

Di- μ -chlorido-bis[aquachlorido[2,2'-thio-bis(pyridine *N*-oxide)- κ O]copper(II)]

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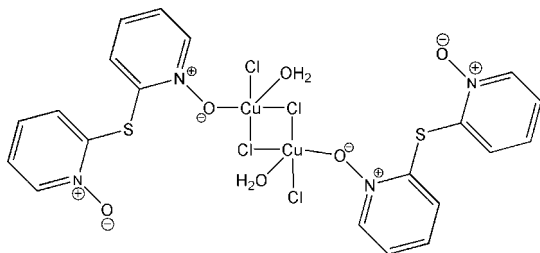
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 Key indicators: single-crystal X-ray study; $T = 294$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; R factor = 0.040; wR factor = 0.088; data-to-parameter ratio = 13.2.

The crystal structure of the title compound, $[\text{Cu}_2\text{Cl}_4(\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2\text{S})_2(\text{H}_2\text{O})_2]$, comprises neutral centrosymmetric μ -chloride-bridged dinuclear units. Each Cu^{II} ion is pentacoordinated by three chloride ligands, a pyridine *N*-oxide O atom and a water molecule. Intra- and intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds occur between the coordinated water molecules and the uncoordinated and coordinated pyridine *N*-oxide groups of the 2,2'-thiobis(pyridine *N*-oxide) ligands, respectively.

Related literature

For the potential of pyridine *N*-oxide-based building blocks in the construction of coordination polymers and crystal engineering, see: Sun *et al.* (2008) and references cited therein. For details of hydrogen-bond motifs, see: Bernstein *et al.* (1995). For a copper-catalysed example of *in situ* S—S and S—Csp² bond cleavage and rearrangement of an related disulfide, see: Wang *et al.* (2007).



Experimental

Crystal data

 $[\text{Cu}_2\text{Cl}_4(\text{C}_{10}\text{H}_8\text{N}_2\text{O}_2\text{S})_2(\text{H}_2\text{O})_2]$
 $M_r = 745.40$

 Monoclinic, $P2_1/c$
 $a = 6.7552$ (18) Å

 $b = 11.430$ (3) Å
 $c = 17.375$ (3) Å
 $\beta = 95.516$ (17)°
 $V = 1335.4$ (6) Å³
 $Z = 2$

 Mo $K\alpha$ radiation
 $\mu = 2.19$ mm⁻¹
 $T = 294$ K
 $0.27 \times 0.21 \times 0.19$ mm

Data collection

 Siemens P4 four-circle diffractometer
 Absorption correction: ψ scan (ABSPsiScan in PLATON; Spek, 2009)
 $T_{\text{min}} = 0.529$, $T_{\text{max}} = 0.663$
 3316 measured reflections

 2349 independent reflections
 1736 reflections with $I > 2(I)$
 $R_{\text{int}} = 0.058$
 3 standard reflections every 97 reflections
 intensity decay: none

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.088$
 $S = 1.02$
 2349 reflections
 178 parameters
 2 restraints

 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.40$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.53$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O2}-\text{H2A}\cdots\text{O1}^{\text{i}}$	0.81 (2)	2.13 (2)	2.919 (4)	167 (5)
$\text{O2}-\text{H2B}\cdots\text{O11}^{\text{ii}}$	0.82 (2)	1.97 (2)	2.789 (5)	177 (5)

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

Data collection: XSCANS (Bruker, 1999); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: DIAMOND (Brandenburg, 2008); software used to prepare material for publication: SHELXL97.

Professor William S. Sheldrick is gratefully acknowledged for generous support. RWS thanks Dr Tobias van Almsick for helpful discussions.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2439).

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supplementary materials

Acta Cryst. (2009). E65, m460 [doi:10.1107/S1600536809011076]

Di- μ -chlorido-bis{aquachlorido[2,2'-thiobis(pyridine *N*-oxide)- κO]copper(II)}

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Comment

Pyridine-*N*-oxide based ligands have attracted a considerable interest in crystal engineering and the synthesis of coordination polymers (Sun *et al.*, 2008).

The title compound, namely bis(μ -chlorido)-diaqua-dichlorido- bis(2,2'-thiobis(pyridine-*N*-oxide- κO)-dicopper(II), is a neutral dinuclear complex with a central Cu_2Cl_2 -ring exhibiting C_1 point symmetry (Fig. 1). The unit cell contains two molecules which reside on a crystallographic centre of inversion. Each Cu^{2+} ion adopts a distorted square-pyramidal coordination sphere. Two equatorial *cis*-coordination sites are occupied by the two bridging chlorido ligands. Another chlorido ligand in monodentate coordination mode and an oxygen atom of the pyridine-*N*-oxide group of the 2,2'-thiobis(pyridine-*N*-oxide) are located at the remaining two *cis*-sites. A water molecule binds to the axial position. The molecular geometry parameters are within normal ranges. The dihedral angle $\text{Cu}(\mu\text{-Cl})_2/\text{CuClO}(\text{N-oxide})$ is $17.0(1)^\circ$. The angle between the mean planes of the rings N1—C6 and N11—C16 is $66.4(1)^\circ$.

The coordinated water molecule forms an intramolecular hydrogen bond to O11 of the non-coordinating pyridine-*N*-oxide group of the 2,2'-thiobis(pyridine-*N*-oxide) ligand. The graph set here is $S(12)$ (Bernstein *et al.*, 1995). The second water hydrogen atom is involved in an intermolecular hydrogen bond to O1 of the coordinating pyridine-*N*-oxide group with a centrosymmetric $R^2_2(8)$ motif. This leads to the formation of infinite chains *via* hydrogen bonding extending in the [100] direction with a period corresponding to the crystallographic *a* axis. Hydrogen bonding details are listed in Table 2.

To the best of our knowledge the title compound is the first coordination compound and the first crystal structure comprising 2,2'-thiobis(pyridine-*N*-oxide).

Experimental

A dark-yellow crystal of the title compound suitable for X-ray diffraction was obtained when equimolar amounts of CuCl_2 and 2,2'-dithiobis(pyridine-*N*-oxide) (Aldrich) were dissolved in methanol and the solution was left at ambient temperature. The crystal was found within dark-green unidentified material. The origin of the new 2,2'-thiobis(pyridine-*N*-oxide) ligand is not clear. Either a trace impurity in the starting material or an *in situ* cleavage and rearrangement of S—S and $\text{S—C}(sp^2)$ bonds can be considered. A copper catalysed example of the latter with an related disulfide was reported by Wang *et al.* (2007). As far we can ascertain no synthetic route to 2,2'-thiobis(pyridine-*N*-oxide) has been reported in the literature.

Refinement

The crystal structure was refined by full-matrix least-squares refinement on F^2 . Anisotropic displacement parameters were introduced for all non-hydrogen atoms. Hydrogen atoms were placed at geometrically positions and refined with the ap-

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appropriate riding model. The water hydrogen atoms were located in a difference Fourier synthesis and refined with O—H distances of 0.82 (2) Å and U_{iso} 1.2 times that of the parent oxygen atom.

Figures

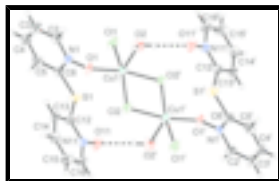


Fig. 1. ORTEP diagram of the title compound with 50% probability of the displacement ellipsoids. Hydrogen atoms are drawn at arbitrary size. Hydrogen bonds are represented by dashed lines. For the symmetry codes see Table 1.

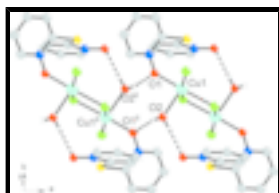


Fig. 2. Hydrogen bonding interactions between to adjacent molecules in the crystal structure of the title compound. Hydrogen bonds are represented by dashed lines. For the symmetry codes see Table 2.

Di- μ -chlorido-bis[aquachlorido[2,2'-thiobis(pyridine *N*-oxide)- κ O]copper(II)]

Crystal data

[Cu₂Cl₄(C₁₀H₈N₂O₂S)₂(H₂O)₂]

$M_r = 745.40$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 6.7552$ (18) Å

$b = 11.430$ (3) Å

$c = 17.375$ (3) Å

$\beta = 95.516$ (17)°

$V = 1335.4$ (6) Å³

$Z = 2$

$F_{000} = 748$

$D_x = 1.854$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 25 reflections

$\theta = 5.1$ – 18.0°

$\mu = 2.19$ mm⁻¹

$T = 294$ K

Prism, dark-yellow

$0.27 \times 0.21 \times 0.19$ mm

Data collection

Siemens P4 four-circle diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 294$ K

ω scans

Absorption correction: ψ scan (ABSPsiScan in PLATON; Spek, 2009)

$T_{\text{min}} = 0.529$, $T_{\text{max}} = 0.663$

3316 measured reflections

2349 independent reflections

1736 reflections with $I > 2(I)$

$R_{\text{int}} = 0.058$

$\theta_{\text{max}} = 25.0^\circ$

$\theta_{\text{min}} = 2.1^\circ$

$h = -8 \rightarrow 1$

$k = -1 \rightarrow 13$

$l = -20 \rightarrow 20$

3 standard reflections

every 97 reflections

intensity decay: none

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.040$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.088$	$w = 1/[\sigma^2(F_o^2) + (0.0347P)^2]$
$S = 1.02$	where $P = (F_o^2 + 2F_c^2)/3$
2349 reflections	$(\Delta/\sigma)_{\max} < 0.001$
178 parameters	$\Delta\rho_{\max} = 0.40 \text{ e } \text{\AA}^{-3}$
2 restraints	$\Delta\rho_{\min} = -0.53 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.36057 (7)	0.52270 (5)	0.07537 (3)	0.02340 (16)
Cl1	0.42569 (17)	0.52142 (11)	0.20449 (6)	0.0365 (3)
Cl2	0.34708 (15)	0.57187 (10)	-0.05629 (6)	0.0273 (3)
S1	0.42443 (17)	0.79699 (11)	0.11518 (7)	0.0343 (3)
O1	0.1176 (4)	0.6210 (3)	0.07498 (15)	0.0272 (7)
O2	0.1784 (5)	0.3623 (3)	0.05848 (18)	0.0325 (8)
H2A	0.086 (5)	0.372 (4)	0.026 (2)	0.039*
H2B	0.231 (7)	0.305 (3)	0.040 (2)	0.039*
N1	0.0804 (5)	0.6857 (3)	0.13620 (19)	0.0250 (8)
C2	-0.0843 (6)	0.6616 (4)	0.1706 (2)	0.0290 (11)
H2	-0.1683	0.6013	0.1521	0.035*
C3	-0.1287 (7)	0.7269 (4)	0.2335 (3)	0.0378 (12)
H3	-0.2435	0.7108	0.2572	0.045*
C4	-0.0060 (7)	0.8142 (4)	0.2611 (3)	0.0386 (12)
H4	-0.0342	0.8569	0.3043	0.046*
C5	0.1619 (7)	0.8391 (4)	0.2242 (3)	0.0352 (11)

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H5	0.2461	0.8996	0.2423	0.042*
C6	0.2049 (6)	0.7744 (4)	0.1606 (2)	0.0250 (10)
O11	0.6518 (4)	0.8360 (3)	0.00176 (19)	0.0412 (9)
N11	0.4647 (5)	0.8581 (3)	-0.0254 (2)	0.0315 (9)
C12	0.3202 (7)	0.8442 (4)	0.0239 (2)	0.0276 (11)
C13	0.1254 (6)	0.8656 (4)	-0.0018 (2)	0.0292 (11)
H13	0.0267	0.8566	0.0315	0.035*
C14	0.0761 (7)	0.9005 (4)	-0.0771 (3)	0.0378 (12)
H14	-0.0560	0.9141	-0.0951	0.045*
C15	0.2246 (8)	0.9151 (4)	-0.1254 (3)	0.0425 (13)
H15	0.1930	0.9400	-0.1761	0.051*
C16	0.4167 (8)	0.8932 (4)	-0.0992 (3)	0.0395 (13)
H16	0.5161	0.9024	-0.1322	0.047*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0210 (3)	0.0273 (3)	0.0224 (3)	0.0022 (3)	0.0041 (2)	-0.0021 (2)
Cl1	0.0376 (7)	0.0499 (7)	0.0224 (6)	0.0122 (6)	0.0045 (5)	0.0007 (5)
Cl2	0.0246 (6)	0.0331 (6)	0.0249 (6)	0.0063 (5)	0.0050 (4)	-0.0017 (5)
S1	0.0216 (6)	0.0443 (7)	0.0370 (7)	-0.0053 (6)	0.0028 (5)	0.0023 (6)
O1	0.0223 (16)	0.0342 (17)	0.0250 (16)	0.0056 (14)	0.0018 (13)	-0.0109 (14)
O2	0.0259 (19)	0.0323 (19)	0.038 (2)	-0.0022 (16)	-0.0030 (15)	-0.0023 (16)
N1	0.0210 (19)	0.029 (2)	0.0253 (19)	0.0026 (17)	0.0042 (16)	-0.0004 (17)
C2	0.021 (2)	0.031 (3)	0.036 (3)	-0.001 (2)	0.006 (2)	0.000 (2)
C3	0.029 (3)	0.053 (3)	0.033 (3)	0.006 (3)	0.008 (2)	-0.001 (2)
C4	0.046 (3)	0.042 (3)	0.030 (3)	0.008 (3)	0.011 (2)	-0.006 (2)
C5	0.041 (3)	0.028 (3)	0.037 (3)	-0.005 (2)	-0.001 (2)	-0.005 (2)
C6	0.019 (2)	0.030 (2)	0.027 (2)	0.001 (2)	0.0029 (19)	0.0001 (19)
O11	0.0196 (17)	0.047 (2)	0.059 (2)	-0.0015 (16)	0.0111 (16)	-0.0083 (17)
N11	0.023 (2)	0.026 (2)	0.047 (2)	-0.0057 (17)	0.0112 (18)	-0.0080 (19)
C12	0.028 (3)	0.022 (2)	0.035 (3)	-0.008 (2)	0.011 (2)	-0.007 (2)
C13	0.020 (2)	0.032 (3)	0.037 (3)	-0.002 (2)	0.012 (2)	-0.002 (2)
C14	0.037 (3)	0.037 (3)	0.040 (3)	-0.002 (2)	0.002 (2)	0.007 (2)
C15	0.048 (3)	0.049 (3)	0.030 (3)	-0.006 (3)	0.007 (2)	0.002 (2)
C16	0.049 (3)	0.045 (3)	0.028 (3)	-0.010 (3)	0.020 (2)	-0.004 (2)

Geometric parameters (\AA , $^\circ$)

Cu1—O1	1.988 (3)	C3—H3	0.9300
Cu1—O2	2.212 (3)	C4—C5	1.386 (6)
Cu1—Cl1	2.2443 (12)	C4—H4	0.9300
Cu1—Cl2 ⁱ	2.3031 (12)	C5—C6	1.384 (6)
Cu1—Cl2	2.3489 (12)	C5—H5	0.9300
Cl2—Cu1 ⁱ	2.3031 (12)	O11—N11	1.331 (5)
S1—C12	1.758 (5)	N11—C16	1.353 (6)
S1—C6	1.764 (4)	N11—C12	1.369 (5)
O1—N1	1.339 (4)	C12—C13	1.370 (6)

O2—H2A	0.81 (2)	C13—C14	1.378 (6)
O2—H2B	0.82 (2)	C13—H13	0.9300
N1—C2	1.341 (5)	C14—C15	1.379 (6)
N1—C6	1.359 (5)	C14—H14	0.9300
C2—C3	1.381 (6)	C15—C16	1.357 (7)
C2—H2	0.9300	C15—H15	0.9300
C3—C4	1.355 (7)	C16—H16	0.9300
O1—Cu1—O2	91.10 (12)	C3—C4—H4	120.4
O1—Cu1—Cl1	95.13 (8)	C5—C4—H4	120.4
O2—Cu1—Cl1	100.39 (9)	C6—C5—C4	120.3 (4)
O1—Cu1—Cl2 ⁱ	169.61 (9)	C6—C5—H5	119.9
O2—Cu1—Cl2 ⁱ	93.77 (9)	C4—C5—H5	119.9
Cl1—Cu1—Cl2 ⁱ	93.00 (4)	N1—C6—C5	118.5 (4)
O1—Cu1—Cl2	84.65 (8)	N1—C6—S1	119.4 (3)
O2—Cu1—Cl2	95.75 (9)	C5—C6—S1	121.9 (3)
Cl1—Cu1—Cl2	163.86 (5)	O11—N11—C16	121.7 (4)
Cl2 ⁱ —Cu1—Cl2	85.74 (4)	O11—N11—C12	117.8 (4)
Cu1 ⁱ —Cl2—Cu1	94.26 (4)	C16—N11—C12	120.5 (4)
C12—S1—C6	99.6 (2)	N11—C12—C13	119.7 (4)
N1—O1—Cu1	121.8 (2)	N11—C12—S1	110.7 (3)
Cu1—O2—H2A	111 (4)	C13—C12—S1	129.6 (3)
Cu1—O2—H2B	117 (3)	C12—C13—C14	119.9 (4)
H2A—O2—H2B	100 (5)	C12—C13—H13	120.1
O1—N1—C2	117.9 (4)	C14—C13—H13	120.1
O1—N1—C6	120.1 (3)	C13—C14—C15	119.3 (5)
C2—N1—C6	122.0 (4)	C13—C14—H14	120.3
N1—C2—C3	119.6 (4)	C15—C14—H14	120.3
N1—C2—H2	120.2	C16—C15—C14	120.1 (5)
C3—C2—H2	120.2	C16—C15—H15	120.0
C4—C3—C2	120.4 (4)	C14—C15—H15	120.0
C4—C3—H3	119.8	N11—C16—C15	120.5 (4)
C2—C3—H3	119.8	N11—C16—H16	119.7
C3—C4—C5	119.2 (4)	C15—C16—H16	119.7

Symmetry codes: (i) $-x+1, -y+1, -z$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O2—H2A \cdots O1 ⁱⁱ	0.81 (2)	2.13 (2)	2.919 (4)	167 (5)
O2—H2B \cdots O11 ⁱ	0.82 (2)	1.97 (2)	2.789 (5)	177 (5)

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

Fig. 1

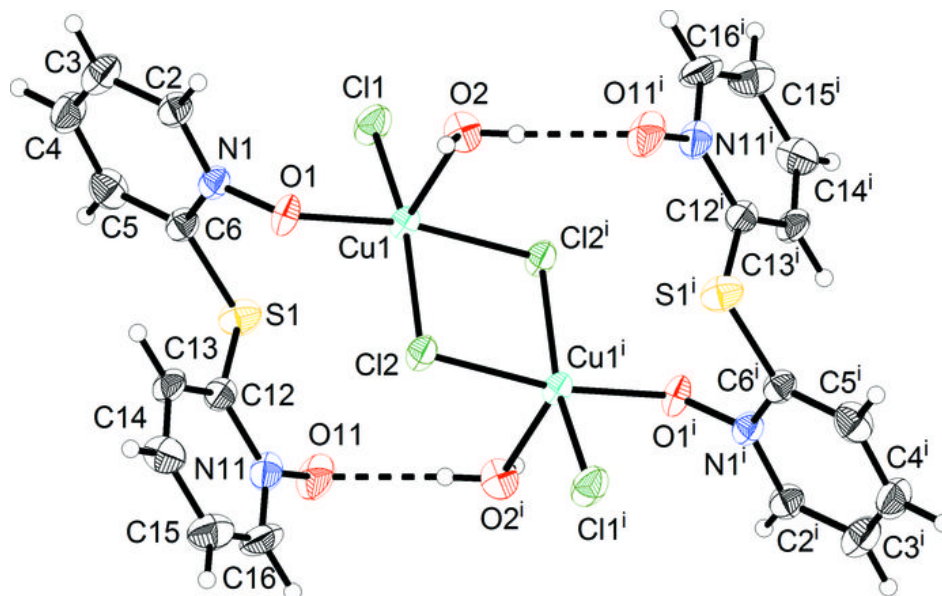


Fig. 2

