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Tetraaquatetrakis[2-(2-hydroxyethylamino)-ethanolato]tetracopper(II) tetranitrate 14/3-hydrate

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The structure of the title complex, $[Cu_4(C_4H_{10}NO_2)_4(H_2O)_4](NO_3)_4 \cdot 14/3\,H_2O$, consists of tetranuclear $[Cu_4(Hdea)_4(H_2O)_4]^{4+}$ cations (H_2dea is diethanolamine), uncoordinated nitrate anions and water molecules. Each copper centre in the two independent cations (one on a twofold rotation axis and the other with $\bar{4}$ crystallographic symmetry) is similarly coordinated by two alkoxo O atoms, one amine N atom of the monodeprotonated Hdea ligands and one O atom from a water molecule in a square-planar geometry [Cu—O/N bond lengths are in the range 1.939 (6)–2.045 (8) Å]. The two axial positions of the Cu atoms are occupied by a weakly bound ethanol group of the chelating Hdea ligand and an alkoxo O atom from a neighbouring Hdea ligand [average Cu—O = 2.532 (7) Å]. The coordination geometry of the Cu atoms can, therefore, be best described as distorted elongated octahedral. The intermolecular hydrogen bonds that involve OH and NH groups of the ligands, uncoordinated NO_3^- anions and water molecules reinforce the crystal structure by forming an extended three-dimensional network.

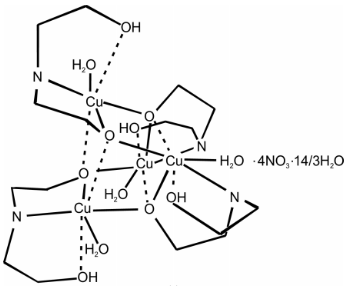
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.014 Å
H-atom completeness 84%
Disorder in solvent or counterion
R factor = 0.064
wR factor = 0.087
Data-to-parameter ratio = 9.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

We have recently succeeded in the preparation of a number of new Cu/M (M = Pb, Co, Zn, Ni) mixed-metal complexes by reacting copper powder with a salt of another metal (or metal oxide and ammonium salt) in a non-aqueous solution of an amino alcohol (Kovbasyuk *et al.*, 1998; Vinogradova *et al.*, 2001; Makhankova, Vassilyeva, Kokozay, Reedijk *et al.*, 2002; Makhankova, Vassilyeva, Kokozay, Skelton *et al.*, 2002; Vinogradova *et al.*, 2002). However, the direct interaction of metallic copper and nickel nitrate in the presence of diethanolamine (H_2dea) in CH_3OH, in air, did not result in the desired Cu/Ni mixed-metal compound, but afforded the tetranuclear copper complex $[Cu_4(Hdea)_4(H_2O)_4](NO_3)_4 \cdot 14/3H_2O$, (I).



(I)

The structure of (I) has been crystallographically investigated previously (Ivanova & Kokozei, 1994). However, the small amount of data afforded a structure of low precision,

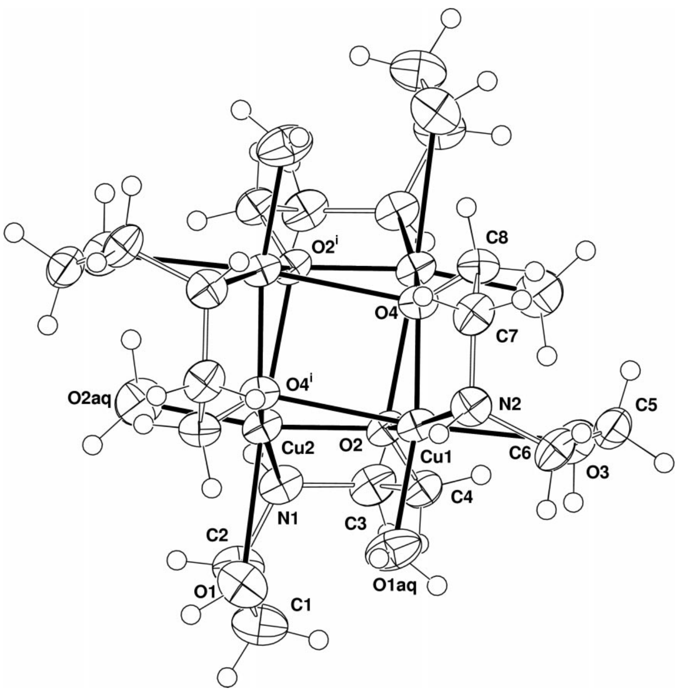


Figure 1
The molecular structure of one of the two crystallographically independent tetranuclear cations in (I), with 50% displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as small spheres of arbitrary radii.

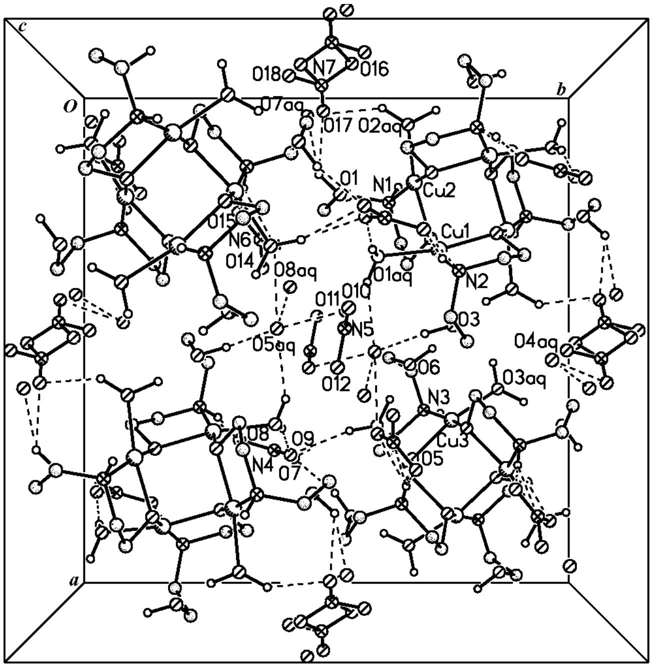


Figure 2
A packing diagram for (I), showing the hydrogen-bonding scheme (H atoms of the CH_2 groups, C1—C12, have been omitted for clarity).

with H atoms on the ligand O and N atoms not being located, and there was also some difficulty in determining the number and location of the nitrate ions. With the availability of a diffractometer with a CCD detector and low-temperature device, a better and significantly different model has been obtained in the present determination, with the location of the nitrate ions and ligand H atoms, allowing the number of charges on the cation to be assigned.

In the structure of (I), the three independent metal atoms, Cu1, Cu2 and Cu3, form two crystallographically inequivalent tetranuclear $[Cu_4(Hdea)_4(H_2O)_4]^{4+}$ cations, with largely similar structural data (Fig. 1 and Table 1). The cation containing Cu1 and Cu2 lies on a twofold axis and that formed from Cu3 has $\overline{4}$ symmetry. Each copper centre is similarly coordinated by two alkoxo O atoms, one amine N atom of the monodeprotonated Hdea ligands and one O atom from a water molecule in a square-planar geometry [Cu—O/N bond lengths are in the range 1.939 (6)–2.045 (8) Å]. As shown in the *Scheme*, the two axial positions of the Cu atoms are occupied by a weakly bound ethanol group of the chelating Hdea ligand and an alkoxo O atom from a neighbouring Hdea ligand [average Cu—O = 2.532 (7) Å]. The geometry of the Cu atoms can, therefore, be best described as distorted elongated octahedral. Each Hdea ligand adopts a chelating-bridging mode, forming five-membered rings with the ethanol group weakly coordinated, a coordination mode that is common for dinuclear copper complexes of this ligand (Karadag *et al.*, 2001; Madarasz *et al.*, 2000; Yilmaz *et al.*, 2001). However, in (I), the triply bridging function of the alkoxo O atoms is realised and results in the formation of a Cu_4O_4 cluster made up of a copper tetrahedron interlocked with an oxygen tetrahedron, closely related to the cubane-type structure (see Fig. 1). The bridged Cu···Cu distances lie in the range 3.172 (1)–3.213 (1) Å. All faces of the heterocubane core are remarkably non-planar, their edges are of different length and the least-squares rhombohedral planes of the faces are mutually non-orthogonal. In the structure of another copper tetramer $[Cu_4(Hdea)_4(OAc)_4]$ published recently (Saalfrank *et al.*, 2001), four copper centres are linked in a different way by bridging O atoms in an *anti*-tricyclo[4.2.0.0^{2,5}]octane-like fashion.

The X-ray investigation shows possible intra- and intermolecular hydrogen bonds involving the OH and NH groups of the ligands, coordinated and uncoordinated water molecules and uncoordinated NO_3^- anions, as indicated by the O···O and O···N distances (Table 2). The hydrogen bonding reinforces the crystal structure by forming an extended three-dimensional network (Fig. 2).

All bond distances and angles within the monodeprotonated diethanolamine are as expected.

Experimental

To synthesize (I), copper powder (0.32 g, 5 mmol), $Ni(NO_3)_2\cdot 4H_2O$ (2.90 g, 10 mmol), NH_4NO_3 (0.8 g, 10 mmol), CH_3OH (20 ml) and H_2dea (2 ml) were heated to 333 K and magnetically stirred until total dissolution of Cu was observed (20 min). Dark blue crystals of (I), adequate for an X-ray crystallographic study, were isolated the next day as a first crop (0.49 g).

Crystal data

$[\text{Cu}_4(\text{C}_4\text{H}_{10}\text{NO}_2)_4(\text{H}_2\text{O})_4]$-
$(\text{NO}_3)_4\cdot 14/3\text{H}_2\text{O}$
$M_r = 1074.85$
Tetragonal, $P4_2/n$
$a = 17.797$ (2) Å
$c = 20.600$ (2) Å
$V = 6524.7$ (12) Å^3
$Z = 6$
$D_x = 1.641$ Mg m$^{-3$}
Mo Kα radiation
Cell parameters from 8192 reflections
$\theta = 2.4$–$23.6°$
$\mu = 2.03$ mm^{-1}
$T = 150$ K
Tetragonal prism, dark blue
0.35 × 0.14 × 0.11 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.67$, $T_{\max} = 0.84$
63965 measured reflections
6674 independent reflections
3803 reflections with $F > 4\sigma(F)$
$R_{\text{int}} = 0.077$
$\theta_{\max} = 26.4°$
$h = -22 \rightarrow 22$
$k = -22 \rightarrow 22$
$l = -25 \rightarrow 25$

Refinement

Refinement on F
$R = 0.064$
$wR = 0.087$
$S = 1.04$
3803 reflections
397 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F) + 0.003F^2]$
$(\Delta/\sigma)_{\max} = 0.011$
$\Delta\rho_{\max} = 1.46$ e Å^{-3}
$\Delta\rho_{\min} = -0.86$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—O2	1.964 (5)	Cu2—O2*aq*	1.992 (8)
Cu1—O3	2.544 (6)	Cu2—O2$^{\text{i}}$	2.562 (5)
Cu1—O4	1.946 (5)	Cu2—O4$^{\text{i}}$	1.974 (5)
Cu1—N2	2.022 (6)	Cu3—O5	1.939 (6)
Cu1—O1*aq*	2.010 (7)	Cu3—O6	2.475 (7)
Cu1—O4$^{\text{i}}$	2.520 (5)	Cu3—N3	2.045 (8)
Cu2—O1	2.558 (7)	Cu3—O3*aq*	1.989 (8)
Cu2—O2	1.942 (5)	Cu3—O5$^{\text{ii}}$	2.531 (6)
Cu2—N1	2.032 (7)	Cu3—O5$^{\text{iii}}$	1.977 (6)
O2—Cu1—O3	92.6 (2)	O2—Cu2—O4$^{\text{i}}$	87.3 (2)
O2—Cu1—O4	87.5 (2)	N1—Cu2—O2*aq*	94.6 (3)
O2—Cu1—N2	166.9 (3)	N1—Cu2—O2$^{\text{i}}$	117.8 (2)
O2—Cu1—O1*aq*	94.5 (3)	N1—Cu2—O4$^{\text{i}}$	166.3 (3)
O2—Cu1—O4$^{\text{i}}$	73.0 (2)	O2*aq*—Cu2—O2$^{\text{i}}$	89.9 (3)
O3—Cu1—O4	94.1 (2)	O2*aq*—Cu2—O4$^{\text{i}}$	95.1 (3)
O3—Cu1—N2	77.2 (2)	O2$^{\text{i}}$—Cu2—O4$^{\text{i}}$	71.86 (19)
O3—Cu1—O1*aq*	95.7 (3)	O5—Cu3—O6	95.3 (2)
O3—Cu1—O4$^{\text{i}}$	164.23 (17)	O5—Cu3—N3	84.5 (3)
O4—Cu1—N2	85.0 (2)	O5—Cu3—O3*aq*	168.8 (3)
O4—Cu1—O1*aq*	169.8 (3)	O5—Cu3—O5$^{\text{ii}}$	82.7 (2)
O4—Cu1—O4$^{\text{i}}$	79.1 (2)	O5—Cu3—O5$^{\text{iii}}$	86.8 (2)
N2—Cu1—O1*aq*	94.7 (3)	O6—Cu3—N3	77.5 (3)
N2—Cu1—O4$^{\text{i}}$	115.9 (2)	O6—Cu3—O3*aq*	95.8 (3)
O1*aq*—Cu1—O4$^{\text{i}}$	92.0 (3)	O6—Cu3—O5$^{\text{ii}}$	164.0 (2)
O1—Cu2—O2	95.3 (2)	O6—Cu3—O5$^{\text{iii}}$	92.0 (2)
O1—Cu2—N1	76.0 (2)	N3—Cu3—O3*aq*	96.6 (4)
O1—Cu2—O2*aq*	95.9 (3)	N3—Cu3—O5$^{\text{ii}}$	117.9 (3)
O1—Cu2—O2$^{\text{i}}$	164.66 (18)	N3—Cu3—O5$^{\text{iii}}$	165.6 (3)
O1—Cu2—O4$^{\text{i}}$	93.4 (2)	O3*aq*—Cu3—O5$^{\text{ii}}$	87.0 (3)
O2—Cu2—N1	85.1 (2)	O3*aq*—Cu3—O5$^{\text{iii}}$	94.2 (3)
O2—Cu2—O2*aq*	168.3 (3)	O5$^{\text{ii}}$—Cu3—O5$^{\text{iii}}$	72.1 (2)
O2—Cu2—O2$^{\text{i}}$	80.0 (2)		

Symmetry codes: (i) $\frac{1}{2} - x, \frac{3}{2} - y, z$; (ii) $\frac{3}{2} - x, \frac{3}{2} - y, z$; (iii) $y, \frac{3}{2} - x, \frac{1}{2} - z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1O$\cdots$O17	0.96	2.10	2.77 (2)	125
O1—H1O$\cdots$O7*aq*	0.96	2.02	2.83 (4)	141
O3—H3O$\cdots$O5*aq*$^{\text{iv}}$	0.96	1.76	2.71 (1)	171
O6—H6O$\cdots$O7$^{\text{iii}}$	0.98	1.89	2.852 (9)	165
N1—H1$\cdots$O8$^{\text{v}}$	0.94	1.96	2.875 (8)	164
N2—H2$\cdots$O8$^{\text{vi}}$	0.94	2.04	2.950 (8)	162
O1*aq*—H1*aqA*$\cdots$O1	0.90	2.25	3.06 (1)	149
O2*aq*—H2*aqB*$\cdots$O3$^{\text{i}}$	0.94	2.10	3.05 (1)	174
O2*aq*—H2*aqA*$\cdots$O17	0.89	2.10	2.94 (3)	157
O5*aq*$\cdots$O10$^{\text{viii}}$	–	–	2.92 (2)	–
O17$\cdots$O4*aq*$^{\text{viii}}$	–	–	2.79 (4)	–
O4*aq*$\cdots$O12$^{\text{viii}}$	–	–	2.72 (2)	–
O4*aq*$\cdots$O6*aq*$^{\text{ix}}$	–	–	2.71 (4)	–
O4*aq*$\cdots$O7*aq*$^{\text{v}}$	–	–	2.70 (4)	–
O5*aq*$\cdots$O13$^{\text{x}}$	–	–	2.68 (3)	–
O5*aq*$\cdots$O8*aq*$^{\text{x}}$	–	–	2.73 (2)	–

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

All non-H atoms were assigned anisotropic displacement parameters, except for the O atoms of half-weighted solvent water molecules, *viz*. O6*aq*, O7*aq* and O8*aq*. H atoms on O and N atoms were found in difference maps, while those of the remainder of the cation were placed in calculated positions and fixed in the refinement. For water molecules O1*aq*–O3*aq*, H atoms were refined with their geometry restrained to ideal values, but those for the solvent water molecules O4*aq*–O8*aq* were not located. Nitrates N6 and N7 are half-weighted, with water molecules O8*aq* and O7*aq* occupying the other half of the sites. The N7/O16/O17/O18 nitrate anion and the O7*aq* solvent water were modelled to be disordered about a crystallographic inversion centre. All nitrate ions were refined as rigid bodies. Several other peaks in a difference map, such as that at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, which was modelled as an *Aq*(8) in the original structure determination, refined with oxygen population less than $\frac{1}{4}$ with an insignificant decrease in the *R* factor, and hence these sites as possible solvent water molecules were ignored. The maximum electron-density peak is 0.56 Å from Cu2.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT* and *Xtal*3.5 (Hall *et al.*, 1995); program(s) used to solve structure: *Xtal*3.5; program(s) used to refine structure: *Xtal*3.5 *CRYLSQ*; molecular graphics: *Xtal*3.5; software used to prepare material for publication: *Xtal*3.5 *BONDLA CIFIO*.

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