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Crystal structure of 2-(1*H*-imidazol-3-ium-4-yl)ethanaminium dichloride, a re-determination

Samira Louhibi,[a] Imene Belfilali,[a] Leila Boukli-Hacene[a]* and Thierry Roisnel[b]

[a]Laboratoire de Chimie Inorganique et Environnement, Universite de Tlemcen, BP119, 13000, Tlemcen, Algeria, and [b]Centre de Diffractometrie X, UMR 6226 CNRS, Unite Sciences Chimiques de Rennes, Universite de Rennes I, 263 Avenue du General Leclerc, 35042 Rennes, France. *Correspondence e-mail: l_bouklihacene@mail.univ-tlemcen.dz, lilibou25@yahoo.fr

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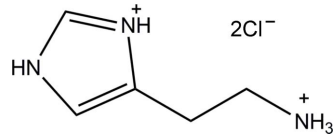
The crystal structure of the title molecular salt, $C_5H_{11}N_3^{+}\cdot 2Cl^{-}$, was redetermined. In comparison with the previous study [Bonnet *et al.* (1975). *Bull. Soc. Fr. Mineral. Crist.* **98**, 208–213.], the positions of some H atoms were corrected, allowing a more accurate description of the hydrogen-bonding scheme. In addition, the absolute structure was also determined. The maximum differences in terms of bond lengths and angles between the two determinations are 0.022 Å and 1.43°, respectively. The organic cation display a *anti* conformation of the protonated amine function and the imidazolium ring. The dihedral angle between the imidazolium plane and the plane through the C—C—N side chain is 29.58 (3)°. In the crystal, the organic cations and Cl^{-} anions are stacked alternatively into layers parallel to (100). N—H···Cl hydrogen bonds between all H atoms of the ammonium group and both N—H groups of the imidazolium ring and the Cl^{-} acceptor anions lead to the linkage of organic and inorganic layers into a three-dimensional network.

Keywords: crystal structure; histamine; redetermination; hydrogen bonding.

CCDC reference: 1051848

1. Related literature

Histamine [2-(1*H*-imidazol-4-yl)ethanamine] is a biogenic amine present in essentially all mammalian tissues and involved in several defense mechanisms of the body. It plays a role in various physiological processes, such as control of gastric acid secretion, neurotransmission, regulation of the microcirculation, and modulation of inflammatory (Cooper *et al.*, 1990; Barnes, 2001) and immunological reactions (Schwartz *et al.*, 1991; Bachert *et al.*, 1998; Emanuel *et al.*, 1999). The contribution of histamine in these physiological and pathological processes and the use in pharmacology make it an interesting substance in biochemistry (Leurs *et al.*, 1995; Galoppin & Ponvert, 1997; O'Mahony *et al.*, 2011; Jadidi-Niaragh & Mirshafiey, 2010; Gustiananda *et al.*, 2012). The structure of the title compound has been determined previously by Bonnet *et al.* (1975) who reported lattice parameters of a =7.596 (6), b = 12.706 (8), c = 4.457 (4) Å, β = 91.64 (5)° at room temperature. For the structure of the histamine copper(II) chloride complex and its catalytic activity study, see: Belfilali *et al.* (2015*a*), and for the structure of monopronated histamine with Cl^{-} as counter-anion, see: Belfilali *et al.* (2015*b*).



2. Experimental

2.1. Crystal data

$C_5H_{11}N_3^{+}\cdot 2Cl^{-}$
M_r = 184.07
Monoclinic, $P2_1$
a = 4.4358 (2) Å
b = 12.6281 (4) Å
c = 7.5588 (3) Å
β = 91.910 (1)°
V = 423.18 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.70 mm^{-1}
T = 150 K
0.43 × 0.32 × 0.09 mm

2.2. Data collection

Bruker APEXII CCD, diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2006)
T_{min} = 0.825, T_{max} = 0.939
3729 measured reflections
1855 independent reflections
1815 reflections with $I > 2\sigma(I)$
R_{int} = 0.024

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.058
S = 1.08
1855 reflections
106 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Absolute structure: Flack (1983), 841 Friedel pairs
Absolute structure parameter: 0.06 (5)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···Cl1^{i}	0.92 (3)	2.19 (3)	3.1071 (17)	171 (2)
N1—H1B···Cl1	0.95 (3)	2.34 (3)	3.1930 (17)	150 (2)
N1—H1C···Cl2^{i}	0.89 (3)	2.44 (3)	3.1768 (16)	141 (2)
N6—H6···Cl2^{ii}	0.88 (3)	2.28 (3)	3.1046 (16)	157 (2)
N8—H8···Cl2^{iii}	0.84 (3)	2.28 (3)	3.1157 (15)	169 (3)

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

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: WM5220).

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supporting information

Acta Cryst. (2015). E**71**, o844–o845 [https://doi.org/10.1107/S2056989015018848]

Crystal structure of 2-(1*H*-imidazol-3-ium-4-yl)ethanaminium dichloride, a re-determination

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S1. Synthesis and crystallization

A stoichiometric mixture of histamine dihydrochloride (1.0 mmol) and 3-ethoxy-4-hydroxybenzaldehyde was irradiated in a microwave oven at 200 Watt for 10 minutes. The reaction mixture was then allowed to attain room temperature and the obtained crystals were separated by filtration.

S2. Refinement

Hydrogen atoms linked to nitrogen atoms were found from Fourier difference maps and were refined with distance restraints in the range 0.84 (3) - 0.95 (3) Å and with a common U_{iso} parameter of 0.05 Å^2. C-bound hydrogen atoms were refined with calculated positions, with C—H = 0.95 and $U(H)_{iso} = 1.2U_{eq}(C)$ for aromatic H atoms and with C—H = 0.99 and $U(H)_{iso} = 1.2U_{eq}(C)$ for methylene H atoms.

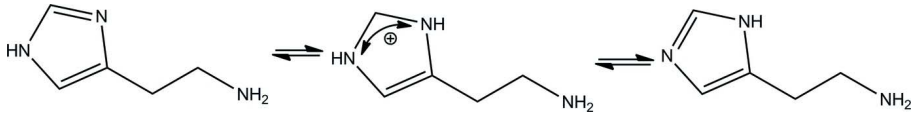

Figure 1

Tautomeric forms of histamine.

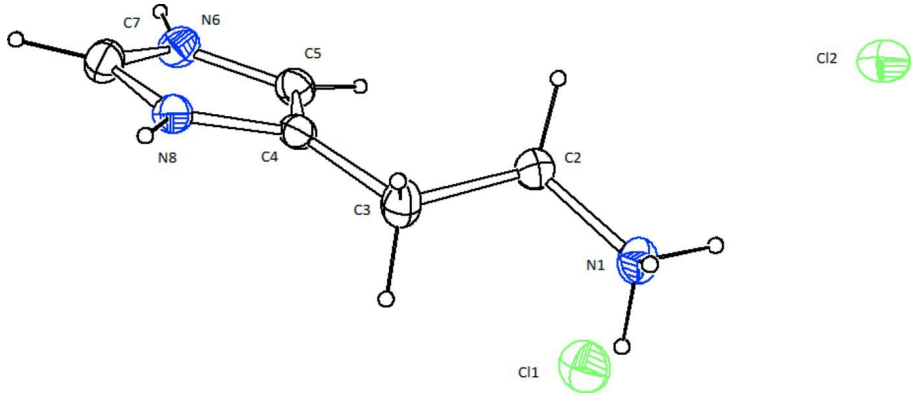

Figure 2

The molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

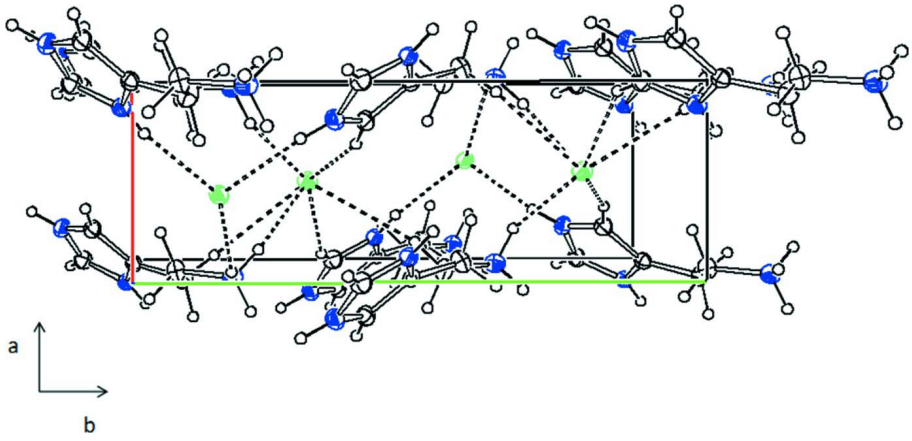

Figure 3

Part of the crystal structure with hydrogen bonds shown as dashed lines.

2-(1*H*-imidazol-3-ium-4-yl)ethanaminium dichloride

Crystal data

$C_5H_{11}N_3^{+}\cdot 2Cl^-$
$M_r = 184.07$
Monoclinic, $P2_1$
Hall symbol: P 2yb
$a = 4.4358$ (2) Å
$b = 12.6281$ (4) Å
$c = 7.5588$ (3) Å
$\beta = 91.910$ (1)°
$V = 423.18$ (3) Å^3
$Z = 2$
$F(000) = 192$
$D_x = 1.445$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2786 reflections
$\theta = 2.7$–$27.5°$
$\mu = 0.70$ mm^{-1}
$T = 150$ K
Prism, colourless
0.43 × 0.32 × 0.09 mm

Data collection

Bruker APEXII CCD, diffractometer
Graphite monochromator
CCD rotation images, thin slices scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2006)
$T_{min} = 0.825$, $T_{max} = 0.939$
3729 measured reflections
1855 independent reflections
1815 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.1°$
$h = -5\rightarrow5$
$k = -16\rightarrow13$
$l = -9\rightarrow9$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.058$
$S = 1.08$
1855 reflections
106 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0327P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e Å^{-3}
Absolute structure: Flack (1983), 841 Friedel pairs
Absolute structure parameter: 0.06 (5)

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.9759 (4)	0.18301 (13)	0.4308 (2)	0.0201 (3)
H1A	1.115 (6)	0.232 (2)	0.472 (3)	0.05*
H1B	0.787 (6)	0.217 (2)	0.441 (3)	0.05*
H1C	1.015 (6)	0.179 (2)	0.316 (4)	0.05*
C2	0.9990 (5)	0.07908 (15)	0.5236 (2)	0.0209 (4)
H2A	1.2044	0.0497	0.5125	0.025*
H2B	0.853	0.0285	0.469	0.025*
C3	0.9317 (4)	0.09457 (15)	0.7190 (2)	0.0214 (4)
H3A	1.053	0.1545	0.7669	0.026*
H3B	0.716	0.1127	0.7299	0.026*
C4	1.0019 (4)	−0.00243 (13)	0.8252 (2)	0.0160 (3)
C5	1.1983 (4)	−0.08313 (15)	0.8024 (2)	0.0189 (3)
H5	1.3185	−0.0945	0.7025	0.023*
N6	1.1904 (3)	−0.14577 (12)	0.95191 (19)	0.0206 (3)
H6	1.284 (6)	−0.206 (2)	0.964 (3)	0.05*
C7	0.9952 (4)	−0.10582 (15)	1.0615 (2)	0.0211 (4)
H7	0.9475	−0.1342	1.1736	0.025*
N8	0.8764 (3)	−0.01892 (12)	0.98803 (17)	0.0168 (3)
H8	0.745 (6)	0.021 (2)	1.031 (4)	0.05*
Cl1	0.47163 (8)	0.32961 (3)	0.59693 (5)	0.02068 (11)
Cl2	0.43148 (9)	0.15270 (3)	0.11930 (5)	0.01937 (11)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0192 (7)	0.0233 (9)	0.0178 (7)	−0.0004 (6)	0.0021 (6)	0.0025 (6)
C2	0.0264 (9)	0.0187 (9)	0.0175 (9)	−0.0022 (7)	0.0010 (7)	−0.0001 (7)
C3	0.0267 (9)	0.0202 (9)	0.0174 (8)	0.0047 (8)	0.0036 (7)	0.0012 (7)
C4	0.0168 (7)	0.0158 (8)	0.0155 (7)	−0.0017 (7)	0.0002 (6)	−0.0027 (6)
C5	0.0208 (8)	0.0177 (8)	0.0183 (8)	0.0006 (7)	0.0026 (6)	−0.0036 (7)
N6	0.0214 (7)	0.0173 (8)	0.0233 (7)	0.0014 (6)	0.0018 (6)	0.0014 (6)
C7	0.0225 (9)	0.0215 (9)	0.0195 (7)	−0.0013 (7)	0.0008 (7)	0.0033 (7)
N8	0.0167 (7)	0.0168 (7)	0.0173 (7)	−0.0009 (6)	0.0032 (5)	−0.0017 (5)
Cl1	0.01948 (19)	0.0235 (2)	0.01936 (17)	−0.00067 (18)	0.00474 (13)	−0.00219 (16)
Cl2	0.01775 (18)	0.0187 (2)	0.02194 (18)	−0.00186 (17)	0.00442 (13)	−0.00354 (15)

Geometric parameters (Å, º)

N1—C2	1.490 (2)	C4—C5	1.355 (3)
N1—H1A	0.92 (3)	C4—N8	1.383 (2)
N1—H1B	0.95 (3)	C5—N6	1.381 (2)
N1—H1C	0.89 (3)	C5—H5	0.95
C2—C3	1.530 (2)	N6—C7	1.319 (2)
C2—H2A	0.99	N6—H6	0.88 (3)
C2—H2B	0.99	C7—N8	1.331 (2)
C3—C4	1.492 (2)	C7—H7	0.95
C3—H3A	0.99	N8—H8	0.84 (3)
C3—H3B	0.99		
C2—N1—H1A	113.7 (15)	H3A—C3—H3B	107.9
C2—N1—H1B	113.9 (15)	C5—C4—N8	106.22 (14)
H1A—N1—H1B	105 (2)	C5—C4—C3	132.25 (16)
C2—N1—H1C	112.9 (18)	N8—C4—C3	121.30 (14)
H1A—N1—H1C	103 (2)	C4—C5—N6	107.03 (15)
H1B—N1—H1C	108 (2)	C4—C5—H5	126.5
N1—C2—C3	109.22 (15)	N6—C5—H5	126.5
N1—C2—H2A	109.8	C7—N6—C5	109.26 (15)
C3—C2—H2A	109.8	C7—N6—H6	126.0 (18)
N1—C2—H2B	109.8	C5—N6—H6	124.3 (17)
C3—C2—H2B	109.8	N6—C7—N8	108.21 (15)
H2A—C2—H2B	108.3	N6—C7—H7	125.9
C4—C3—C2	111.78 (14)	N8—C7—H7	125.9
C4—C3—H3A	109.3	C7—N8—C4	109.27 (14)
C2—C3—H3A	109.3	C7—N8—H8	126.6 (18)
C4—C3—H3B	109.3	C4—N8—H8	124.2 (18)
C2—C3—H3B	109.3		
N1—C2—C3—C4	−170.28 (15)	C4—C5—N6—C7	0.6 (2)
C2—C3—C4—C5	26.5 (3)	C5—N6—C7—N8	−0.2 (2)
C2—C3—C4—N8	−159.79 (15)	N6—C7—N8—C4	−0.27 (19)
N8—C4—C5—N6	−0.70 (17)	C5—C4—N8—C7	0.61 (17)
C3—C4—C5—N6	173.73 (18)	C3—C4—N8—C7	−174.57 (16)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···Cl1^{i}	0.92 (3)	2.19 (3)	3.1071 (17)	171 (2)
N1—H1*B*···Cl1	0.95 (3)	2.34 (3)	3.1930 (17)	150 (2)
N1—H1*C*···Cl2^{i}	0.89 (3)	2.44 (3)	3.1768 (16)	141 (2)
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Symmetry codes: (i) *x*+1, *y*, *z*; (ii) −*x*+2, *y*−1/2, −*z*+1; (iii) *x*, *y*, *z*+1.