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# Hexa-$\mu$-chloro-$\mu_4$-oxo-tetrakis[(4,5-dihydro-2-methyl-1,2-thiazole-$\kappa N$)copper(II)]

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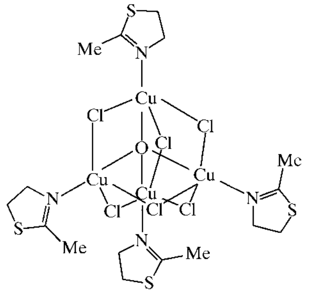
The title compound, $[Cu_4Cl_6O(C_4H_7NS)_4]$, was obtained by the reaction of $CuCl_2\cdot 2H_2O$ with 2-methyl-2-thiazoline in methanol. The complex has twofold crystallographic symmetry and contains a tetrahedron of four Cu$^{II}$ atoms coordinating a central $\mu_4$-O atom, with the six edges of the tetrahedron bridged by Cl atoms. Distance ranges are Cu—O 1.917 (4)–1.920 (4) and Cu—Cl 2.370 (2)–2.445 (2) Å.

## Comment

The magnetic properties of polynuclear paramagnetic transition metal ions and their presence at the active sites of a number of metalloproteins have attracted the attention of inorganic and bioinorganic chemists for many years (Marsh *et al.*, 1983; Halfen & Tolman, 1994). Among the ligands that allow the formation of tetranuclear copper(II) complexes are the thiazole derivatives, whose reaction products with $CuCl_2$ have been extensively studied (Hodgson, 1984; Marsh *et al.*, 1983, 1988). In contrast, relatively little information is available on the reaction of Cu$^{II}$ with thiazoline derivatives, which have an almost similar structure to that of thiazoles. The present study is part of a systematic investigation on the reaction products of $CuCl_2$ and $CuBr_2$ with thiazolines.



(I)

The molecular structure of the title compound, (I), along with the atomic numbering scheme, is shown in Fig. 1, while selected bond lengths and angles are given in Table 1. Selected intramolecular contact distances are given in Table 2. The central $Cu_4OCl_6$ unit is of the same type as that found in many related complexes (Bertrand, 1967; Belford *et al.*, 1972; Gill & Sterns, 1970; Guy *et al.*, 1988). The four Cu$^{II}$ atoms are arranged tetrahedrally around a central O atom, and are also bridged in pairs by Cl atoms. Each Cu$^{II}$ atom is fivefold coordinated by three Cl atoms, the central O atom and the N atom from a 2-methyl-2-thiazoline ligand (2m-2tzn hereafter), in an arrangement close to trigonal bipyramidal (TBP). The percentage trigonal distortions from the square pyramidal (SP) geometry of the atomic arrangements around the two independent Cu$^{II}$ atoms are $\tau$ = 77.5 and 77.7% for Cu1 and Cu2, respectively [$\tau$ = 0% for ideal SP and $\tau$ = 100% for ideal TBP geometries (Addison *et al.*, 1984)].

The $Cu_4OCl_6$ cluster has been reported to possess various point-group symmetries, for example, $\overline{4}3m$ (Bertrand, 1967), 2 (Belford *et al.*, 1972) or 1 (Gill & Sterns, 1970). In the present case, the point-group symmetry is 2, with the twofold axis passing through atoms Cl2, O and Cl3 (Fig. 1). The observed bond lengths and angles in the cluster are in fair agreement with those observed in related complexes.

The two symmetrically independent 2m-2tzn rings, which are approximately perpendicular to each other [91.7 (3)°], have almost identical geometries, with most of the corresponding bond lengths and angles coinciding within experimental error. The only significant differences appear between the bond lengths C3—S1 and C7—S2 [1.81 (1) and 1.73 (2) Å, respectively], and between the bond angles C2—C3—S1 and C6—C7—S2 [104.1 (6) and 107.8 (8)°, respectively]. The two 2m-2tzn rings differ also in the degree of planarity. Thus, while the ring attached to Cu1 appears slightly puckered, with a maximum atomic deviation from the mean plane of 0.18 (1) Å, (atom C2), the ring attached to Cu2 is perfectly planar within experimental error. The C1—N1 and C5—N2 bonds, of length 1.26 (1) and 1.28 (1) Å, respectively, are substantially shorter than the adjacent C2—N1 and C6—N2 bonds, of length

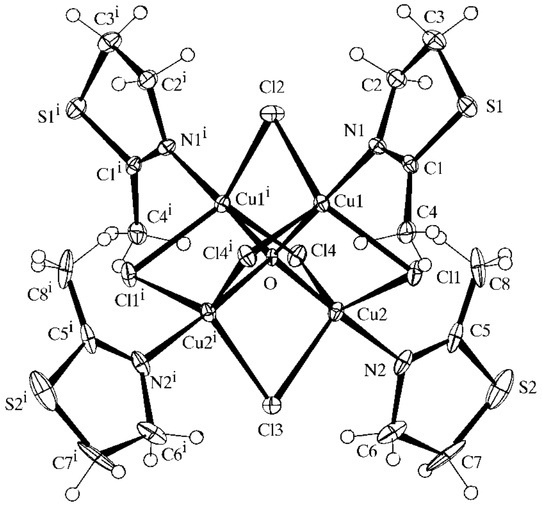


**Figure 1**
*DIAMOND* (Bergerhoff, 1996) plot of the title molecule with the atomic numbering scheme. Displacement ellipsoids are at the 30% probability level. [Symmetry code: (i) $-x, y, -z + \frac{1}{2}$.]

1.46 (1) and 1.45 (1) Å, respectively, indicating that the primary resonance structures in the two 2m-2tzn rings have the double bond located between C1 and N1, and between C5 and N2, respectively. Atoms N1 and N2 are pyramidally coordinated by C1, C2, Cu1 and C5, C6, Cu2, respectively, the corresponding deviations from their basal planes being 0.108 (8) and 0.07 (1) Å.

In the crystal structure of the title compound, no unusual intermolecular contact distances are observed, so that the molecular packing may be attributed to normal van der Waals interactions.

## Experimental

The title compound was synthesized by mixing a solution of copper(II) chloride dihydrate (1 mmol) in methanol (10 ml) with a solution of the ligand 2-methyl-2-thiazoline (4 mmol) in methanol (5 ml), the reaction being carried out at 291 K. The light-brown solution was left overnight at 291 K, whereupon brown rhombic crystals formed.

*Crystal data*

$[Cu_4Cl_6O(C_4H_7NS)_4]$
$M_r = 887.52$
Orthorhombic, *Pbcn*
$a = 10.3705\ (18)$ Å
$b = 14.903\ (2)$ Å
$c = 20.375\ (4)$ Å
$V = 3148.9\ (9)$ Å$^3$
$Z = 4$
$D_x = 1.872$ Mg m$^{-3}$
$D_m = 1.87$ Mg m$^{-3}$
$D_m$ measured by flotation in a mixture of $CCl_4$ and $CH_3I$
Mo $K\alpha$ radiation
Cell parameters from 15 reflections
$\theta = 8.2–11.5°$
$\mu = 3.46$ mm$^{-1}$
$T = 293\ (2)$ K
Plate, brown
0.23 × 0.13 × 0.04 mm

*Data collection*

Upgraded Philips PW1100 diffractometer
$\theta/2\theta$ scans
Absorption correction: $\psi$ scan (*EMPIR*; Stoe & Cie, 1988)
$T_{min} = 0.448$, $T_{max} = 0.652$
5588 measured reflections
2775 independent reflections
1273 reflections with $I > 2\sigma(I)$
$R_{int} = 0.101$
$\theta_{max} = 25°$
$h = -12 \rightarrow 12$
$k = -17 \rightarrow 17$
$l = 0 \rightarrow 24$
3 standard reflections
frequency: 120 min
intensity decay: 10%

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Cl1—Cu1 | 2.370 (2) | Cl4—Cu1$^{i}$ | 2.445 (2) |
| Cl1—Cu2 | 2.402 (2) | N1—Cu1 | 1.991 (7) |
| Cl2—Cu1 | 2.393 (2) | N2—Cu2 | 1.972 (7) |
| Cl3—Cu2 | 2.434 (3) | O1—Cu2 | 1.917 (4) |
| Cl4—Cu2 | 2.381 (3) | O1—Cu1 | 1.920 (4) |
| | | | |
| Cu1—Cl1—Cu2 | 80.51 (8) | Cl1—Cu1—Cl2 | 129.89 (8) |
| Cu1$^{i}$—Cl2—Cu1 | 83.73 (11) | O1—Cu1—Cl4$^{i}$ | 83.78 (10) |
| Cu2$^{i}$—Cl3—Cu2 | 81.08 (10) | N1—Cu1—Cl4$^{i}$ | 99.8 (2) |
| Cu2—Cl4—Cu1$^{i}$ | 80.96 (8) | Cl1—Cu1—Cl4$^{i}$ | 111.86 (10) |
| Cu2$^{i}$—O1—Cu2 | 111.2 (3) | Cl2—Cu1—Cl4$^{i}$ | 114.74 (7) |
| Cu2$^{i}$—O1—Cu1 | 109.53 (4) | O1—Cu2—N2 | 176.1 (3) |
| Cu2—O1—Cu1 | 106.99 (4) | O1—Cu2—Cl4 | 85.62 (11) |
| Cu2$^{i}$—O1—Cu1$^{i}$ | 106.99 (4) | N2—Cu2—Cl4 | 91.1 (2) |
| Cu2—O1—Cu1$^{i}$ | 109.53 (4) | O1—Cu2—Cl1 | 85.02 (8) |
| Cu1—O1—Cu1$^{i}$ | 112.6 (3) | N2—Cu2—Cl1 | 95.5 (2) |
| O1—Cu1—N1 | 176.4 (2) | Cl4—Cu2—Cl1 | 129.46 (10) |
| O1—Cu1—Cl1 | 85.88 (13) | O1—Cu2—Cl3 | 83.85 (18) |
| N1—Cu1—Cl1 | 92.2 (2) | N2—Cu2—Cl3 | 99.7 (3) |
| O1—Cu1—Cl2 | 81.83 (18) | Cl4—Cu2—Cl3 | 120.05 (7) |
| N1—Cu1—Cl2 | 97.1 (2) | Cl1—Cu2—Cl3 | 108.08 (7) |

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

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.127$
$S = 0.90$
2775 reflections
162 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0540P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.020$
$\Delta\rho_{max} = 0.71$ e Å$^{-3}$
$\Delta\rho_{min} = -0.60$ e Å$^{-3}$

**Table 2**
Selected intramolecular contact distances (Å).

| | | | |
|---|---|---|---|
| Cu1···Cu2 | 3.083 (1) | Cu1···Cu2$^{i}$ | 3.133 (1) |
| Cu1···Cu1$^{i}$ | 3.195 (1) | Cu2···Cu2$^{i}$ | 3.164 (1) |

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

For one atom, C7, the ratio of maximum/minimum principal r.m.s. atomic displacements was found to be fairly large (5.54), indicating possible disorder. An attempt, however, to refine C7 as a split atom proved unsuccessful; therefore, its anisotropic displacement parameters were retained, since the refinement converged smoothly, leading to chemically reasonable positions for all atoms. The H atoms were placed geometrically at their ideal positions and allowed to ride with isotropic displacement parameters equal to $1.2U_{eq}$ of the parent atoms. An extinction correction was not deemed necessary. Some geometrical calculations were performed using *Xtal*3.2 (Hall *et al.*, 1992).

Data collection: *DIF*4 (Stoe & Cie, 1988); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1988); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1502). Services for accessing these data are described at the back of the journal.

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