Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Hexa-μ_2-chloro-μ_4-oxo-tetrakis-[(2-ethyltetrazole-κN^4)copper(II)]

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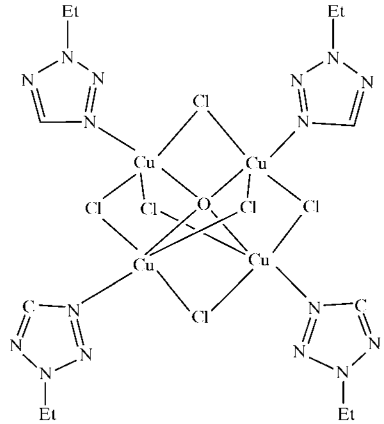
Received 14 June 2004
Accepted 18 June 2004
Online 21 July 2004

In the title molecular complex, [$Cu_4Cl_6O(2\text{-}EtTz)_4$], where 2-EtTz is 2-ethyltetrazole ($C_3H_6N_4$), the central O atom is located on the $\overline{4}$ symmetry site and is tetrahedrally coordinated to four Cu atoms, with Cu—O distances of 1.8966 (4) Å. A very slight distortion of Cu_4O from a regular tetrahedron is observed [two Cu—O—Cu angles are 108.76 (3)° and four others are 109.828 (13)°]. Each Cu atom is connected to three others *via* the Cl atoms, forming a slightly distorted Cl octahedron around the O atom, with O···Cl distances of 2.9265 (7) Å for Cl atoms lying on the twofold axis and 2.9441 (13) Å for those in general positions. The Cu atom has a distorted trigonal–bipyramidal environment, with three Cl atoms in the equatorial plane, and with the N atom of the 2-ethyltetrazole ligand and the μ_4-O atom in axial positions. The Cu atom is displaced out of the equatorial plane by *ca* 0.91 Å towards the coordinated N atom of the 2-ethyltetrazole ligand.

Comment

Tetranuclear complexes of copper(II) with the composition $Cu_4OX_6L_4$ (where X is Cl or Br, and L is Cl, Br or ligands containing N-, O- or P-donors) have been the subject of numerous investigations, mainly because of their unusual magnetic properties, which are caused by the existence of two different exchange interaction channels, Cu—O—Cu and Cu—X—Cu, and which depend on the nature of the ligand L (Carlin, 1986; Atria *et al.*, 1999). The high thermodynamic stability of such complexes is reflected in their frequent formation as by-products on preparing $CuX_2{\cdot}nL$ adducts starting from the corresponding copper(II) halide hydrate and compound L (Norman & Rose, 1989; Virovets *et al.*, 2001).

We have recently shown that $Cu_4OX_6L_4$ complexes are also formed in the attempt to synthesize copper(II) chloride complexes with 2-substituted tetazoles, especially on slow crystallization (Degtyarik *et al.*, 2003). Three such complexes, with L = 2-methyl-, 2-ethyl- and 2-allyltetrazole, have been obtained. This paper presents the crystal structure of one of them, namely [$Cu_4OCl_6(2\text{-}EtTz)_4$], (I), where 2-EtTz is 2-ethyltetrazole (Fig. 1).



(I)

The molecule of (I) consists of a tetrahedron of Cu atoms bonded to a central O atom. Each Cu atom is connected to three others through bridging Cl atoms, and to the 2-ethyltetrazole ligand *via* atom N4. The O and Cl1 atoms lie on Wyckoff sites $\overline{4}$ and 2, respectively; all others are in general positions.

The crystallographic site symmetry of the central O atom imposes $\overline{4}$ symmetry on the Cu_4O tetrahedron and of course on the molecule as a whole. The tetrahedron has Cu—O bond lengths of 1.8966 (4) Å, and two Cu—O—Cu angles of 108.76 (3) Å (the $\overline{4}$ axis lies on the intersection of the planes of these angles) and four others of 109.828 (13) Å. The Cu···Cu distances corresponding to the above Cu—O—Cu angles are 3.0835 (7) and 3.1039 (7) Å, respectively.

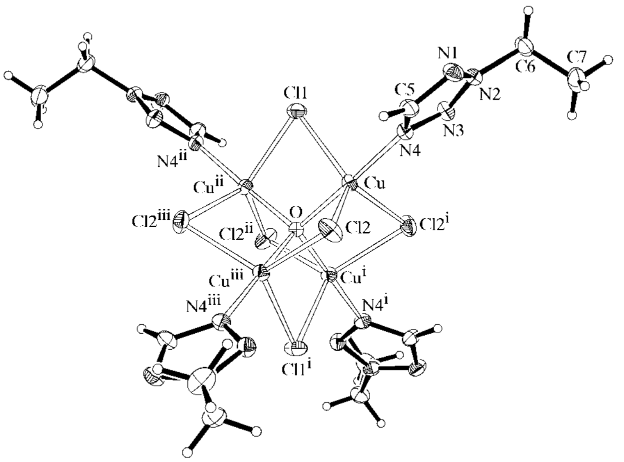


Figure 1
The structure of the molecule of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The $\overline{4}$ axis runs along O···Cl1. Symmetry codes are as given in Table 1.

DOI: 10.1107/S0108270104014921

The six Cl atoms of the molecule form a slightly distorted octahedron around the O atom, with two axial O$\cdots$Cl1 distances of 2.9441 (13) Å and four equatorial O$\cdots$Cl2 distances of 2.9265 (7) Å. The Cl2$\cdots$O$\cdots$Cl2 equatorial–equatorial angles are either 90.124 (2) or 174.68 (3)°, and the Cl1$\cdots$O$\cdots$Cl2 axial–equatorial angles are 92.662 (16) or 87.338 (16)°.

The Cu atom has a distorted trigonal–bipyramidal coordination (Table 1), with a τ descriptor of 0.88 (extreme values are 0 for a square pyramid and 1 for a trigonal bipyramid; Addison *et al.*, 1984). The axial positions of the bipyramid are occupied by the O atom and atom N4 of one 2-ethyltetrazole ligand, with Cu—O and Cu—N4 bond lengths of 1.8966 (4) and 1.972 (2) Å, respectively. The equatorial plane is occupied by one Cl1 atom [Cu—Cl1 2.4002 (9) Å] and two Cl2 atoms [Cu—Cl2 2.3827 (8) and 2.4344 (7) Å]. The axial–axial O—Cu—N4 angle of the bipyramid deviates slightly from 180°, with a value of 178.20 (6)°. The Cl2—Cu—Cl2 and Cl2—Cu—Cl1 equatorial–equatorial angles are 118.652 (19) and 113.95 (3)°, respectively. The axial–equatorial angles fall into two groups, with O—Cu—Cl values in the range 84.04 (2)–85.65 (3)° and N4—Cu—Cl in the range 93.20 (6)–97.70 (6)°, which reflects the fact that the Cu atom is displaced out of the plane of the three equatorial Cl atoms by *ca* 0.91 Å towards atom N4 of the 2-ethyltetrazole ligand. The Cu—Cl1—Cu and Cu—Cl2—Cu bridges are characterized by angles of 79.93 (4) and 80.23 (3)°, respectively.

The tetrazole ring of the 2-ethyltetrazole ligand in (I) is essentially planar, with a mean deviation from the least-squares plane of 0.0005 (16) Å. The tetrazole ring geometry is similar to those found previously for complexes of 2-substituted tetrazoles, namely $[\mathrm{Ni(2\text{-}MeTz)_6}](\mathrm{BF_4})_2$ (2-MeTz = 2-methyltetrazole; van den Heuvel *et al.*, 1983), $[\mathrm{Zn}L_3](\mathrm{ClO_4})_2$ [L = 1,2-bis(tetrazol-2-yl)ethane; Bronisz, 2002], $[\mathrm{CuCl_2}(2\text{-}^t\mathrm{BuTz})]$ (2-^tBuTz = 2-*tert*-buthyltetrazole; Lyakhov, Gaponik, Degtyarik & Ivashkevich, 2003*a*), $[\mathrm{CuCl_3(2\text{-}AlTz)_4}]$ (2-AlTz = 2-allyltetrazole; Lyakhov, Gaponik, Degtyarik *et al.*, 2003) and $[\mathrm{CuCl_2(2\text{-}EtTz)_2}]$ (2-EtTz = 2-ethyltetrazole; Lyakhov, Gaponik, Degtyarik & Ivashkevich, 2003*b*). Table 2 compares the tetrazole ring bond lengths in (I) with those for these previously investigated complexes of 2-substituted tetrazoles found in an analysis of search results from the Cambridge Structural Database (CSD, Version 5.24, November 2002 release; Allen, 2002).

Because of a lack of hydrogen bonds in the structure of (I), only van der Waals interactions are responsible for the crystal packing.

Experimental

2-Ethyltetrazole (1.57 g, 0.016 mol) was added to a solution of $\mathrm{CuCl_2{\cdot}2H_2O}$ (2.82 g, 0.0165 mol) in methanol (20 ml). The reaction mixture was stirred for 1 h and was then kept in air at room temperature. Two months later, a mixture of needle-like green and prismatic brown crystals had formed, from which prismatic brown crystals of (I) (0.52 g, yield *ca* 15%) could be separated. Analysis found: Cu 29.1, Cl 23.1%; calculated: Cu 29.0, Cl 24.3%. These values correspond to the composition $[\mathrm{Cu_4Cl_6O(2\text{-}EtTz)_4}]$.

Crystal data

$[\mathrm{Cu_4Cl_6O(C_3H_6N_4)_4}]$
$M_r = 875.37$
Tetragonal, $I4_1/a$
$a = 16.069\ (2)$ Å
$c = 11.836\ (4)$ Å
$V = 3056.2\ (12)$ Å^3
$Z = 4$
$D_x = 1.902$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 18.1$–$21.4°$
$\mu = 3.31$ mm^{-1}
$T = 293\ (2)$ K
Prism, dark brown
0.40 × 0.38 × 0.35 mm

Data collection

Nicolet *R*3*m* four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{\min} = 0.281$, $T_{\max} = 0.312$
2607 measured reflections
2243 independent reflections
1938 reflections with $I > 2\sigma(I)$

$R_{\mathrm{int}} = 0.025$
$\theta_{\max} = 30.0°$
$h = 0 \rightarrow 22$
$k = 0 \rightarrow 22$
$l = -1 \rightarrow 16$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.093$
$S = 1.05$
2243 reflections
90 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.048P)^2 + 3.5779P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.64$ e Å^{-3}
$\Delta\rho_{\min} = -0.55$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu—O	1.8966 (4)	Cu—Cl1	2.4002 (9)
Cu—N4	1.972 (2)	Cu—Cl2$^{\mathrm{i}}$	2.4344 (7)
Cu—Cl2	2.3827 (8)		
O—Cu—N4	178.20 (6)	N4—Cu—Cl2$^{\mathrm{i}}$	97.70 (6)
O—Cu—Cl2	85.50 (2)	Cl2—Cu—Cl2$^{\mathrm{i}}$	118.652 (19)
N4—Cu—Cl2	94.05 (6)	Cl1—Cu—Cl2$^{\mathrm{i}}$	113.95 (3)
O—Cu—Cl1	85.65 (3)	Cu—Cl1—Cu$^{\mathrm{ii}}$	79.93 (4)
N4—Cu—Cl1	93.20 (6)	Cu—Cl2—Cu$^{\mathrm{iii}}$	80.23 (2)
Cl2—Cu—Cl1	125.21 (3)	Cu$^{\mathrm{ii}}$—O—Cu	108.76 (3)
O—Cu—Cl2$^{\mathrm{i}}$	84.04 (2)	Cu$^{\mathrm{ii}}$—O—Cu$^{\mathrm{i}}$	109.828 (13)

Symmetry codes: (i) $\frac{5}{4} - y, x - \frac{3}{4}, \frac{5}{4} - z$; (ii) $2 - x, \frac{1}{2} - y, z$; (iii) $\frac{3}{4} + y, \frac{5}{4} - x, \frac{5}{4} - z$.

Table 2
Comparison of tetrazole ring bond lengths (Å) in (I) and the corresponding mean values for five metal(II) complexes of 2-substituted tetrazoles found in a CSD survey.

Bond	(I)	Mean from CSD
N1—N2	1.329 (3)	1.322 (2)
N1═C5	1.319 (3)	1.319 (10)
N2—N3	1.304 (3)	1.303 (3)
N3═N4	1.323 (3)	1.323 (2)
N4—C5	1.333 (3)	1.334 (5)

The H atoms were placed in geometrically calculated positions, with C—H distances in the range 0.93–0.97 Å, and refined using a riding model, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.5U_{\mathrm{eq}}(\mathrm{C})$ for the methyl group and $1.2U_{\mathrm{eq}}(\mathrm{C})$ for the other H atoms.

Data collection: *R3m Software* (Nicolet, 1980); cell refinement: *R3m Software*; data reduction: *R3m Software*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics:

ORTEP-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1637). Services for accessing these data are described at the back of the journal.

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