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Hexa- μ_2 -chlorido- μ_4 -oxido-tetrakis[(3-methyl-5-phenyl-1*H*-pyrazole- κ N²)-copper(II)]

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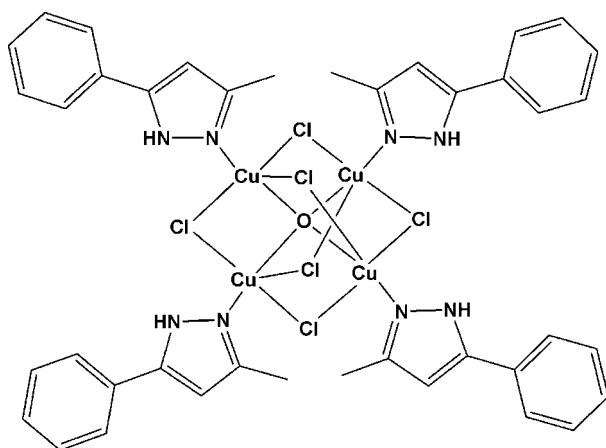
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.018$ Å; R factor = 0.067; wR factor = 0.194; data-to-parameter ratio = 15.2.

The title compound, $[\text{Cu}_4\text{Cl}_6\text{O}(\text{C}_{10}\text{H}_{10}\text{N}_2)_4]$, contains four Cu^{II} atoms which are bridged by six chloride anions. The central O atom is located on a crystallographic fourfold roto-inversion axis. Each Cu^{II} atom is coordinated by an N atom of a neutral monodentate 3-methyl-5-phenylpyrazole ligand, three Cl^- anions, and one O^{2-} anion. The geometry at each Cu^{II} atom is distorted trigonal-bipyramidal, with the three Cl^- ions in the equatorial plane and the N and O atoms in the axial positions.

Related literature

For the formation of trispyrazolylborate anions, see: Tekeste & Vahrenkamp (2007); Jacobsen & Cohen (2004); Puerta & Cohen (2003); Parkin (2004). For the formation of dinuclear copper compounds, see: He & Sykes (2007). For the formation of tetranuclear compounds, see: Keij *et al.* (1991); Liu *et al.* (2003); Chiarella *et al.* (2009).



Experimental

Crystal data

$[\text{Cu}_4\text{Cl}_6\text{O}(\text{C}_{10}\text{H}_{10}\text{N}_2)_4]$
 $M_r = 1115.66$
Tetragonal, $P4/n$
 $a = 14.5460$ (6) Å
 $c = 11.1686$ (7) Å
 $V = 2363.1$ (3) Å³

$Z = 2$
Mo $K\alpha$ radiation
 $\mu = 2.16$ mm⁻¹
 $T = 293$ K
 $0.30 \times 0.30 \times 0.30$ mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2006)
 $T_{\text{min}} = 0.564$, $T_{\text{max}} = 0.564$

14047 measured reflections
2072 independent reflections
1184 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.080$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.067$
 $wR(F^2) = 0.194$
 $S = 1.17$
2072 reflections

136 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.72$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.56$ e Å⁻³

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008), *WinGX* (Farrugia, 1999) and *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2649).

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supporting information

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Hexa- μ_2 -chlorido- μ_4 -oxido-tetrakis[(3-methyl-5-phenyl-1*H*-pyrazole- κN^2)copper(II)]

Hongshan He

S1. Comment

5-Methyl-3-phenylpyrazole has been widely used as starting material for the preparation of the trispyrazolylborate anion (Tekeste & Vahrenkamp, 2007; Jacobsen & Cohen, 2004; Puerta & Cohen, 2003; Parkin, 2004). It can form a dimeric complex (He & Sykes, 2007). Reported here is a new complex when it reacts with copper chloride.

In the title compound, (I), six chloride ions hold four copper ions together with an O atom encapsulated in the center (Fig. 1). The coordination geometry around each Cu^{II} is identical to each other with three Cl⁻ in the equatorial positions and N and O atoms in the axial positions. The distances between Cu1 and three Cl atoms are 2.361 (2), 2.514 (3) and 2.377 (2) Å. The distances between Cu1 and O1 and N1 are 1.9052 (10) and 1.953 (8) Å, respectively. The N1, Cu1 and O1 atoms fall almost in a line with an angle of 177.9 (5)°. The oxygen atom is located on a crystallographic fourfold roto-inversion axis.

S2. Experimental

5-Methyl-3-phenylpyrazole (16.0 mg, 0.1 mmol), prepared according to the literature (Puerta & Cohen, 2003), was dissolved in dichloromethane (10 ml) at room temperature. To this solution, copper(II) chloride dihydrate (8.7 mg, 0.05 mmol) in methanol (2 ml) was added. The resulting solution was stirred for two hours. The mixture was filtered and the filtrate kept at room temperature. Brown crystals were obtained after one week by slow evaporation.

S3. Refinement

All H atoms are geometrically constrained and refined in riding mode as follows: methyl $d(C-H) = 0.96$ Å, $U_{iso}(H) = 1.5U_{eq}(C)$; aromatic $d(C-H) = 0.93$ Å, $U_{iso}(H) = 1.2U_{eq}(C)$; $d(N-H) = 0.86$ Å, $U_{iso}(H) = 1.5U_{eq}(N)$.

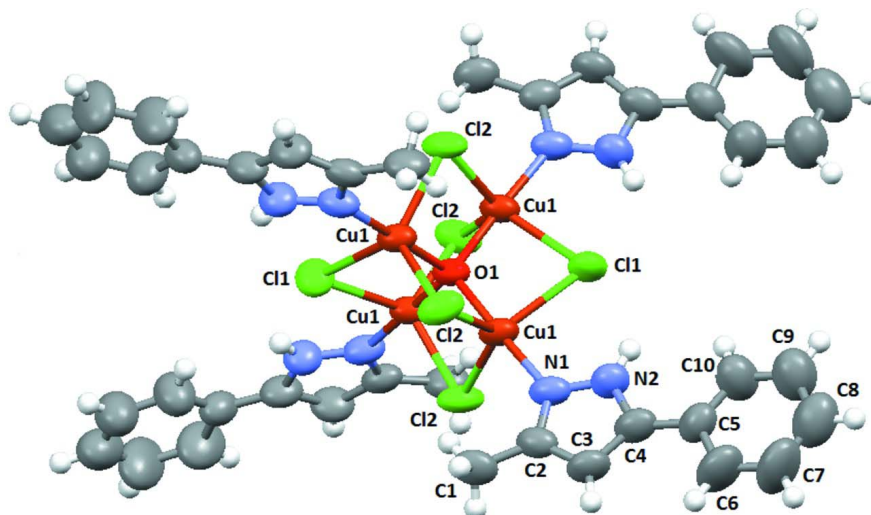


Figure 1

The structure of the title compound with displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms are drawn as small circles of arbitrary radii.

Hexa- μ_2 -chlorido- μ_4 -oxido-tetrakis[(3-methyl-5-phenyl-1H-pyrazole- κN^2)copper(II)]

Crystal data

[Cu₄Cl₆O(C₁₀H₁₀N₂)₄]

$M_r = 1115.66$

Tetragonal, $P4/n$

Hall symbol: -P 4a

$a = 14.5460$ (6) Å

$c = 11.1686$ (7) Å

$V = 2363.1$ (3) Å³

$Z = 2$

$F(000) = 1124$

$D_x = 1.568$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 16570 reflections

$\theta = 2.3$ – 25.0°

$\mu = 2.16$ mm⁻¹

$T = 293$ K

Block, brown

$0.30 \times 0.30 \times 0.30$ mm

Data collection

Bruker APEXII CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2006)

$T_{\min} = 0.564$, $T_{\max} = 0.564$

14047 measured reflections

2072 independent reflections

1184 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.080$

$\theta_{\max} = 25.0^\circ$, $\theta_{\min} = 2.3^\circ$

$h = -17 \rightarrow 17$

$k = -17 \rightarrow 17$

$l = -13 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.067$

$wR(F^2) = 0.194$

$S = 1.17$

2072 reflections

136 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0526P)^2 + 14.3478P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.72$ e Å⁻³

$\Delta\rho_{\min} = -0.56$ e Å⁻³

Extinction correction: *SHELXL97* (Sheldrick, 2008), $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0028 (8)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.72083 (7)	0.14541 (7)	0.90461 (11)	0.0567 (5)
Cl2	0.57726 (15)	0.14864 (15)	1.0031 (3)	0.0729 (8)
Cl1	0.7500	0.2500	0.7295 (3)	0.0705 (10)
N2	0.6784 (5)	0.0507 (5)	0.6812 (8)	0.070 (2)
H2	0.6890	0.1006	0.6424	0.084*
N1	0.6896 (5)	0.0413 (5)	0.8019 (8)	0.063 (2)
O1	0.7500	0.2500	1.0000	0.052 (3)
C1	0.6666 (7)	-0.0801 (7)	0.9515 (11)	0.079 (3)
H1A	0.6904	-0.0337	1.0042	0.119*
H1B	0.7046	-0.1340	0.9560	0.119*
H1C	0.6050	-0.0954	0.9749	0.119*
C2	0.6663 (6)	-0.0449 (6)	0.8269 (10)	0.063 (3)
C3	0.6412 (7)	-0.0918 (7)	0.7231 (11)	0.075 (3)
H3	0.6232	-0.1530	0.7177	0.090*
C4	0.6481 (7)	-0.0296 (7)	0.6292 (11)	0.072 (3)
C5	0.6268 (7)	-0.0344 (7)	0.5035 (11)	0.075 (3)
C6	0.5923 (10)	-0.1170 (9)	0.4580 (14)	0.120 (5)
H6	0.5854	-0.1677	0.5079	0.143*
C7	0.5686 (12)	-0.1228 (12)	0.3385 (15)	0.139 (6)
H7	0.5476	-0.1786	0.3084	0.166*
C8	0.5748 (10)	-0.0512 (12)	0.2651 (15)	0.122 (5)
H8	0.5571	-0.0566	0.1854	0.146*
C9	0.6072 (10)	0.0301 (11)	0.3078 (14)	0.120 (5)
H9	0.6116	0.0811	0.2579	0.144*
C10	0.6331 (9)	0.0355 (9)	0.4244 (13)	0.104 (4)
H10	0.6568	0.0911	0.4516	0.125*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0436 (6)	0.0403 (6)	0.0863 (9)	-0.0028 (4)	-0.0010 (6)	-0.0064 (5)
Cl2	0.0424 (12)	0.0602 (14)	0.116 (2)	-0.0100 (10)	0.0079 (13)	-0.0219 (14)
Cl1	0.088 (2)	0.0405 (17)	0.082 (2)	-0.0115 (16)	0.000	0.000

N2	0.074 (5)	0.056 (5)	0.081 (6)	-0.014 (4)	0.002 (5)	-0.006 (4)
N1	0.051 (4)	0.043 (4)	0.096 (7)	-0.004 (3)	0.011 (4)	0.000 (4)
O1	0.039 (3)	0.039 (3)	0.077 (8)	0.000	0.000	0.000
C1	0.065 (6)	0.058 (6)	0.114 (10)	-0.016 (5)	0.001 (6)	0.009 (6)
C2	0.046 (5)	0.051 (5)	0.092 (8)	-0.001 (4)	0.009 (5)	0.008 (5)
C3	0.076 (7)	0.047 (5)	0.102 (9)	-0.013 (5)	0.000 (6)	-0.012 (6)
C4	0.066 (6)	0.054 (6)	0.097 (9)	-0.016 (5)	0.009 (6)	-0.012 (6)
C5	0.073 (7)	0.074 (7)	0.078 (8)	-0.017 (5)	0.013 (6)	-0.017 (6)
C6	0.149 (13)	0.090 (9)	0.119 (12)	-0.040 (9)	0.014 (10)	-0.039 (8)
C7	0.180 (16)	0.130 (14)	0.106 (13)	-0.057 (12)	0.008 (12)	-0.049 (11)
C8	0.108 (11)	0.142 (14)	0.115 (12)	-0.035 (10)	0.011 (9)	-0.029 (12)
C9	0.128 (12)	0.127 (12)	0.104 (11)	-0.037 (10)	-0.004 (9)	0.003 (10)
C10	0.122 (11)	0.096 (9)	0.095 (10)	-0.032 (8)	-0.014 (8)	0.004 (8)

Geometric parameters (Å, °)

Cu1—O1	1.9052 (10)	C1—H1C	0.9600
Cu1—N1	1.953 (8)	C2—C3	1.394 (14)
Cu1—Cl2	2.361 (2)	C3—C4	1.388 (14)
Cu1—Cl2 ⁱ	2.377 (2)	C3—H3	0.9300
Cu1—Cl1	2.514 (3)	C4—C5	1.439 (15)
Cl2—Cu1 ⁱⁱ	2.377 (2)	C5—C10	1.350 (15)
Cl1—Cu1 ⁱⁱⁱ	2.514 (3)	C5—C6	1.397 (15)
N2—N1	1.365 (11)	C6—C7	1.38 (2)
N2—C4	1.377 (11)	C6—H6	0.9300
N2—H2	0.8600	C7—C8	1.33 (2)
N1—C2	1.328 (10)	C7—H7	0.9300
O1—Cu1 ⁱⁱⁱ	1.9052 (10)	C8—C9	1.359 (18)
O1—Cu1 ⁱ	1.9052 (10)	C8—H8	0.9300
O1—Cu1 ⁱⁱ	1.9052 (10)	C9—C10	1.358 (18)
C1—C2	1.482 (15)	C9—H9	0.9300
C1—H1A	0.9600	C10—H10	0.9300
C1—H1B	0.9600		
O1—Cu1—N1	177.9 (3)	H1B—C1—H1C	109.5
O1—Cu1—Cl2	85.45 (7)	N1—C2—C3	110.7 (10)
N1—Cu1—Cl2	94.8 (2)	N1—C2—C1	121.5 (10)
O1—Cu1—Cl2 ⁱ	84.98 (7)	C3—C2—C1	127.8 (9)
N1—Cu1—Cl2 ⁱ	96.7 (2)	C4—C3—C2	106.9 (8)
Cl2—Cu1—Cl2 ⁱ	120.86 (5)	C4—C3—H3	126.6
O1—Cu1—Cl1	85.08 (7)	C2—C3—H3	126.6
N1—Cu1—Cl1	93.0 (3)	N2—C4—C3	104.9 (9)
Cl2—Cu1—Cl1	119.98 (8)	N2—C4—C5	121.4 (10)
Cl2 ⁱ —Cu1—Cl1	117.06 (8)	C3—C4—C5	133.6 (9)
Cu1—Cl2—Cu1 ⁱⁱ	81.32 (8)	C10—C5—C6	115.7 (12)
Cu1 ⁱⁱⁱ —Cl1—Cu1	77.85 (12)	C10—C5—C4	126.0 (10)
N1—N2—C4	111.7 (8)	C6—C5—C4	118.3 (12)
N1—N2—H2	124.1	C7—C6—C5	119.6 (15)

C4—N2—H2	124.1	C7—C6—H6	120.2
C2—N1—N2	105.8 (8)	C5—C6—H6	120.2
C2—N1—Cu1	131.9 (8)	C8—C7—C6	122.0 (15)
N2—N1—Cu1	122.0 (6)	C8—C7—H7	119.0
Cu1 ⁱⁱⁱ —O1—Cu1	112.00 (7)	C6—C7—H7	119.0
Cu1 ⁱⁱⁱ —O1—Cu1 ⁱ	108.22 (3)	C7—C8—C9	119.3 (16)
Cu1—O1—Cu1 ⁱ	108.22 (3)	C7—C8—H8	120.3
Cu1 ⁱⁱⁱ —O1—Cu1 ⁱⁱ	108.22 (3)	C9—C8—H8	120.3
Cu1—O1—Cu1 ⁱⁱ	108.22 (3)	C10—C9—C8	118.9 (15)
Cu1 ⁱ —O1—Cu1 ⁱⁱ	112.00 (7)	C10—C9—H9	120.6
C2—C1—H1A	109.5	C8—C9—H9	120.6
C2—C1—H1B	109.5	C5—C10—C9	124.4 (13)
H1A—C1—H1B	109.5	C5—C10—H10	117.8
C2—C1—H1C	109.5	C9—C10—H10	117.8
H1A—C1—H1C	109.5		
O1—Cu1—Cl2—Cu1 ⁱⁱ	1.12 (6)	Cl1—Cu1—O1—Cu1 ⁱⁱ	119.21 (2)
N1—Cu1—Cl2—Cu1 ⁱⁱ	-176.7 (3)	N2—N1—C2—C3	0.8 (10)
Cl2 ⁱ —Cu1—Cl2—Cu1 ⁱⁱ	82.50 (10)	Cu1—N1—C2—C3	174.0 (6)
Cl1—Cu1—Cl2—Cu1 ⁱⁱ	-80.53 (11)	N2—N1—C2—C1	-177.8 (8)
O1—Cu1—Cl1—Cu1 ⁱⁱⁱ	0.0	Cu1—N1—C2—C1	-4.6 (13)
N1—Cu1—Cl1—Cu1 ⁱⁱⁱ	179.1 (2)	N1—C2—C3—C4	-1.1 (11)
Cl2—Cu1—Cl1—Cu1 ⁱⁱⁱ	81.86 (9)	C1—C2—C3—C4	177.3 (9)
Cl2 ⁱ —Cu1—Cl1—Cu1 ⁱⁱⁱ	-81.80 (9)	N1—N2—C4—C3	-0.6 (11)
C4—N2—N1—C2	-0.1 (10)	N1—N2—C4—C5	176.7 (9)
C4—N2—N1—Cu1	-174.1 (6)	C2—C3—C4—N2	1.0 (11)
Cl2—Cu1—N1—C2	-60.9 (8)	C2—C3—C4—C5	-175.8 (11)
Cl2 ⁱ —Cu1—N1—C2	61.0 (8)	N2—C4—C5—C10	-0.3 (18)
Cl1—Cu1—N1—C2	178.7 (8)	C3—C4—C5—C10	176.0 (13)
Cl2—Cu1—N1—N2	111.4 (6)	N2—C4—C5—C6	-177.1 (11)
Cl2 ⁱ —Cu1—N1—N2	-126.7 (6)	C3—C4—C5—C6	-0.7 (19)
Cl1—Cu1—N1—N2	-9.0 (6)	C10—C5—C6—C7	1 (2)
Cl2—Cu1—O1—Cu1 ⁱⁱⁱ	-120.66 (8)	C4—C5—C6—C7	178.0 (13)
Cl2 ⁱ —Cu1—O1—Cu1 ⁱⁱⁱ	117.77 (8)	C5—C6—C7—C8	-2 (3)
Cl1—Cu1—O1—Cu1 ⁱⁱⁱ	0.0	C6—C7—C8—C9	1 (3)
Cl2—Cu1—O1—Cu1 ⁱ	120.13 (9)	C7—C8—C9—C10	1 (2)
Cl2 ⁱ —Cu1—O1—Cu1 ⁱ	-1.44 (8)	C6—C5—C10—C9	1 (2)
Cl1—Cu1—O1—Cu1 ⁱ	-119.21 (2)	C4—C5—C10—C9	-175.8 (13)
Cl2—Cu1—O1—Cu1 ⁱⁱ	-1.45 (8)	C8—C9—C10—C5	-2 (2)
Cl2 ⁱ —Cu1—O1—Cu1 ⁱⁱ	-123.01 (9)		

Symmetry codes: (i) $-y+1, x-1/2, -z+2$; (ii) $y+1/2, -x+1, -z+2$; (iii) $-x+3/2, -y+1/2, z$.