis, *viz.* $C30-H30 \cdots Cg1^v$, where $Cg1$ is the centroid of the ring containing atom N11 [symmetry code: (v) $x + 1, y, z$] (Table 2 and Fig. 4). The other is an offset stacking between two parallel N7-containing pyridine rings, in which the smallest separation is 3.361 (12) Å between atoms C25 and $C25^{iv}$ [symmetry code: (iv) $1 - x, -y, 1 - z$].

Experimental

The $H_4\text{heap}$ ligand was synthesized according to the method of Ojima & Nonoyama (1988). $[Cu_2(\text{H}_2\text{heap}^{2-})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $[Cu(\text{bpy})_2](\text{ClO}_4)_2$ were prepared according to the methods of Zhu *et al.* (2007) and Jaeger & Dijk (1936), respectively. $[Cu_2(\text{H}_2\text{heap}^{2-})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (32.5 mg, 0.05 mmol) was dissolved in methanol (6 ml) and the solution was heated under reflux with stirring. After 10 min, a methanol solution (0.5 ml) containing piperidine (8.5 mg, 0.1 mmol) was added. After 30 min, a methanol solution (5 ml) of $[Cu(\text{bpy})_2](\text{ClO}_4)_2$ (28.7 mg, 0.1 mmol) was added dropwise to the mixture, which was then heated under reflux with stirring at 323 K for 5 h. The resulting light-green solution was filtered. Green crystals of (I) of a size suitable for X-ray analysis were obtained from the filtrate after one week by slow evaporation at room temperature. Analysis calculated for $C_{52}H_{54}Cl_4Cu_4N_{12}O_{20}$: C 39.96, H 3.48, N 10.75%; found: C 40.03, H 3.30, N 10.86%.

Crystal data

$[Cu_4(C_{12}H_{22}N_4O_4)(C_{10}H_8N_2)_4](ClO_4)_4$	$\beta = 109.39 (3)^\circ$
$M_r = 1563.03$	$V = 6375 (2) \text{ \AA}^3$
Monoclinic, $P2_1/c$	$Z = 4$
$a = 14.617 (3) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 33.273 (7) \text{ \AA}$	$\mu = 1.57 \text{ mm}^{-1}$
$c = 13.897 (3) \text{ \AA}$	$T = 296 \text{ K}$
	$0.15 \times 0.07 \times 0.05 \text{ mm}$

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.915 (4)	Cu3—N8	2.025 (6)
Cu1—O3	1.970 (4)	Cu4—O4	1.941 (5)
Cu1—N1	1.977 (6)	Cu4—N9	1.972 (7)
Cu1—N2	1.930 (5)	Cu4—N10	2.023 (6)
Cu2—O2	1.960 (4)	Cu4—N11	2.206 (5)
Cu2—O4	1.905 (4)	Cu4—N12	2.003 (6)
Cu2—N3	1.936 (5)	C6—O2	1.277 (7)
Cu2—N4	1.986 (6)	C6—N2	1.284 (8)
Cu3—O1	1.935 (4)	C6—C7	1.528 (8)
Cu3—N5	2.184 (6)	C7—O3	1.270 (7)
Cu3—N6	2.012 (6)	C7—N3	1.266 (8)
Cu3—N7	1.986 (6)		
O1—Cu1—N2	175.4 (2)	O1—Cu3—N8	152.4 (2)
O3—Cu1—N1	174.3 (3)	N5—Cu3—N6	77.8 (2)
O3—Cu1—N2	85.02 (19)	N6—Cu3—N7	174.7 (2)
N1—Cu1—N2	96.2 (2)	N7—Cu3—N8	80.6 (2)
O2—Cu2—N4	173.3 (3)	O4—Cu4—N10	148.3 (2)
O4—Cu2—N3	173.6 (2)	N9—Cu4—N10	80.8 (3)
O4—Cu2—N4	85.3 (2)	N9—Cu4—N12	171.6 (2)
N3—Cu2—N4	96.6 (2)	N11—Cu4—N12	77.5 (2)

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

$Cg1$ is the centroid of the pyridine ring containing atom N11.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C1—H1B \cdots O18 ⁱ	0.97	2.53	3.228 (12)	129
C15—H15 \cdots O14	0.93	2.49	3.317 (11)	148
C22—H22 \cdots O17	0.93	2.46	3.111 (12)	127
C31—H31 \cdots O13 ⁱⁱ	0.93	2.52	3.396 (13)	157
C30—H30 \cdots Cg1 ⁱⁱⁱ	0.93	2.58	3.470 (9)	160

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

Table 3
The puckering parameters of some chelate rings in (I).

No.	Size of ring	Determining atoms	Q (Å)	θ (°)	φ (°)
1	5	Cu1/O1/N1/C1/C2	0.323 (9)		113.9 (11)
2	5	Cu2/O4/N4/C11A/C12	0.379 (10)		115.0 (11)
3	5	Cu2/O4/N4/C11B/C12	0.334 (15)		295.5 (17)
4	6	Cu1/N1/N2/C3—C5	0.466 (10)	128.5 (10)	336.1 (12)
5	6	Cu2/N3/N4/C8/C9A/C10A	0.52 (2)	55.6 (16)	208.4 (19)
6	6	Cu2/N3/N4/C8/C9B/C10B	0.55 (5)	129 (3)	18 (4)

Data collection

Bruker APEX CCD area-detector diffractometer	31167 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	11536 independent reflections
$T_{\min} = 0.799, T_{\max} = 0.926$	6688 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.054$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.068$	20 restraints
$wR(F^2) = 0.188$	H-atom parameters constrained
$S = 1.03$	$\Delta\rho_{\max} = 0.75 \text{ e \AA}^{-3}$
11536 reflections	$\Delta\rho_{\min} = -0.47 \text{ e \AA}^{-3}$
853 parameters	

All H atoms were placed in calculated positions, with N—H = 0.91 Å and C—H = 0.93 (aromatic) or 0.97 Å (methylene), and refined in riding mode with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier atom})$. The C

atoms of one substituent of the oxamide group in the heap^{4-} anion are disordered over two sets of positions (C9A–C11A and C9B–C11B), the occupancies of which were refined and then fixed at 0.7 and 0.3, respectively. The perchlorate anions containing atoms Cl1 and Cl2 each have three disordered O atoms, the components of which were refined isotropically. The occupancies of atoms O6A–O8A and O6B–O8B were fixed at 0.4 and 0.6, respectively, and those of atoms O10A–O12A and O10B–O12B are equal at 0.5. To obtain reasonable bond lengths, DFIX restraints (SHELXL97; Sheldrick, 2008) were applied to the disordered parts. In the perchlorate anions containing atoms Cl1 and Cl2, the Cl–O bonds and O···O distances were restrained to 1.4 (1) and 2.3 (1) Å, respectively, while in the disordered parts of the heap^{4-} ligand, the C–C and N–C bonds were restrained to 1.54 (1) and 1.47 (1) Å, respectively.

Data collection: SMART (Bruker, 2002); cell refinement: SAINT (Bruker, 2002); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: XP (Siemens, 1994); software used to prepare material for publication: WinGX (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3251). Services for accessing these data are described at the back of the journal.

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