

Redetermination of *catena*-poly[bis-[chloro(μ -pyridine *N*-oxide- κ^2 O:O)-copper(II)]-di- μ -chloro]

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Key indicators

Single-crystal X-ray study

$T = 293$ K

Mean $\sigma(\text{C}-\text{C}) = 0.005$ Å

R factor = 0.035

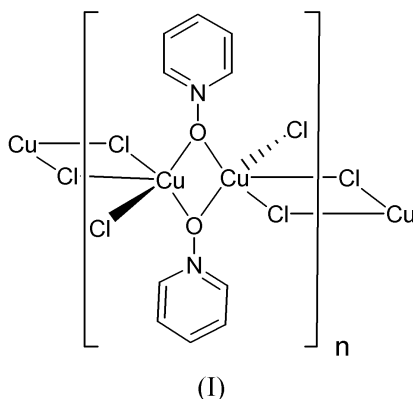
wR factor = 0.087

Data-to-parameter ratio = 18.1

The title compound, $[\text{Cu}_2\text{Cl}_4(\text{C}_5\text{H}_5\text{NO})_2]_n$, is a one-dimensional polymer in which the Cu^{II} atoms are alternately bridged by two O atoms [$\text{Cu}\cdots\text{Cu} = 3.2131(10)$ Å] and two Cl atoms [$\text{Cu}\cdots\text{Cu} = 3.7061(11)$ Å]. The metal centers display a very distorted coordination geometry, with the four stronger bonds defining a CuCl_2O_2 polyhedron midway between square planar and tetrahedral, which serves as the base of a pyramid, while the loosely bound Cl atom in the bridge occupies the apex. The simultaneous presence of a good hydrogen-bond acceptor and an adequate C–H donor leads to a network of C–H \cdots Cl interactions.

Comment

After a long period of neglect, weak hydrogen bonds involving C–H groups have become a current focus of interest, mainly because of the accumulated evidence of the role they play in the self-assembly of organic molecules. Although this state of affairs occurs mainly in the absence of stronger interactions, when ionic groups (like halides) are present, these C–H \cdots halogen contacts can occur in such large quantity as to become significant, even in the presence of the more important stabilizing forces (*viz.* Coulomb). We present here a simple example of this, namely the structure of $[\text{CuCl}_2(\text{C}_5\text{H}_5\text{NO})_2]_n$, (I), a polymeric copper complex that has Cl and pyridine *N*-oxide as ligands. In (I), the simultaneous presence of a good hydrogen-bond acceptor and an adequate C–H donor leads to a very complex stabilizing hydrogen-bonding network that determines the packing geometry. It must be emphasized that the structure of (I) has been known for some time (Schafer *et al.*, 1965; Sager *et al.*, 1967), but the precision attainable at that time (final R values 0.15 and 0.084, respectively), did not allow a detailed hydrogen-bonding analysis. Therefore, a new structure determination seemed justified.



Compound (I) is a one-dimensional polymer, the dimeric units $[\text{CuCl}_2(\text{C}_5\text{H}_5\text{NO})_2]$ being the elemental links that define the chains through a weak $\text{Cu}-\text{Cl}$ interaction joining them (Fig. 1 and Table 1) are built up around a center of symmetry, and each copper cation is strongly bonded to two independent chloride ions [$\text{Cu1}-\text{Cl1} = 2.1881(9) \text{ \AA}$ and $\text{Cu1}-\text{Cl2} = 2.1973(9) \text{ \AA}$] and two O atoms from two symmetry-related pyridine *N*-oxide ligands [$\text{Cu1}-\text{O1} = 2.0055(19) \text{ \AA}$ and $\text{Cu1}-\text{O1}(-x, 1-y, 1-z) = 1.9579(18) \text{ \AA}$], which act as bridging agents. These four bonds adopt a geometry somewhere between square planar and tetrahedral, as evidenced by the bond angles around atom Cu1 (Table 1) and the dihedral angle between the $\text{O1}-\text{Cu1}-\text{O1}(-x, 1-y, 1-z)$ and $\text{Cl1}-\text{Cu1}-\text{Cl2}$ planes [$32.2(1)^\circ$]. In spite of being far from planar, the group constitutes the distorted 'square' base of a pyramid of which the remaining $\text{Cu}-\text{Cl2}(1-x, 1-y, 1-z)$ bond [$2.8150(10) \text{ \AA}$] is the apical bond.

The alternating Cu_2O_2 and Cu_2Cl_2 loops that result develop along the *a* axis, around the two non-equivalent centers of symmetry in the structure. The bridging loops are strictly planar, as required by symmetry, and define a very twisted chain, as shown by the dihedral angle between loop planes [$85.7(1)^\circ$] and the angle between neighboring $\text{Cu}\cdots\text{Cu}$ vectors [$113.5(1)^\circ$].

Even though the $\text{Cu}\cdots\text{Cu}$ distance in the Cu_2O_2 loop [$3.213(1) \text{ \AA}$] appears rather long when compared with the mean value for all Cu_2O_2 bridges [$3.11(19) \text{ \AA}$ for *ca* 1500 cases in the November 2002 version of the Cambridge Structural Database (CSD; Allen, 2002)], this distance is still on the short side when compared with the average from the 29 cases with closely related pyridine *N*-oxide bridges [$3.38(15) \text{ \AA}$]. On the other hand, the Cu_2Cl_2 loop presents a $\text{Cu}\cdots\text{Cu}$ distance of $3.706(1)$, significantly longer than the mean for some 130 similar cases in the CSD [$3.35(28) \text{ \AA}$].

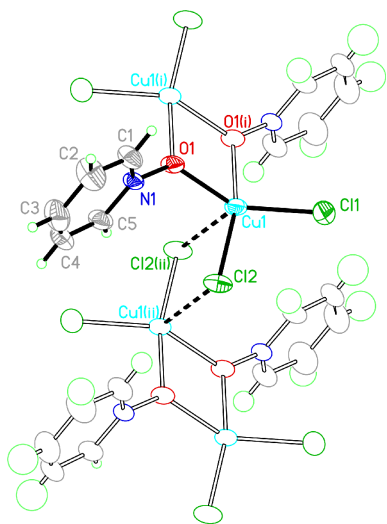


Figure 1
The molecular structure of (I), showing the dimeric unit and (in heavy broken lines) the long $\text{Cu1}-\text{Cl2}$ interaction leading to the chain formation. The asymmetric unit of the structure is shown as full displacement ellipsoids (50% probability level); symmetry-related atoms are shown as open ellipsoids. For symmetry codes refer to Table 1.

The pyridine *N*-oxide group is planar to within 0.002 \AA , and binds at $69.76(7)^\circ$ to the Cu_2O_2 loop plane. In general terms, the structure does not depart from that expected, and its most interesting feature resides in its self-assembly into a three-dimensional structure. This process is achieved through a dense network of weak $\text{C}-\text{H}\cdots\text{Cl}$ contacts, involving all of the available H atoms in the structure (Table 2). At a first glance, this process could appear as a simple stacking of the one-dimensional arrays (Fig. 2), but a closer examination suggests that this stacking is subtly directed by the $\text{C}-\text{H}\cdots\text{Cl}$ contacts; the lateral view in Fig. 3 shows the formation of planar sheets roughly parallel to (102), formed by interleaved pyridine *N*-oxide groups and Cl^- ions linked by a dense network of weak $\text{C}-\text{H}\cdots\text{Cl}$ contacts (see also Fig. 4). The negatively charged planes have interplanar distances of about 3.25 \AA , and between two adjacent structures a plane of Cu^{2+} cations builds up. Fig. 4 shows a detailed view of the hydrogen

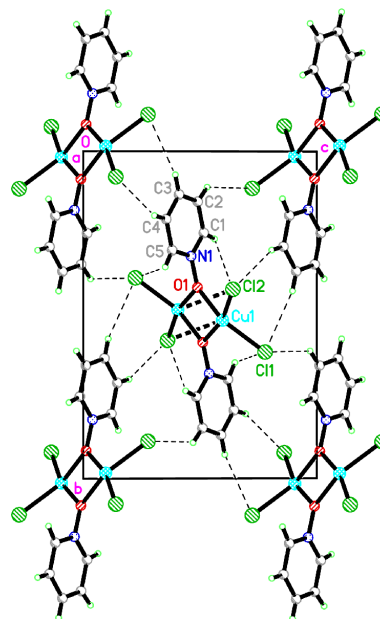


Figure 2
Packing view of (I) along the *a* axis, showing chains in projection. Each chain interacts with its four next-nearest neighbors.

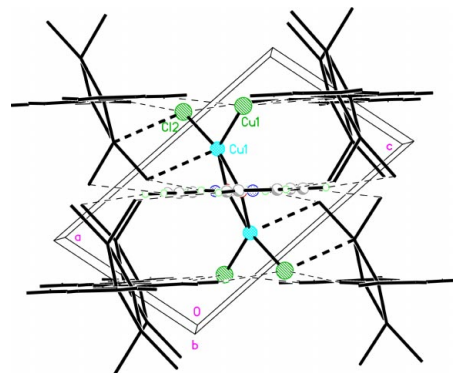


Figure 3
Packing view of (I) (lateral view). The planes formed by the ligands are clearly seen, leaving the cations 'sandwiched' in between.

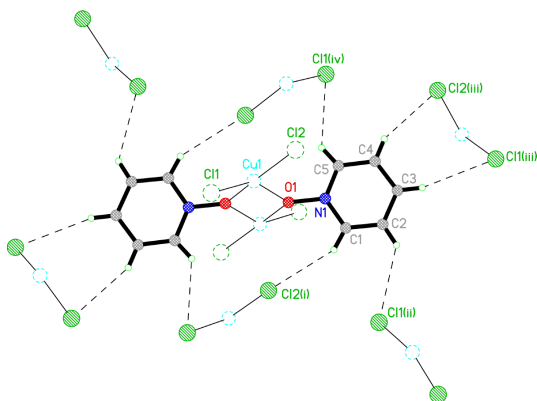


Figure 4
Schematic view of one of the 'anionic' planes, showing the distribution of C—H...Cl contacts. Atoms lying in the plane are represented by heavy full lines; those above/below the plane are shown as broken circles. For symmetry codes refer to Table 2.

bonds arising in the anionic planes. The dense and even distribution of weak C—H...Cl hydrogen contacts in the plane is apparent. The two pairs of chlorine anions in the reference dimer (Fig. 3, center) happen to correspond to the next nearest planes in the upwards (downwards) directions in the figure, thus providing an intricate interweaving of molecules. Copper cations lie 'sandwiched' between the planes.

In order to investigate how common such C—H...Cl contacts are, we made a search in the CSD, looking for cases in which an aromatic H atom interacts with a chlorine ion at less than the sum of their van der Waals radii (in this instance set at 2.90 Å). The search provided *ca* 20 000 cases, the mean value of the Cl...H distance being 2.80 (8) Å. The upper limit for the interaction, however, seemed to be far from obvious, and situations were found that could only be attributable to a genuine interaction, with Cl...H distances in the range 3.4–3.5 Å and C—H...Cl angles largely in excess of 150°.

Experimental

Pyridine *N*-oxide (1 mmol) in methanol was added slowly, with stirring, to a methanol solution of CuCl₂·2H₂O (1 mmol). The resulting solution was refluxed for 30 min. After 2 d at room temperature, green crystals of (I) were obtained. Elemental analysis for (I) calculated: C 26.16, H 2.20%; found: C 26.3, H 2.2%.

Crystal data

[Cu ₂ Cl ₄ (C ₅ H ₅ NO) ₂]	$D_x = 2.022 \text{ Mg m}^{-3}$
$M_r = 459.08$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 123 reflections
$a = 5.7929 (18) \text{ \AA}$	$\theta = 3.1\text{--}24.7^\circ$
$b = 13.509 (4) \text{ \AA}$	$\mu = 3.53 \text{ mm}^{-1}$
$c = 9.980 (3) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 105.049 (5)^\circ$	Parallelepiped, dark green
$V = 754.2 (4) \text{ \AA}^3$	$0.60 \times 0.20 \times 0.18 \text{ mm}$
$Z = 2$	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	1664 independent reflections
φ and ω scans	1478 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2002)	$R_{\text{int}} = 0.034$
$T_{\text{min}} = 0.27, T_{\text{max}} = 0.53$	$\theta_{\text{max}} = 27.6^\circ$
5290 measured reflections	$h = -7 \rightarrow 7$
	$k = -17 \rightarrow 17$
	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.087$
 $S = 1.08$
 1664 reflections
 92 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0478P)^2 + 0.1682P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.012$
 $\Delta\rho_{\text{max}} = 0.60 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.62 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Cu1—O1 ⁱ	1.9579 (18)	Cu1—Cl2	2.1973 (9)
Cu1—O1	2.0055 (19)	Cu1—Cl2 ⁱⁱ	2.8150 (10)
Cu1—Cl1	2.1881 (9)		
O1 ⁱ —Cu1—O1	71.67 (9)	Cl1—Cu1—Cl2	99.54 (3)
O1 ⁱ —Cu1—Cl1	94.28 (6)	O1 ⁱ —Cu1—Cl2 ⁱⁱ	86.04 (7)
O1—Cu1—Cl1	145.98 (6)	O1—Cu1—Cl2 ⁱⁱ	93.68 (7)
O1 ⁱ —Cu1—Cl2	165.94 (6)	Cl1—Cu1—Cl2 ⁱⁱ	116.68 (4)
O1—Cu1—Cl2	97.74 (6)	Cl2—Cu1—Cl2 ⁱⁱ	85.44 (3)

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

Table 2

Hydrogen-bonding geometry (Å, °).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
C1—H1A...Cl2 ⁱⁱⁱ	0.93	2.86	3.649 (3)	143
C2—H2A...Cl1 ^{iv}	0.93	2.96	3.624 (4)	139
C3—H3A...Cl1 ^v	0.93	2.94	3.846 (3)	164
C4—H4A...Cl2 ^v	0.93	2.76	3.622 (3)	155
C5—H5A...Cl1 ⁱⁱ	0.93	2.65	3.406 (3)	139

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

H atoms were included at idealized positions and refined in the riding-model approximation [C—H = 0.93 Å; $U_{\text{iso}} = 1.2U_{\text{eq}}$ (parent atom)].

Data collection: SMART-NT (Bruker, 2001); cell refinement: SMART-NT; data reduction: SAINT-NT (Bruker, 2002); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XP in SHELXTL-PC (Sheldrick, 1994); software used to prepare material for publication: SHELXL97.

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