

## Doxylaminium tetrachlorocuprate(II)

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The structure of the title compound, 2-[1-(dimethylammonioethoxy)-1-phenylethyl]pyridinium tetrachlorocuprate(II), ( $C_{17}H_{24}N_2O$ )[ $CuCl_4$ ], contains dihydro cations of doxylamine hydrogen bonded to two Cl atoms in two different  $CuCl_4^{2-}$  anions, with  $Cl \cdots N$  distances of 3.101 (9) and 3.253 (10) Å. The ethereal O atom is involved in intramolecular hydrogen bonds, with  $O \cdots N$  distances of 2.517 (11) and 2.757 (12) Å. The molecular dimensions in the cation are as expected and the  $CuCl_4^{2-}$  anion has a flattened tetrahedral geometry.

### Comment

Doxylamine,  $C_{17}H_{22}N_2O$ , is a chiral tertiary aminoalkyl ether effective on the  $H_1$  receptor site (Casy, 1991). Unlike the crystal structures of the tetrachlorozincate and tetrachlorocobaltate salts of doxylamine, which have been reported from our laboratory in a centrosymmetric space group (Parvez & Sabir, 1998), this antihistamine has now been crystallized as a dihydro-cation, with the  $CuCl_4^{2-}$  anion in a non-centrosymmetric space group. In this paper, we report the structure of doxylamine tetrachlorocuprate(II), (I).

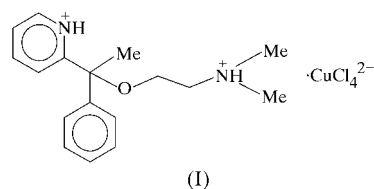


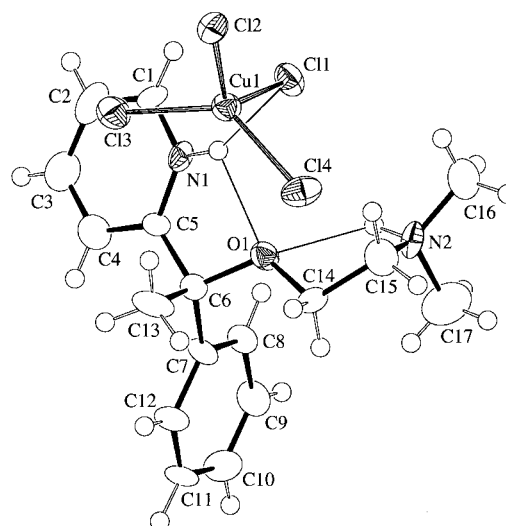
Fig. 1 shows an *ORTEPII* (Johnson, 1976) drawing of (I). The molecular dimensions in the doxylamine dication are normal. The important mean bond distances are:  $C_{sp^3}-C_{sp^3}$  1.497 (17),  $C_{sp^3}-C_{sp^2}$  1.514 (9),  $C-C_{aromatic}$  1.378 (15),  $C-C_{pyridyl}$  1.376 (19),  $N-C_{sp^3}$  1.469 (14),  $N-C_{sp^2}$  1.324 (2) and  $O-C_{sp^3}$  1.429 (16) Å. The pyridyl and phenyl rings are essentially planar with the maximum deviations of atoms from the least-squares planes being 0.007 (8) and 0.019 (9) Å, respectively. The dihedral angle between these planes in (I) is 82.9 (3)°; the corresponding angles in the structures of the tetrachlorozincate and tetrachlorocobaltate salts of doxylamine are 87.68 (14) and 88.1 (2)°, respectively (Parvez & Sabir, 1998).

The atoms C6, O1, C14 and C15 of the side chain in (I) are nearly coplanar and are fully extended, with N2 lying in a non-extended conformation. This is in contrast to the conformation adopted by the corresponding atoms in the structures of the tetrachlorozincate and tetrachlorocobaltate salts of doxylamine, which were essentially planar, with deviations of 0.042 (2) and 0.058 (4) Å, respectively (Parvez & Sabir, 1998).

It is interesting to note that in (I), O1 is hydrogen bonded to two H atoms, one H from the pyridyl ring [ $O1 \cdots N1$  2.517 (11) Å] and one H from the ammonium N atom [ $O1 \cdots N2$  2.757 (12) Å]. A similar pattern of hydrogen bonding has been observed in the structures of the tetrachlorozincate and tetrachlorocobaltate salts of doxylamine (Parvez & Sabir, 1998). The N—H groups are also hydrogen bonded to the Cl atoms of two  $CuCl_4^{2-}$  anions, with  $N \cdots Cl$  distances of 3.101 (9) Å for the pyridinyl N and 3.253 (10) Å for the ammonium N atom. Similar bifurcated hydrogen bonding has been found in the structure of chloropyramine tetrachlorocuprate(II) (Parvez & Sabir, 1997). The structure of (I) is stabilized by hydrogen bonding involving the ethereal O atom, both N atoms of the cations and two Cl atoms of the anions; details of the hydrogen-bonding geometry are presented in Table 2.

The  $CuCl_4^{2-}$  anion shows a flattened tetrahedral geometry. The Cu—Cl bond lengths for Cl atoms not involved in hydrogen bonding are identical [2.206 (3) and 2.210 (3) Å], while those involved in hydrogen bonds are significantly longer, with values of 2.248 (4) and 2.299 (3) Å. The Cl—Cu—Cl bond angles lie in two ranges; four are in the range 99.92 (13)–102.57 (12)°, and the remaining two angles are 123.09 (13) and 132.81 (14)°.

The crystal structures of a number of closely related compounds have been determined, *e.g.* diphenhydramine (Glaser & Maartmann-Moe, 1990), the diphenhydramine thiourea complex (Wiedenfeld & Knoch, 1987), carboxamine maleate (Bertolasi *et al.*, 1980) and clemastine hydrogen fumarate (Parvez & Wendling, 1991).



**Figure 1**  
*ORTEPII* (Johnson, 1976) drawing of (I) with displacement ellipsoids at the 50% probability level.

## Experimental

The title compound was synthesized by adding  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (1.0 mmol) to doxylamine succinate (2.0 mmol) (Sigma Inc.) in ethanol (20 ml). HCl was added until the pH was 2–3. The solution was evaporated slowly at room temperature, and yellow prismatic crystals separated after a few days.

### Crystal data

$(\text{C}_{17}\text{H}_{24}\text{N}_2\text{O})[\text{CuCl}_4]$	$D_x = 1.539 \text{ Mg m}^{-3}$
$M_r = 477.72$	Mo $K\alpha$ radiation
Monoclinic, $Cc$	Cell parameters from 25 reflections
$a = 16.807(2) \text{ \AA}$	$\theta = 10.0\text{--}20.0^\circ$
$b = 9.3006(16) \text{ \AA}$	$\mu = 1.59 \text{ mm}^{-1}$
$c = 13.7677(10) \text{ \AA}$	$T = 170(2) \text{ K}$
$\beta = 106.682(10)^\circ$	Prismatic, yellow
$V = 2061.5(5) \text{ \AA}^3$	$0.45 \times 0.23 \times 0.18 \text{ mm}$
$Z = 4$	

### Data collection

Rigaku AFC-6S diffractometer	1140 reflections with $I > 2\sigma(I)$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 25.0^\circ$
Absorption correction: empirical $\psi$ scan (3 reflections) (North <i>et al.</i> , 1968)	$h = 0 \rightarrow 20$
$T_{\text{min}} = 0.54$ , $T_{\text{max}} = 0.76$	$k = 0 \rightarrow 11$
1901 measured reflections	$l = -16 \rightarrow 15$
1821 independent reflections (plus 80 Friedel-related reflections)	3 standard reflections every 200 reflections intensity decay: 0.6%

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.059P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.044$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.128$	$(\Delta/\sigma)_{\text{max}} < 0.01$
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.53 \text{ e \AA}^{-3}$
1901 reflections	$\Delta\rho_{\text{min}} = -0.63 \text{ e \AA}^{-3}$
229 parameters	Absolute structure: (Flack, 1983)
H-atom parameters constrained	Flack parameter = $-0.02(4)$

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Cu1—Cl3	2.206 (3)	N1—C1	1.322 (14)
Cu1—Cl2	2.210 (3)	N1—C5	1.326 (13)
Cu1—Cl4	2.248 (4)	N2—C16	1.449 (16)
Cu1—Cl1	2.299 (3)	N2—C15	1.478 (15)
O1—C14	1.413 (12)	N2—C17	1.479 (17)
O1—C6	1.445 (13)		
Cl3—Cu1—Cl2	100.62 (13)	C14—O1—C6	116.1 (8)
Cl3—Cu1—Cl4	132.81 (14)	C1—N1—C5	125.4 (10)
Cl2—Cu1—Cl4	102.57 (12)	C16—N2—C15	112.9 (10)
Cl3—Cu1—Cl1	100.86 (12)	C16—N2—C17	109.7 (11)
Cl2—Cu1—Cl1	123.09 (13)	C15—N2—C17	113.3 (11)
Cl4—Cu1—Cl1	99.92 (13)		

H atoms were located from difference maps and were placed at geometrically idealized positions (N—H = 0.88 and 0.93  $\text{\AA}$ , and C—H = 0.95–0.99  $\text{\AA}$ ) utilizing a riding model, and a torsional parameter was refined for each Me group. The non-methyl and methyl H

**Table 2**

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

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
N1—H1 $\cdots$ Cl1	0.88	2.30	3.101 (9)	152
N2—H2 $\cdots$ Cl4 <sup>i</sup>	0.93	2.50	3.253 (10)	138
N1—H1 $\cdots$ O1	0.88	2.12	2.517 (11)	107
N2—H2 $\cdots$ O1	0.93	2.31	2.757 (12)	109

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

atoms were assigned isotropic displacement parameters 1.2 and 1.5 times, respectively, the displacement parameters of the atoms to which they were attached.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1994); program(s) used to solve structure: *SAPI91* (Fan, 1991); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *TEXSAN*; software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1314). Services for accessing these data are described at the back of the journal.

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