Structure of 4-(2-Ammonioethyl)-1-methyl-3H^+-imidazolium Tetrachlorocuprate(II)

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Abstract. $C_6H_{13}N_3^{2+}.CuCl_4^{2-}$, $M_r = 332.55$, monoclinic, $P2_1/c$, $a = 10.849$ (4), $b = 15.339$ (4), $c = 7.876$ (2) Å, $\beta = 108.76$ (3)°, $V = 1241.0$ (7) Å^3, $Z = 4$, $D_x = 1.780$ Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu = 2.64$ mm^{-1}, $F(000) = 668$, $T = 295$ K, final $R = 0.032$ for 2688 independent reflections. The structure was determined by the heavy-atom method. It consists of methylhistamine dications and $[CuCl_4]^{2-}$ anions connected by five N—H···Cl hydrogen bonds. The anions are distinctly distorted with Cl—Cu—Cl angles between 98.7 and 134.3° while Cu—Cl distances vary from 2.22 to 2.27 Å. The geometry and electron distribution of the methylimidazole ring as well as the conformation of the side chain resemble those found in the crystal structures of histamine dications.

Introduction. All methyl-substituted histamines generally show decreased activity at histamine receptors but the differences in their activity in different tissues allowed at least two types of histamine responses to be distinguished: H_1 (Ash & Schild, 1966) and H_2 (Black, Duncan, Durant, Ganellin & Parsons, 1972). Recently, a third type of histamine receptor has been proposed (Arrang, Garbarg & Schwartz, 1983, 1987; Van der Werf, Bijloo, Van der Vliet, Bast & Timmerman, 1987). Ganellin's work on the conformation of histamine and methylhistamines in relation to their activities showed that the *trans* conformer is dominant in aqueous solution for both mono- and dication forms and that N-methylation has little influence on the conformation of the histamine frame (Ganellin, 1973; Ganellin, Pepper, Port & Richards, 1973; Ganellin, Port & Richards, 1973). The present study was undertaken to estimate the electronic effects of τ-methylation on the imidazole system.

Experimental. Crystallized from methanol solution by slow evaporation. A single crystal of dimensions $0.52 \times 0.30 \times 0.10$ mm was used for data collection and accurate cell-parameter determination on a CAD-4 diffractometer with graphite-monochromatized Mo $K\alpha$

radiation, θ up to 27°. Unit-cell parameters determined by least squares from 2θ values of 25 reflections in the θ range 9–12°. 2688 independent intensities [1969 considered observed with $I > 3\sigma(I)$ used for structure refinement] were measured with $\omega/2\theta$ scan technique; $h_{max} = 13$, $k_{max} = 19$, $\pm l_{max} = 9$. Three standards monitored during data collection did not show significant change of intensity. The data were corrected for absorption, following the method of North, Phillips & Mathews (1968), the minimum transmission factor was 0.673. The structure was solved by Patterson method and refined by full-matrix least squares with anisotropic temperature factors for non-H and isotropic for H atoms. The final R (wR) was 0.032 (0.040), $S = 1.42$ and $(\Delta/\sigma)_{max} = 0.15$ for non-H atoms and 0.51 for H atoms.* The weighting scheme applied was $w^{-1} = \sigma^2(F_o) + 0.04|F_o|^2$. $\rho_{max} = 0.22$ e Å^{-3} in final map. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974) and the programs used in the calculations were those of the *SDP* system (Frenz, 1978) and *PARST* (Nardelli, 1983).

Discussion. The final thermal and positional parameters are listed in Table 1 and bond lengths, valency angles and some torsion angles in Table 2. The values, compared with those found in other histamine dications (Veidis. Palenik, Schaffrin & Trotter, 1969; Yamane, Ashida & Kakudo, 1973; Bonnet & Jeannin, 1972), show that indeed N$^\tau$ methylation of the histamine does not much alter either the imidazole-ring geometry or its electron distribution. As pointed out by Ganellin, Pepper, Port & Richards (1973) and confirmed in this study the τ-methyl group also has little direct steric effect on the conformation of the side chain. The C(4)—C(6)—C(3)—N(2) torsional angle is

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Table 1. *Fractional atomic coordinates* (× 10^5 *for* Cu *and* Cl, × 10^4 *for* N *and* C *and* × 10^3 *for* H *atoms*) *and equivalent isotropic* (*isotropic for* H) *temperature factors* ($Å^2$)

$$B_{eq} = \tfrac{4}{3}(a^{*2}B_{11} + \ldots + b^*c^*B_{23}\cos\alpha^*).$$

	x	y	z	$B_{eq}(B_{iso})$
Cu	21555 (3)	−9647 (2)	−8944 (4)	2.416 (7)
Cl(1)	23315 (8)	−22287 (5)	5718 (10)	3.16 (2)
Cl(2)	31947 (8)	−3660 (6)	−26137 (11)	4.28 (2)
Cl(3)	28001 (8)	−537 (5)	15050 (10)	2.92 (2)
Cl(4)	1228 (8)	−10052 (6)	−28264 (11)	3.56 (2)
N(1)	4160 (2)	2918 (1)	−118 (3)	2.27 (5)
N(2)	−852 (2)	1082 (2)	−3252 (3)	2.95 (5)
N(3)	3544 (3)	1596 (2)	−544 (4)	3.51 (6)
C(1)	4979 (3)	3690 (2)	547 (5)	3.90 (8)
C(2)	4517 (3)	2107 (2)	349 (4)	3.17 (7)
C(3)	346 (3)	1431 (2)	−1947 (4)	3.10 (7)
C(4)	2532 (3)	2082 (2)	−1602 (4)	2.63 (6)
C(5)	2934 (3)	2922 (2)	−1323 (4)	2.75 (6)
C(6)	1305 (3)	1704 (3)	−2825 (4)	3.87 (7)
H(11)	575 (4)	357 (3)	120 (5)	6.8 (11)
H(12)	529 (4)	391 (2)	−40 (5)	6.0 (11)
H(13)	457 (4)	411 (2)	68 (5)	6.4 (11)
H(2)	534 (3)	194 (2)	124 (4)	2.7 (7)
H(21)	−114 (3)	133 (2)	−388 (4)	4.1 (8)
H(22)	−151 (5)	83 (4)	−257 (7)	12.5 (18)
H(23)	−66 (5)	63 (3)	−386 (7)	10.3 (15)
H(3)	359 (4)	109 (3)	−51 (5)	7.1 (12)
H(31)	8 (3)	194 (2)	−145 (4)	5.0 (9)
H(32)	61 (4)	100 (2)	−129 (5)	6.0 (11)
H(5)	254 (3)	345 (2)	−184 (4)	3.1 (7)
H(61)	151 (3)	120 (2)	−341 (4)	4.6 (9)
H(62)	90 (4)	207 (3)	−354 (6)	8.4 (13)

Table 2. *Bond lengths* (Å), *valency and selected torsional angles* (°) *and hydrogen-bond parameters with e.s.d.'s in parentheses*

Cu–Cl(1)	2.2326 (7)	Cl(1)–Cu–Cl(2)	134.32 (3)
Cu–Cl(2)	2.2206 (8)	Cl(1)–Cu–Cl(3)	98.68 (3)
Cu–Cl(3)	2.2725 (7)	Cl(1)–Cu–Cl(4)	103.25 (3)
Cu–Cl(4)	2.2423 (7)	Cl(2)–Cu–Cl(3)	99.93 (3)
N(1)–C(1)	1.473 (4)	Cl(2)–Cu–Cl(4)	100.31 (3)
N(1)–C(2)	1.319 (3)	Cl(3)–Cu–Cl(4)	123.66 (3)
N(1)–C(5)	1.364 (3)	C(1)–N(1)–C(2)	124.7 (3)
N(2)–C(3)	1.475 (4)	C(1)–N(1)–C(5)	125.9 (3)
N(3)–C(2)	1.322 (4)	C(2)–N(1)–C(5)	109.4 (2)
N(3)–C(4)	1.367 (4)	C(2)–N(3)–C(4)	110.4 (2)
C(3)–C(6)	1.483 (4)	N(1)–C(2)–N(3)	107.3 (3)
C(4)–C(5)	1.354 (4)	N(2)–C(3)–C(6)	111.8 (3)
C(4)–C(6)	1.488 (4)	N(3)–C(4)–C(5)	105.4 (2)
		N(3)–C(4)–C(6)	123.9 (3)
N(2)–C(3)–C(6)–C(4)	178.7 (3)	C(5)–C(4)–C(6)	130.6 (3)
C(3)–C(6)–C(4)–N(3)	80.2 (4)	N(1)–C(5)–C(4)	107.5 (2)
C(3)–C(6)–C(4)–C(5)	−102.9 (4)	C(3)–C(6)–C(4)	115.1 (3)

Hydrogen bonds

X–H···Y	X–H (Å)	X···Y (Å)	H···Y (Å)	X–H···Y (°)	Y
N(3)–H(3)···Cl(2)	0.78 (5)	3.385 (3)	2.73 (4)	143 (4)	x, y, z
			2.53	140	
N(3)–H(3)···Cl(3)	0.78 (5)	3.240 (3)	2.68 (5)	130 (4)	x, y, z
			2.53	126	
N(2)–H(23)···Cl(4)	0.90 (5)	3.355 (3)	2.69 (5)	131 (4)	x, y, z
			2.61	129	
N(2)–H(21)···Cl(1)	0.62 (3)	3.278 (3)	2.69 (3)	159 (3)	−x, ½+y,
			2.31	156	−z−½
N(2)–H(22)···Cl(3)	1.09 (6)	3.274 (3)	2.20 (6)	167 (5)	−x, −y, −z
			2.26	168	

The lower values for H···Y distances and X–H···Y angles are normalized for N–H distance of 1.03 Å (Taylor & Kennard, 1983).

178.8 (3)° while the angle between the imidazole ring and the plane defined by the three non-H atoms of the side chain is 78.1 (2)°, close to the values observed in the structure of the only known histamine monocation (89.7°; Prout, Critchley & Ganellin, 1974) and in one of the histamine dications (82.5°; Veidis, Palenik, Schaffrin & Trotter, 1969). In three other known structures of the histamine dication the values of the interplanar angle are smaller: 30° in the dibromide (Decou, 1964), 7° in the tetrachlorocobaltate (Bonnet & Jeannin, 1972), 4.4 and 9.2° in the sulfate (Yamane, Ashida & Kakudo, 1973). The similarity of the conformations of some diprotonated histamines, τ-methylhistamine and monoprotonated histamine, which is supposed to predominate in the physiological environment (Ganellin, Pepper, Port & Richards, 1973), suggests that either the τ-methyl group sterically hinders histamine–receptor interactions or an H atom at $N^τ$ is essential for these interactions and not the conformation itself. The findings are in agreement with a proton-transfer process proposed for the activation of the H_2 receptor (Weinstein, Chou, Johnson, Kang & Green, 1976; Weinstein, Mazurek, Osman & Topiol, 1986).

The crystal structure of the title complex is built up of τ-methylhistamine dications and $[CuCl_4]^{2-}$ anions connected by five N–H···Cl hydrogen bonds (Fig. 1). As there are four acceptor atoms (Cl) and four H atoms at positively charged N atoms, one of the bonds is bifurcated and one Cl atom participates in two hydrogen bonds. The mean N···Cl and H···Cl distances and N–H···Cl angles are 3.24 to 3.39, 2.2 to 2.7 Å and 130 to 167° (Table 2), respectively. The
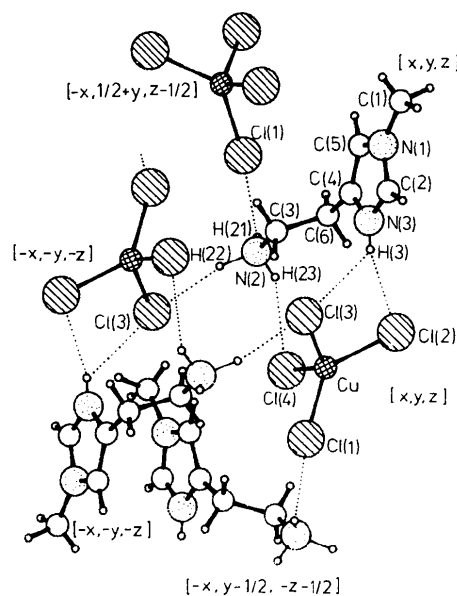

Fig. 1. Hydrogen bonds, general view of ions and numbering of atoms. The drawing was made with *PLUTO* (Motherwell, 1979).

$[CuCl_4]^{2-}$ anions are distinctly distorted. The Cl—Cu—Cl angles vary from 98·72 (4) to 134·32 (5)° and Cu—Cl bond lengths from 2·221 (1) to 2·272 (1) Å owing to different crystal environments.

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Structure of Dichloro[tetrakis(triphenylphosphine oxide)]iron(III) Tetrachloroferrate(III)

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Abstract. $C_{72}H_{60}Cl_2FeO_4P_4^+.Cl_4Fe^-$, $M_r = 1437\cdot53$, monoclinic, $P2_1/c$, $a = 14\cdot002$ (4), $b = 27\cdot718$ (7), $c = 18\cdot317$ (5) Å, $\beta = 104\cdot48$ (5)°, $V = 6883$ (4) Å^3, $Z = 4$, $D_m = 1\cdot389$ (1), $D_x = 1\cdot387$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 7\cdot47$ cm^{-1}, $F(000) = 2952$, room temperature, $R = 0\cdot0643$ for 6807 reflections. The structure consists of $[FeCl_2(OPPh_3)_4]^+$ cations (Ph = phenyl group) and $FeCl_4^-$ anions; the iron(III) atom in the complex cation is octahedrally coordinated by four O atoms from OPPh$_3$ ligands and by two Cl ligands with Fe—O interatomic distances in the range 2·005 (4)–2·019 (4) Å, and Fe—Cl distances 2·347 (2) and 2·353 (2) Å. The Cl—Fe—O bond angles in the cation are near to 90°, the Cl—Fe—Cl angle is 177·7 (1)°. The iron(III) atom in the anion is tetrahedrally coordinated by four Cl ligands with Fe—Cl distances in the range 2·111 (5)–2·217 (5) Å and Cl—Fe—Cl angles ranging from 104·3 (2) to 113·8 (2)°.

Introduction. Oxidation of triphenylphosphine (PPh$_3$) to triphenylphosphine oxide (OPPh$_3$) with O$_2$ in the presence of Fe compounds has been studied for Fe^{z+} + X^- + PPh$_3$ + O$_2$ + solvent systems ($z = 0$, 2 or 3; X = Cl, Br and NCS) (Ondrejkovičová, 1984). With acetonitrile as solvent, PPh$_3$ was oxidized to OPPh$_3$ (Vančová, Ondrejkovičová & Ondrejovič, 1984) and FeX_3(OPPh$_3$)$_2$ compounds were formed showing