

Hexa- μ -chloro- μ_4 -oxo-tetrakis- {[5-(2,4,6-trimethylphenyl)pyrazole- κN^2]copper(II)}

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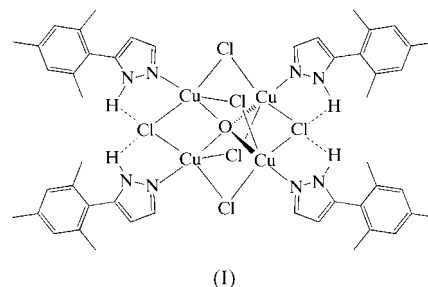
The title compound, $[\text{Cu}_4\text{Cl}_6\text{O}(\text{C}_{12}\text{H}_{14}\text{N}_2)_4]$, is a new example of the well known $[\text{Cu}_4(\mu_4\text{-O})(\mu\text{-X})_6L_4]$ class of complex (X^- is Cl^- , Br^- or I^- , and L is a monodentate ligand). The molecule has crystallographic C_2 symmetry, with two Cl^- ions on each edge of a Cu_4 tetrahedron. Two of these, on opposite edges of the tetrahedron, accept intramolecular hydrogen bonds from two of the pyrazole N—H donors.

Comment

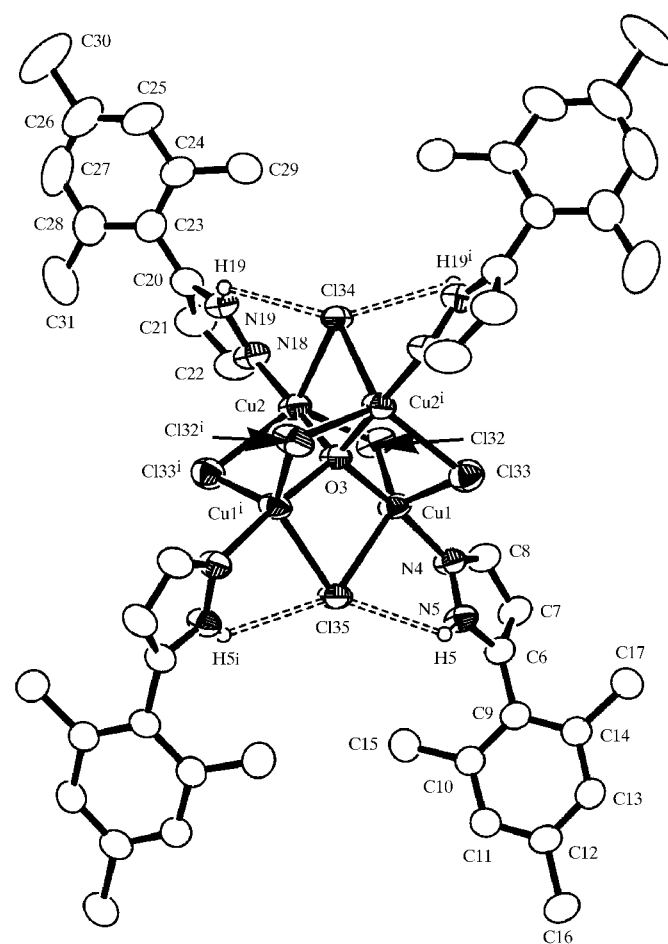
The $[\text{Cu}_4(\mu_4\text{-O})(\mu\text{-X})_6L_4]^{n-}$ structure type is well known, where X^- can be Cl^- , Br^- or I^- and L is a monodentate ligand. The terminal ligand L can be a halide (giving $n = 4$) or a variety of neutral monodentate N or O donors (giving $n = 0$), such as imidazoles (Atria *et al.*, 1999; Clegg *et al.*, 1988), thiazolines (Bolos & Christidis, 2002), pyridines (Gill & Sterns, 1970; Haendler, 1990; Kilbourn & Dunitz, 1967), pyrazines (Näther & Jeß, 2002), amines (Pavlenko *et al.*, 1993), sulfimides (Kelly *et al.*, 1999), phosphine oxides (Jorik *et al.*, 1996) or sulfoxides (Guy *et al.*, 1988) (not a complete list). Only one previous example containing a pyrazole terminal ligand has been structurally characterized, namely $[\text{Cu}_4(\mu_4\text{-O})(\mu\text{-Cl})_6(L^1)_4]$ (L^1 is 3,4-dimethyl-5-phenylpyrazole; Keij *et al.*, 1991). As part of our studies of the reactions of substituted pyrazoles with Cu^{II} salts (Liu *et al.*, 2001; Liu, McAllister *et al.*, 2002; Liu, McLaughlin *et al.*, 2002), we have now isolated the title compound, (I), as a second example with a similar formulation, namely $[\text{Cu}_4(\mu_4\text{-O})(\mu\text{-Cl})_6(L^2)_4]$ [L^2 is 5-(2,4,6-trimethylphenyl)pyrazole].

The approximately tetrahedral cluster core in (I) has crystallographic C_2 symmetry, with the C_2 axis at $(\frac{1}{2}, y, \frac{1}{4})$ passing through atoms Cl34, O3 and Cl35 (Fig. 1). The two unique Cu centres have very similar distorted trigonal-bipyramidal stereochemistries, with τ values of 0.7198 (14) (Cu1) and 0.7560 (12) (Cu2), which are closer to the ideal value of 1 for a trigonal bipyramid than to the value of 0 expected for an ideal

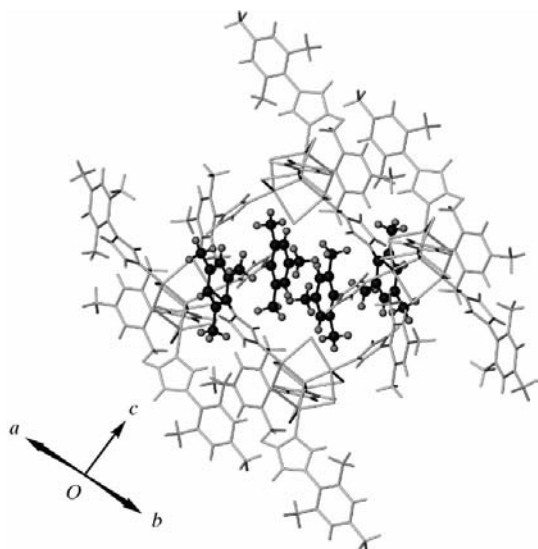
square pyramid (Addison *et al.*, 1984). The Cu—N, Cu—O and Cu—Cl distances in the molecule lie within the usual ranges, but show small differences between the two Cu centres.



Interestingly, the Cu—Cl bonds to the two ligands that accept N—H...Cl hydrogen bonds (see below) are not notably longer than the other Cu—Cl bonds in the molecule, showing that the small Cu—Cl bond-length variations cannot be attributed to this feature of the structure. The Cu—O—Cu angles in the molecule also show small distortions from the tetrahedral angle. These small deviations from ideal tetrahedral molecular symmetry are common in $[\text{Cu}_4(\mu_4\text{-O})(\mu\text{-$


Figure 1

The molecular structure of (I), with 50% probability displacement ellipsoids and the atom-numbering scheme [symmetry code: (i) $1 - x, y, \frac{1}{2} - z$]. All carbon-bound H atoms have been omitted for clarity.


Figure 2

A partial packing diagram for (I), highlighting the association *via* the mesityl substituents to give discrete π - π -stacked tetrads. All atoms are plotted with arbitrary radii.

$X)_6L_4]$ complexes, and have a significant effect on their magnetic properties (Blake *et al.*, 1997, and references therein). The four unique Cu...Cu distances in the structure are in the range 3.0570 (4)–3.1689 (5) Å.

The four L^2 ligands in the molecule form two pairs of intramolecular hydrogen bonds, with N19–H19 and N19ⁱ–H19ⁱ [symmetry code: (i) $1 - x, y, \frac{1}{2} - z$] interacting with atom Cl34, and N5–H5 and N5ⁱ–H5ⁱ with atom Cl35. This is the same pattern of intramolecular hydrogen bonding shown by $[\text{Cu}_4(\mu_4\text{-O})(\mu\text{-Cl})_6(L^1)_4]$ (Keij *et al.*, 1991).

The molecules in the crystal associate through two unique π - π interactions. One is between the aryl groups C23–C28 and C9ⁱⁱ–C14ⁱⁱ [symmetry code: (ii) $1 - x, y + 1, \frac{1}{2} - z$]. The least-squares planes of these two groups have a dihedral angle between them of 5.89 (11)°, and are separated by an average of 3.72 Å. The centroids of the two interacting aryl rings are offset by 1.69 Å. The second π - π interaction is between the opposite face of C23–C28 and C23ⁱⁱⁱ–C28ⁱⁱⁱ [symmetry code: (iii) $1 - x, 2 - y, 1 - z$]. These two rings are coplanar by symmetry and are separated by 3.70 Å, with their centroids offset by 2.59 Å. The effect of these interactions is to associate the molecules into discrete π - π -stacked tetrads, which zigzag along the crystallographic [110] direction (Fig. 2). There are no other significant intermolecular interactions in the lattice.

Experimental

A solution of CuCl_2 (0.13 g, 1.0 mmol) in MeOH (10 ml) was added to a solution of 3-mesitylpyrazole (0.37 g, 2.0 mmol) and NaOH (0.040 g, 1.0 mol) in MeOH (20 ml), yielding an immediate green precipitate. The mixture was stirred overnight and then filtered. Slow concentration of the filtrate by evaporation yielded dark-blue crystals of (I), contaminated by a smaller amount of paler blue $[\text{CuCl}_2(L^2)_4]$.

Elemental analysis of (I), found: C 46.9, H 4.9, N 9.1%; calculated for $\text{C}_{48}\text{H}_{56}\text{Cl}_6\text{Cu}_4\text{N}_8\text{O}$: C 47.0, H 4.6, N 9.1%.

Crystal data

$[\text{Cu}_4\text{Cl}_6\text{O}(\text{C}_{12}\text{H}_{14}\text{N}_2)_4]$
 $M_r = 1227.87$
 Monoclinic, $C2/c$
 $a = 21.6279$ (2) Å
 $b = 11.8266$ (1) Å
 $c = 20.8023$ (3) Å
 $\beta = 96.4448$ (5)°
 $V = 5287.28$ (10) Å³
 $Z = 4$

$D_x = 1.543$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 45 511 reflections
 $\theta = 2.6$ – 27.5 °
 $\mu = 1.93$ mm⁻¹
 $T = 150$ (2) K
 Lath, dark blue
 $0.30 \times 0.24 \times 0.14$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
 Area-detector scans
 Absorption correction: multi-scan (SORTAV; Blessing, 1995)
 $T_{\min} = 0.595$, $T_{\max} = 0.774$
 45 511 measured reflections

6034 independent reflections
 5044 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.075$
 $\theta_{\text{max}} = 27.5$ °
 $h = -27 \rightarrow 28$
 $k = -15 \rightarrow 15$
 $l = -26 \rightarrow 26$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.102$
 $S = 1.05$
 6034 reflections
 311 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.055P)^2 + 4.466P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.49$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.81$ e Å⁻³
 Extinction correction: SHELXL97 (Sheldrick, 1997)
 Extinction coefficient: 0.00148 (15)

Table 1

Selected geometric parameters (Å, °).

Cu1–O3	1.8987 (11)	Cu2–Cl32	2.4517 (7)
Cu1–N4	1.9460 (19)	Cu2–Cl33 ⁱ	2.3944 (7)
Cu1–Cl32	2.3370 (7)	Cu2–Cl34	2.4353 (6)
Cu1–Cl33	2.4226 (7)	Cu1...Cu2	3.0570 (4)
Cu1–Cl35	2.4900 (7)	Cu1...Cu2 ⁱ	3.0873 (4)
Cu2–O3	1.8897 (12)	Cu1...Cu1 ⁱ	3.1689 (5)
Cu2–N18	1.936 (2)	Cu2...Cu2 ⁱ	3.1000 (6)
O3–Cu1–N4	174.93 (8)	N18–Cu2–Cl33 ⁱ	94.33 (7)
O3–Cu1–Cl32	87.19 (4)	O3–Cu2–Cl34	85.37 (5)
N4–Cu1–Cl32	96.36 (6)	N18–Cu2–Cl34	93.31 (6)
O3–Cu1–Cl33	83.66 (2)	Cl33 ⁱ –Cu2–Cl34	131.71 (2)
N4–Cu1–Cl33	97.46 (6)	O3–Cu2–Cl32	84.12 (2)
Cl32–Cu1–Cl33	121.70 (3)	N18–Cu2–Cl32	98.77 (7)
O3–Cu1–Cl35	83.92 (5)	Cl33 ⁱ –Cu2–Cl32	118.77 (3)
N4–Cu1–Cl35	91.01 (6)	Cl34–Cu2–Cl32	106.94 (2)
Cl32–Cu1–Cl35	131.74 (2)	Cu2–O3–Cu2 ⁱ	110.21 (10)
Cl33–Cu1–Cl35	104.297 (19)	Cu2–O3–Cu1	107.593 (12)
O3–Cu2–N18	177.07 (7)	Cu2–O3–Cu1 ⁱ	109.161 (13)
O3–Cu2–Cl33 ⁱ	84.63 (4)	Cu1–O3–Cu1 ⁱ	113.12 (10)

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

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N5–H5...Cl35	0.88	2.56	3.079 (2)	119
N19–H19...Cl34	0.88	2.83	3.274 (2)	113

The slightly high displacement parameters of atoms C26, C27 and C30 may be indicative of a small degree of librational disorder involving these atoms. However, attempts to refine a static disorder model for the C23–C31 mesityl group to take account of this were unsuccessful and the original model has been retained. All H atoms were placed in calculated positions and refined using a riding model, with the methyl group torsion angles being allowed to refine freely. The fixed C–H distances were: C–H(aryl) = 0.95, C–H(methyl) = 0.98 and N–H = 0.88 Å. The H-atom U_{iso} parameters were fixed at $1.2U_{\text{eq}}(\text{C,N})$ for the aryl C–H and the N–H groups, and at $1.5U_{\text{eq}}(\text{C})$ for methyl C–H.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: local program.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1524). Services for accessing these data are described at the back of the journal.

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