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## Key indicators

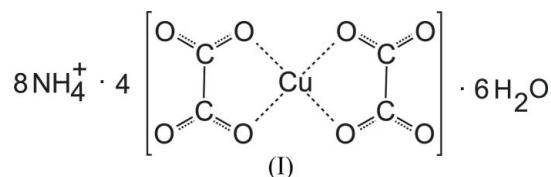
Single-crystal X-ray study  
 $T = 293$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å  
 $R$  factor = 0.032  
 $wR$  factor = 0.061  
Data-to-parameter ratio = 16.4For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.Octaammonium diaqua-hexa- $\mu_2$ -oxalato-  
dioxalatotetracopper(II) tetrahydrate

In the structure of the title compound,  $(\text{NH}_4)_8[\text{Cu}_4(\text{C}_2\text{O}_4)_8(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ , isolated tetramers of  $[\text{Cu}(\text{ox})_2]^{2+}$  (ox is oxalate) are present. Each  $\text{Cu}^{\text{II}}$  ion coordinates to four O atoms in two oxalate ligands and to two more distant O atoms in a neighbouring oxalate ligand or a water molecule. An extensive hydrogen-bonding network connects the tetramers to two unique solvent water molecules and four ammonium ions.

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## Comment

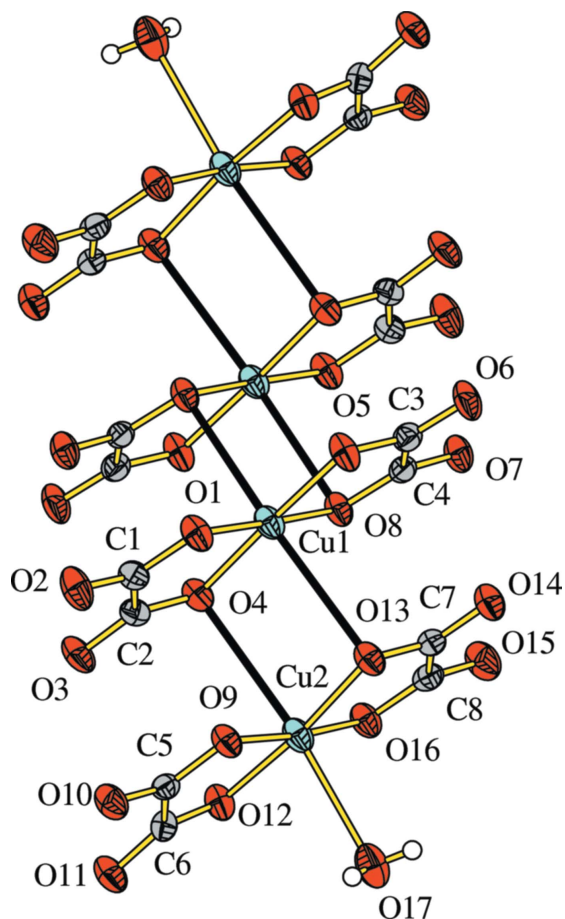
Carboxylate complexes of  $3d$  transition metals ions have been studied for a long time in our department. In particular, complexes of Cu, Ni and Fe have been the subject of investigation. A compound nearly similar in composition to the title compound,  $(\text{NH}_4)_4[\text{Cu}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_{0.5}]_2(\text{H}_2\text{O})_2$ , (I), but crystallizing with a slightly lower water content of two water molecules instead of three, has been the subject of earlier investigations (Viswamitra, 1962; Novosad *et al.*, 2000).



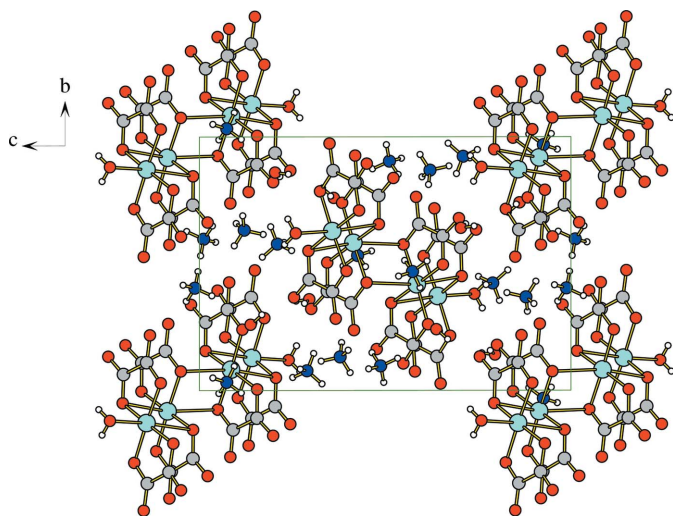
In the structure of (I), isolated tetramers of  $[\text{Cu}(\text{ox})_2]^{2+}$  [ox is oxalate] are formed, while the previously studied compound forms infinite chains of  $[\text{Cu}(\text{ox})_2]^{2+}$  where every second Cu atom coordinates to two water molecules in axial positions. In (I), the two central Cu atoms of the tetramer are coordinated only by oxalate ligands, while the two outer Cu atoms coordinate to a water molecule in the axial position (Fig. 1). Both unique Cu atoms coordinate two oxalate groups in an approximately planar configuration.

The coordination around Cu1 is slightly twisted. The deviations (with s.u.s) of the atoms from the least-squares plane of one of the oxalate complexes are Cu1 – 0.006 (1), O1 0.033 (1), O4 – 0.034 (1), O5 – 0.033 (1) and O8 0.036 (1) Å. In contrast with this, the four closest O atoms coordinating to Cu2 are planar to within less than 0.01 Å, with atom Cu2 deviating by 0.089 (1) Å from this least-squares plane in the direction of O17.

One of the oxalate ligands is planar to within 0.01 (1) Å, while the other three oxalate groups are planar only to within 0.03 (2) Å. These nearly planar  $\text{Cu}(\text{ox})_2$  groups are stacked to complete an elongated  $\text{CuO}_6$  octahedron around each Cu atom with more distant O atoms in neighbouring oxalates or a



**Figure 1**  
The tetrameric copper dioxalate complex of (I), showing 50% probability displacement ellipsoids, with the unique atoms labelled. The long interatomic Cu—O distances between individual Cu(ox)<sub>2</sub> units are shown with black bonds. Two unique water molecules and four unique ammonium ions have been omitted for clarity. H atoms are shown as circles of arbitrary radius. Unlabelled atoms are related to labelled atoms by the symmetry operator (1 - x, 1 - y, 1 - z).



**Figure 2**  
A packing diagram for (I), in a view along the *a* axis. Cu atoms are shown in pale grey-blue, C atoms in grey, H atoms in white, N atoms in blue and O atoms in red.

water molecule (O17), in accordance with a large Jahn–Teller distortion of the Cu<sup>II</sup> ion.

An extensive hydrogen-bonding network (Table 2) connects the tetramers to two unique solvent water molecules and four unique ammonium ions. A packing diagram of (I) is shown in Fig. 2.

## Experimental

Compound (I) was crystallized by slow evaporation of an aqueous solution (50 ml) of ammonium oxalate hydrate (0.0118 g, 0.083 mmol) and copper acetate hydrate (0.0202 g, 0.101 mmol) at ambient temperature. Thin plate-like crystals suitable for X-ray analysis were obtained when the solvent evaporated.

### Crystal data

(NH<sub>4</sub>)<sub>8</sub>[Cu<sub>4</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>8</sub>(H<sub>2</sub>O)<sub>2</sub>].4H<sub>2</sub>O  
*M<sub>r</sub>* = 1210.76  
 Monoclinic, *P*2<sub>1</sub>/*c*  
*a* = 11.1364 (6) Å  
*b* = 11.2806 (6) Å  
*c* = 17.1470 (12) Å  
 $\beta$  = 106.235 (5)°  
*V* = 2068.2 (2) Å<sup>3</sup>

*Z* = 2  
*D<sub>x</sub>* = 1.944 Mg m<sup>-3</sup>  
 Mo K $\alpha$  radiation  
 $\mu$  = 2.16 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Plate, light blue  
 0.50 × 0.20 × 0.05 mm

### Data collection

Oxford Xcalibur-3  $\kappa$  diffractometer  
 with Sapphire-III CCD detector  
 $\omega$  scans at different  $\varphi$   
 Absorption correction: numerical  
 (*X-RED*; Stoe & Cie, 1997)  
*T<sub>min</sub>* = 0.63, *T<sub>max</sub>* = 0.79

37577 measured reflections  
 6003 independent reflections  
 2994 reflections with *I* > 2 $\sigma$ (*I*)  
*R<sub>int</sub>* = 0.067  
 $\theta_{\max}$  = 30.0°

### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.033  
*wR*(*F*<sup>2</sup>) = 0.061  
*S* = 0.84  
 6003 reflections  
 366 parameters

Only H-atom coordinates refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0199P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.40 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.36 \text{ e \AA}^{-3}$

**Table 1**

Selected bond lengths (Å).

Cu1—O1	1.9085 (17)	O5—C3	1.284 (3)
Cu1—O8	1.9262 (17)	O6—C3	1.221 (3)
Cu1—O4	1.9338 (17)	O7—C4	1.223 (3)
Cu1—O5	1.9353 (17)	O8—C4	1.283 (3)
Cu1—O8 <sup>i</sup>	2.7971 (17)	O9—C5	1.285 (3)
Cu1—O13	2.8779 (18)	O10—C5	1.225 (3)
Cu2—O12	1.9300 (17)	O11—C6	1.225 (3)
Cu2—O16	1.9348 (17)	O12—C6	1.278 (3)
Cu2—O9	1.9365 (17)	O13—C7	1.285 (3)
Cu2—O13	1.9403 (17)	O14—C7	1.223 (3)
Cu2—O17	2.542 (2)	O15—C8	1.223 (3)
Cu2—O4	2.9481 (17)	O16—C8	1.279 (3)
O1—C1	1.290 (3)	C1—C2	1.554 (3)
O2—C1	1.215 (3)	C3—C4	1.547 (3)
O3—C2	1.224 (3)	C5—C6	1.545 (3)
O4—C2	1.283 (3)	C7—C8	1.562 (4)

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

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

<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>
O17—H171...O14 <sup>ii</sup>	0.73 (2)	2.27 (2)	2.870 (3)	140 (2)
O17—H171...O15 <sup>ii</sup>	0.73 (2)	2.38 (2)	3.025 (3)	147 (2)
O17—H172...O10 <sup>iii</sup>	0.74 (2)	2.00 (2)	2.733 (3)	169 (2)
N1—H11...O15 <sup>ii</sup>	0.88 (2)	2.03 (2)	2.873 (3)	161 (2)
N1—H12...O11 <sup>iii</sup>	0.87 (2)	2.12 (2)	2.948 (3)	159 (2)
N1—H12...O10 <sup>iii</sup>	0.87 (2)	2.47 (2)	2.930 (3)	114 (2)
N1—H12...O11 <sup>iv</sup>	0.87 (2)	2.54 (2)	3.023 (3)	117 (2)
N1—H13...O13	0.87 (2)	2.16 (2)	2.993 (3)	162 (2)
N1—H14...O3 <sup>iv</sup>	0.88 (2)	2.04 (2)	2.871 (3)	158 (2)
O18—H181...O9 <sup>v</sup>	0.72 (2)	2.20 (2)	2.900 (3)	162 (2)
O18—H182...O6 <sup>vi</sup>	0.73 (2)	2.14 (2)	2.816 (3)	154 (2)
N2—H21...O16 <sup>vii</sup>	0.86 (2)	2.33 (2)	3.025 (3)	138 (2)
N2—H21...O12 <sup>iii</sup>	0.86 (2)	2.50 (2)	2.977 (3)	116 (2)
N2—H22...O18	0.88 (2)	2.10 (2)	2.901 (3)	151 (2)
N2—H22...O16 <sup>iii</sup>	0.88 (2)	2.63 (2)	3.093 (3)	114 (2)
N2—H23...O19	0.87 (2)	2.09 (2)	2.958 (3)	172 (2)
N2—H24...O4 <sup>vii</sup>	0.88 (2)	2.27 (2)	3.118 (3)	162 (2)
O19—H191...O1 <sup>vi</sup>	0.73 (2)	2.17 (2)	2.835 (3)	151 (2)
O19—H192...O14	0.74 (2)	2.23 (2)	2.933 (3)	160 (2)
N3—H31...O2 <sup>vi</sup>	0.88 (2)	1.98 (2)	2.819 (3)	159 (2)
N3—H32...O5	0.86 (2)	2.03 (2)	2.880 (3)	175 (2)
N3—H33...O17 <sup>viii</sup>	0.88 (2)	2.11 (2)	2.989 (3)	172 (2)
N3—H34...O6 <sup>ix</sup>	0.87 (2)	2.14 (2)	2.953 (3)	157 (2)
N3—H34...O7 <sup>ix</sup>	0.87 (2)	2.27 (2)	2.838 (3)	124 (2)
N4—H41...O10 <sup>iv</sup>	0.87 (2)	2.28 (2)	3.020 (3)	143 (2)
N4—H42...O19	0.87 (2)	2.15 (2)	2.965 (3)	155 (2)
N4—H42...O11 <sup>iii</sup>	0.87 (2)	2.38 (2)	2.818 (3)	111 (2)
N4—H43...O3 <sup>iv</sup>	0.87 (2)	2.27 (2)	2.975 (3)	139 (2)
N4—H43...O2 <sup>iv</sup>	0.86 (2)	2.29 (2)	2.945 (3)	133 (2)
N4—H44...O7 <sup>vii</sup>	0.88 (2)	1.90 (2)	2.769 (3)	169 (2)

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

H atoms were located in difference density maps. The O—H and N—H distances were restrained (Table 2) for the water and ammonium ions to retain the previously known geometry of these molecules. The H atoms of the water molecules and ammonium ions were given  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O}, \text{N})$ . The data were cut to  $2\theta = 60^\circ$  in the final refinement, although reflection data were collected up to  $2\theta \simeq 66.8^\circ$ , but with much less than 100% completeness at the highest angles.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *PLATON* (Spek, 2003) and *SHELXL97*.

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