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Redetermination of $[Cu_5Cl_{10}(n\text{-}C_3H_7OH)_2]$

George Pon and Roger D. Willett

Chemistry Department, Washington State University, Pullman, WA 99164, USA

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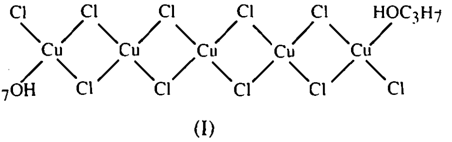
Abstract

The structure of the title compound, octa-μ-chloro-1:2κ^4*Cl*,2:3κ^4*Cl*,3:4κ^4*Cl*,4:5κ^4*Cl*-dichloro-1κ*Cl*,5κ*Cl*-bis(propanol)-1κ*O*,5κ*O*-pentacopper(II), consists of planar bibridged pentameric $Cu_5Cl_{10}L_2$ (L = n-propanol) units. Each Cu^{2+} ion assumes approximate square-planar coordination geometry, with Cu—Cl distances ranging between 2.258 (2) and 2.297 (3) Å. The oligomers form stacks parallel to b through the formation of longer semicoordinate bonds which range in length from 2.687 (2) to 3.158 (3) Å. The stacking pattern leaves one semicoordinate site vacant on the Cu(3) atom. The stacks then aggregate into sheets lying parallel to the ($\bar{1}01$) planes through the formation of semicoordinate Cu(3)—Cl(5) bonds of 2.681 (2) Å. The n-propyl groups separate these sheets. Large atomic displacements of the C atoms [particularly for atoms C(2) and C(3)] indicate substantial disorder of the propyl groups.

Comment

The title pentamer, (I), is one of a series of planar bibridged $Cu_nX_{2n}L_2$ oligomers, with n = 2, 3, 4, 5, 6 or 7, X = Cl^- or Br^-, and L = Cl^-, Br^- or other coordinating ligands (Bond & Willett, 1989; Willett, Bond & Pon, 1990; Bond, Place, Wang, Willett, Liu, Grigereit & Drumheller, 1995). The stacking pattern is denoted as $5(\frac{3}{2},\frac{1}{2})$ in the notation of Geiser, Willett, Lindbeck & Emerson (1986). A phenomenological theory has been developed to describe the stacking pattern (Willett, 1993).



(I)

The structure of the Cu/Cl framework (Fig. 1) and the stacking of the oligomers (Fig. 2) is closely related to that of the parent $CuCl_2$ structure (Wells, 1947). The latter is built up of infinite planar bibridged $(CuCl_2)_n$ chains linked together into layers through semicoordinate bonds. The stacks of pentamers in $Cu_5Cl_{10}L_2$ can be viewed as slabs cut from the $CuCl_2$ layer structure when the n-propanol groups are inserted into the chains. This chain termination effect is a common modification of the parent $CuCl_2$ structure (Weiss & Willett, 1993). In the title compound, however, semicoordinate bonds between the stacks link adjacent stacks to form a herringbone pattern (Fig. 3).

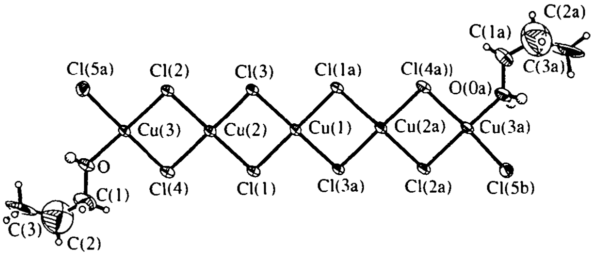


Fig. 1. Displacement ellipsoid illustration of the $[Cu_5Cl_{10}(n\text{-}C_3H_7OH)_2]$ oligomer, with ellipsoids shown at the 50% probability level.

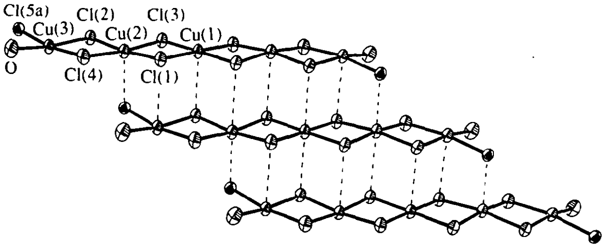


Fig. 2. Displacement ellipsoid illustration of the stacking of the pentamers, with ellipsoids shown at the 50% probability level.

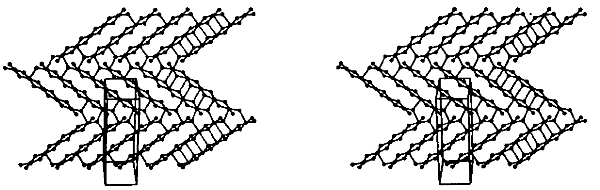


Fig. 3. Stereoview of the sheet structure.

In the present compound, there is less variation in the length of the coordinate Cu—Cl bonds than in other $Cu_nCl_{2n}L_2$ oligomer systems (Willett, 1988). The normal trend of short, long, short, *etc.*, bond-length alternation is found as one proceeds from the end of the oligomer towards the center; however, it is not as pronounced as in other oligomers. In the

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pentamer reported here, the sequence of average Cu—Cl bond lengths is 2.265 (3), 2.292 (3), 2.280 (4), 2.288 (4) and 2.272 (15) Å, while, for example, the sequence observed for a series of $Cu_4Cl_{10}^{2-}$ tetramers is 2.235 (9), 2.328 (28), 2.264 (7) and 2.305 (8) Å.

Experimental

Crystal data

$[Cu_5Cl_{10}(C_3H_8O)_2]$
M_r = 792.4
Monoclinic
$P2_1/n$
a = 10.234 (4) Å
b = 6.023 (2) Å
c = 18.478 (7) Å
β = 94.55 (2)°
V = 1135.4 (8) $Å^3$
Z = 2
D_x = 2.318 Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.54178 Å
Cell parameters from 25 reflections
θ = 33–35°
μ = 16.01 mm^{-1}
T = 295 K
Truncated needle
0.45 × 0.25 × 0.25 mm
Brick red

Data collection

Syntex $P2_1$ upgraded to Nicolet $P3$ diffractometer
ω scans
Absorption correction: ψ scans (*XABS* in *SHELXTL-Plus*; Sheldrick, 1991)
T_{min} = 0.57, T_{max} = 0.94
1545 measured reflections
1291 independent reflections
1091 observed reflections $[|F| > 3\sigma(|F|)]$

R_{int} = 0.063
θ_{max} = 55°
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 6$
$l = -19 \rightarrow 18$
2 standard reflections monitored every 96 reflections intensity decay: no systematic variation

Refinement

Refinement on F
R = 0.0682
wR = 0.0874
S = 1.43
1091 reflections
107 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F) + 0.0030F^2]$
$(\Delta/\sigma)_{max}$ = 0.017

$\Delta\rho_{max}$ = 1.2 e $Å^{-3}$
$\Delta\rho_{min}$ = −1.7 e $Å^{-3}$
Extinction correction: $F^* = F[1 + (0.002\chi \times F^2/\sin 2\theta)]^{-1/4}$
Extinction coefficient: χ = 0.00181 (8)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cu(2)	0.9431 (1)	0.0650 (2)	0.3934 (1)	0.031 (1)
Cu(3)	0.8934 (1)	−0.3926 (2)	0.2951 (1)	0.031 (1)
Cl(3)	0.8644 (2)	0.2037 (4)	0.4969 (1)	0.032 (1)
Cl(4)	1.0378 (2)	−0.1001 (4)	0.2995 (1)	0.038 (1)
Cl(1)	1.0913 (2)	0.3492 (4)	0.4024 (1)	0.033 (1)
Cl(2)	0.8126 (2)	−0.2407 (4)	0.3962 (1)	0.032 (1)
Cu(1)	1	1/2	1/2	0.032 (1)
O	0.9773 (6)	−0.5476 (12)	0.2180 (3)	0.047 (2)
C(1)	1.0807 (18)	−0.492 (3)	0.1736 (11)	0.155 (10)
C(2)	1.0862 (22)	−0.602 (4)	0.1078 (10)	0.179 (12)
C(3)	1.0617 (19)	−0.824 (3)	0.0935 (11)	0.133 (9)
Cl(5)	0.7704 (2)	−0.7011 (4)	0.3068 (1)	0.034 (1)

Table 2. *Selected geometric parameters* (Å, °)

Cu(2)—Cl(3)	2.291 (3)	Cu(2)—Cl(4)	2.282 (3)
Cu(2)—Cl(1)	2.284 (3)	Cu(2)—Cl(2)	2.278 (3)
Cu(2)—Cl(5^{i})	2.687 (2)	Cu(2)—Cl(3^{iii})	3.158 (3)
Cu(3)—Cl(4)	2.297 (3)	Cu(3)—Cl(2)	2.293 (3)
Cu(3)—O	1.957 (7)	Cu(3)—Cl(5)	2.265 (3)
Cu(3)—Cl(5^{ii})	2.681 (2)	Cu(3)—Cl(1^{iv})	3.133 (3)
Cu(1)—Cl(3)	2.258 (2)	Cu(1)—Cl(1)	2.285 (2)
Cu(1)—Cl(2^{i})	3.036 (3)	O—C(1)	1.431 (21)
C(1)—C(2)	1.39 (3)	C(2)—C(3)	1.39 (3)
Cl(3)—Cu(2)—Cl(4)	173.0 (1)	Cl(3)—Cu(2)—Cl(1)	86.6 (1)
Cl(4)—Cu(2)—Cl(1)	93.6 (1)	Cl(3)—Cu(2)—Cl(2)	91.7 (1)
Cl(4)—Cu(2)—Cl(2)	87.2 (1)	Cl(1)—Cu(2)—Cl(2)	172.4 (1)
Cl(3)—Cu(2)—Cl(5^{i})	92.7 (1)	Cl(4)—Cu(2)—Cl(5^{i})	94.3 (1)
Cl(1)—Cu(2)—Cl(5^{i})	93.0 (1)	Cl(2)—Cu(2)—Cl(5^{i})	94.5 (1)
Cl(4)—Cu(3)—Cl(2)	86.4 (1)	Cl(4)—Cu(3)—O	94.2 (2)
Cl(2)—Cu(3)—O	172.2 (2)	Cl(4)—Cu(3)—Cl(5)	170.8 (1)
Cl(2)—Cu(3)—Cl(5)	90.6 (1)	O—Cu(3)—Cl(5)	87.6 (2)
Cl(4)—Cu(3)—Cl(5^{ii})	93.4 (1)	Cl(2)—Cu(3)—Cl(5^{ii})	98.9 (1)
O—Cu(3)—Cl(5^{ii})	88.9 (2)	Cl(5)—Cu(3)—Cl(5^{ii})	95.7 (1)
Cu(2)—Cl(3)—Cu(1)	93.1 (1)	Cu(2)—Cl(4)—Cu(3)	92.9 (1)
Cu(2)—Cl(1)—Cu(1)	92.6 (1)	Cu(2)—Cl(2)—Cu(3)	93.1 (1)
Cl(3)—Cu(1)—Cl(1)	87.4 (1)	Cl(3)—Cu(1)—Cl(3^{v})	180.0 (1)
Cl(1)—Cu(1)—Cl(3^{v})	92.6 (1)	Cl(3)—Cu(1)—Cl(1^{v})	92.6 (1)
Cl(1)—Cu(1)—Cl(1^{v})	180.0 (1)	Cl(3^{v})—Cu(1)—Cl(1^{v})	87.4 (1)
Cu(3)—O—C(1)	133.8 (9)	O—C(1)—C(2)	118.2 (17)
C(1)—C(2)—C(3)	127.5 (20)	Cu(3)—Cl(5)—Cu(2^{ii})	98.2 (1)
Cu(3)—Cl(5)—Cu(3^{vi})	127.4 (1)	Cu(2^{ii})—Cl(5)—Cu(3^{vi})	122.5 (1)

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

Positional parameters were taken from a previous structure determination (Willett & Rundle, 1964). Refinement was carried out with *SHELXTL-Plus* software (Sheldrick, 1991). The O—H bonds were assumed to be disordered. Attempts to model the disorder of the propyl groups did not result in a significant lowering of the R and wR values, and resulted in physically unreal values for the anisotropic displacement parameters.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1198). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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