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Bis[5,5-dichloro-4,6-dioxo-3,7-diaza-1,9-nonanedylbis(dimethylammonium)] Tetrachlorohexa- μ -chloro- μ_4 -oxo-tetra-cuprate(II)

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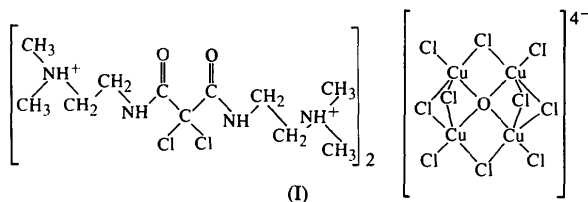
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Abstract

The anion of the title compound, $(C_{11}H_{24}Cl_2N_4O_2)_2^{2-} [Cu_4OCl_{10}]$, contains a tetrahedral oxide ion coordinated to four Cu^{II} ions. Each Cu^{II} ion is in turn coordinated to one terminal and three bridging Cl ions, giving rise to a symmetrical polynuclear cluster. The cation is a diprotonated tetraamine where the central methylene protons have been displaced by Cl ions.

Comment

We present here the structure of the title copper(II) complex, (I), which contains an unusual anion. The complex consists of a $[Cu_4OCl_{10}]^{4-}$ anion (located on a twofold axis) and two cations.



The $[Cu_4OCl_{10}]^{4-}$ polynuclear cluster of the anion contains the oxide ion in a rather unusual environment, *i.e.* tetrahedrally coordinated to four Cu^{II} ions. Similar anions have been reported, for example, $[Cu_4OCl_6L_4]$, where L is triphenylphosphine oxide, pyridine or N,N -diethylnicotinamide (Bertrand & Kelley, 1966; Kilbourn & Dunitz, 1967; El-Toukhy *et al.*, 1984). In (I), the $Cu-\mu_4-O$ distances are 1.917 (3) Å and the $Cu-O-Cu$ angles are between 108.76 (3) and 110.09 (3)°. Thus, the central O atom is only slightly distorted from perfect T_d symmetry. The Cu atoms are essentially in a trigonal-bipyramidal environment, with the terminal $Cl-Cu$ bond lengths of 2.239 (2) and 2.257 (2) Å significantly shorter than the bridging $Cl-Cu$ bond lengths which range from 2.353 (1) to 2.466 (2) Å. The $O-Cu-Cl_{ax}$ angles are virtually linear (*ca* 177°), the $O-Cu-Cl_{eq}$ angles have an average value of *ca* 85° and the $Cl_{ax}-$

$Cu-Cl_{eq}$ angles are all greater than 90°. It is thus apparent that the Cu atoms are displaced out of the equatorial plane away from the oxide towards the axial chlorides.

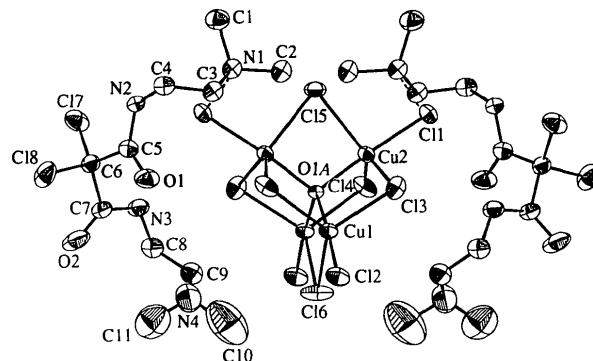


Fig. 1. The structure of the title compound showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

The bond lengths in the cation fall within expected ranges. An interesting feature of the cation is the displacement of the central methylene protons during the isolation of the crystals, which were prepared by slow diffusion of chloroform into an aqueous solution of N,N' -bis[(2-dimethylamino)ethyl]propanediamide and copper(II) chloride. The central methylene protons are quite labile and have been shown to undergo deuterium exchange in D_2O solution because they are situated between two electron-withdrawing amide groups. However, they were not expected to exchange with chlorine. It is possible that coordination of the Cu^{II} ion to the ligand catalyzes this reaction, as it has not been observed in the absence of metal ions. The N1 atom makes a close contact with Cl1, indicating the presence of $N-H\cdots Cl$ hydrogen bonding. The $N\cdots Cl$ distance is 3.166 (6) Å and the $N-H\cdots Cl$ angle is 168°.

Experimental

The title compound was prepared by slow diffusion of chloroform into an aqueous solution of N,N' -bis[2-(dimethylamino)ethyl]propanediamide and copper(II) chloride.

Crystal data

$(C_{11}H_{24}Cl_2N_4O_2)_2^{2-} [Cu_4OCl_{10}]$

$M_r = 1255.2$

Monoclinic

$C2/c$

$a = 14.405 (2) \text{ \AA}$

$b = 15.805 (2) \text{ \AA}$

$c = 20.644 (5) \text{ \AA}$

$\beta = 99.61 (2)^\circ$

$V = 4634 (2) \text{ \AA}^3$

$Z = 4$

$D_x = 1.799 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 24

reflections

$\theta = 16-17^\circ$

$\mu = 2.66 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Prism

$0.43 \times 0.40 \times 0.28 \text{ mm}$

Red

Data collection

Enraf–Nonius CAD-4
diffractometer
 $\omega/2\theta$ scans
Absorption correction:
empirical via ψ scans
(North, Phillips &
Mathews, 1968)
 $T_{\min} = 0.639$, $T_{\max} =$
0.995
3708 measured reflections
3658 independent reflections

3209 observed reflections
[$I > 2\sigma(I)$]
 $R_{\text{int}} = 0.034$
 $\theta_{\text{max}} = 25^\circ$
 $h = -17 \rightarrow 17$
 $k = 0 \rightarrow 18$
 $l = 0 \rightarrow 24$
3 standard reflections
frequency: 60 min
intensity decay: 5.5%

Refinement

Refinement on F
 $R = 0.049$
 $wR = 0.059$
 $S = 1.094$
3209 reflections
255 parameters
H atoms: see text
 $w = 1.538/[\sigma^2(F)$
 $+ 0.001163F^2]$

$(\Delta/\sigma)_{\text{max}} = 0.05$
 $\Delta\rho_{\text{max}} = 1.28 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = 0.59 \text{ e } \text{Å}^{-3}$
Extinction correction: none
Atomic scattering factors
from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV)

N2—C5	1.331 (8)	C7—N3	1.306 (10)
C5—C6	1.554 (8)	C6—C7	1.564 (9)
C5—O1	1.194 (8)	O2—C7	1.192 (10)
C17—C6	1.758 (6)	C6—C18	1.774 (7)
Cu1—O1A—Cu2	108.76 (3)	Cu1—O1A—Cu1 ¹	109.10 (8)
Cu1—O1A—Cu2 ¹	110.09 (3)	Cu2—O1A—Cu2 ¹	110.08 (5)
C12—Cu1—C16	96.07 (6)	C11—Cu2—C15	98.35 (6)
C12—Cu1—C14 ¹	93.36 (8)	C11—Cu2—C14	91.74 (7)
C12—Cu1—C13	98.24 (6)	C11—Cu2—C13	94.59 (6)
C14 ¹ —Cu1—O1A	83.71 (5)	C14—Cu2—O1A	85.48 (5)
C16—Cu1—O1A	83.91 (2)	C15—Cu2—O1A	85.11 (3)
C13—Cu1—O1A	84.64 (5)	C13—Cu2—O1A	85.16 (4)
C12—Cu1—O1A	176.51 (6)	C11—Cu2—O1A	176.25 (5)
Cu1—C13—Cu2	81.18 (5)	Cu2—C14—Cu1 ¹	80.36 (6)
Cu2—C15—Cu2 ¹	79.70 (3)	Cu1—C16—Cu1 ¹	83.13 (2)
N2—C5—C6	116.0 (5)	C6—C7—N3	114.8 (5)
N2—C5—O1	126.1 (6)	O2—C7—N3	125.6 (7)
O1—C5—C6	117.9 (6)	C6—C7—O2	119.0 (6)
C18—C6—C7	107.9 (4)	C5—C6—C7	111.8 (5)

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

Non-H atoms were refined anisotropically. H atoms were included in idealized positions and refined with a common isotropic displacement parameter.

Data collection: *CAD-4 Manual* (Enraf–Nonius, 1988). Cell refinement: *CAD-4 Manual*. Data reduction: *CAD-4 Manual*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL76* (Sheldrick, 1978). Molecular graphics: *ZORTEP* (Zsolnai, 1994).

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Cu1	0.54254 (1)	0.31763 (1)	0.32472 (2)	0.0422 (1)
Cu2	0.60272 (1)	0.45752 (2)	0.23377 (1)	0.0407 (1)
C11	0.7270 (1)	0.5321 (1)	0.2110 (1)	0.050 (1)
C12	0.5832 (1)	0.2355 (1)	0.4133 (1)	0.061 (1)
C13	0.6871 (1)	0.3956 (1)	0.3315 (1)	0.062 (1)
C14	0.5738 (1)	0.3980 (1)	0.1250 (1)	0.063 (1)
C15	1/2	0.5766 (1)	1/4	0.066 (1)
C16	1/2	0.2062 (1)	1/4	0.083 (1)
C17	0.9781 (1)	0.5144 (1)	0.1685 (1)	0.079 (1)
C18	1.0194 (2)	0.4155 (2)	0.0584 (1)	0.094 (1)
O1A	1/2	0.3880 (3)	1/4	0.031 (1)
C1	0.6646 (6)	0.7016 (5)	0.0872 (4)	0.074 (3)
C2	0.5269 (5)	0.6098 (5)	0.0717 (5)	0.078 (3)
N1	0.6317 (4)	0.6139 (3)	0.0762 (3)	0.053 (2)
C3	0.6571 (4)	0.5711 (4)	0.0160 (3)	0.053 (2)
C4	0.7571 (5)	0.5816 (4)	0.0065 (3)	0.053 (2)
N2	0.8284 (3)	0.5468 (3)	0.0590 (2)	0.045 (2)
C5	0.8453 (4)	0.4640 (4)	0.0629 (3)	0.049 (2)
O1	0.7989 (4)	0.4101 (3)	0.0325 (3)	0.078 (2)
C6	0.9356 (4)	0.4365 (4)	0.1103 (3)	0.053 (2)
O2	0.9742 (5)	0.2961 (4)	0.1473 (4)	0.109 (3)
C7	0.9198 (5)	0.3529 (4)	0.1475 (3)	0.054 (2)
N3	0.8530 (4)	0.3566 (3)	0.1831 (3)	0.062 (2)
C8	0.8328 (5)	0.2853 (4)	0.2246 (3)	0.061 (2)
C9	0.7464 (6)	0.2400 (5)	0.2027 (5)	0.080 (3)
N4	0.7386 (6)	0.1960 (6)	0.1395 (5)	0.121 (5)
C10	0.6533 (9)	0.1520 (13)	0.1226 (10)	0.332 (17)
C11	0.8085 (12)	0.1529 (16)	0.1239 (8)	0.239 (13)

Table 2. Selected geometric parameters (Å , $^\circ$)

Cu1—C12	2.239 (2)	Cu2—C11	2.257 (2)
Cu1—O1A	1.917 (3)	Cu2—O1A	1.917 (3)
Cu1—C13	2.404 (2)	Cu2—C13 ¹	2.386 (2)
Cu1—C14 ¹	2.466 (2)	Cu2—C14	2.404 (2)
Cu1—C16	2.353 (1)	Cu2—C15	2.452 (1)

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1210). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Bertrand, J. A. & Kelley, J. A. (1966). *J. Am. Chem. Soc.* **88**, 4746–4747.
- El-Toukhy, A., Cai, G.-Z., Davies, G., Gilbert, T. R., Onan, K. D. & Veidis, M. (1984). *J. Am. Chem. Soc.* **106**, 4596–4605.
- Enraf–Nonius (1988). *CAD-4 Manual*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Kilbourn, B. T. & Dunitz, J. D. (1967). *Inorg. Chim. Acta*, **1**, 209–216.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sheldrick, G. M. (1978). *Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, p. 34. Delft University Press.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Zsolnai, L. (1994). *ZORTEP*. Modified Version of *ORTEP*. University of Heidelberg, Germany.