



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

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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 displays 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.

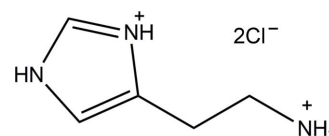
Keywords: crystal structure; histamine; redetermination; hydrogen bonding.

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, $\beta = 91.64$ (5)° at room temperature. For the structure of the histamine copper(II) chloride complex and its catalytic activity study, see: Belfilali *et al.* (2015a), and for the structure of monoprotonated histamine with Cl^- as counter-anion, see: Belfilali *et al.* (2015b).



2. Experimental

2.1. Crystal data

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

2.2. Data collection

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

2.3. Refinement

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

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|----------------------------|----------|--------------|--------------|----------------|
| 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). E71, 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 Å². C-bound hydrogen atoms were refined with calculated positions, with C—H = 0.95 and $U(\text{H})_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$ for aromatic H atoms and with C—H = 0.99 and $U(\text{H})_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$ for methylene H atoms.

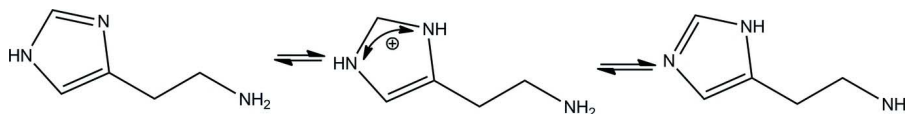


Figure 1

Tautomeric forms of histamine.

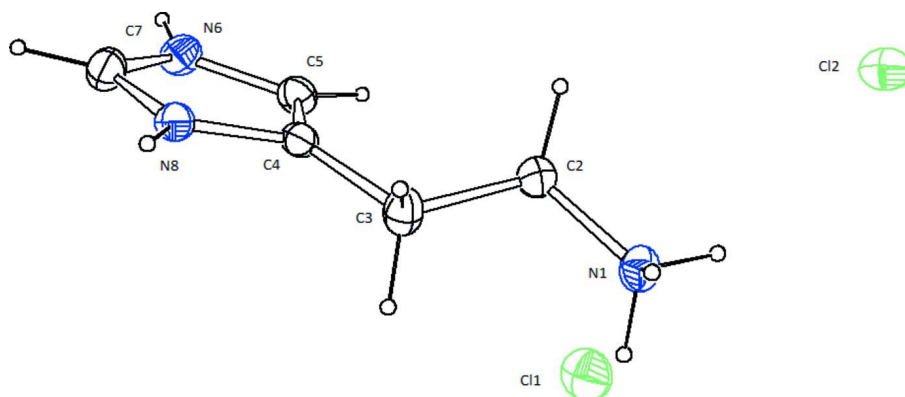


Figure 2

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

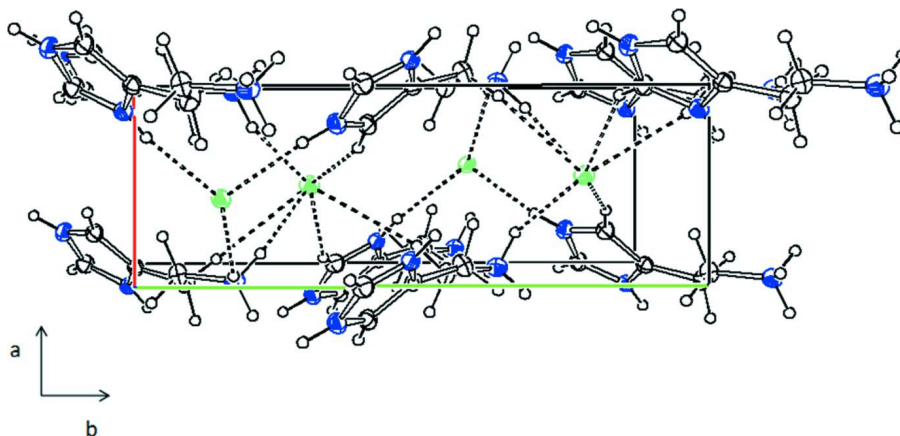


Figure 3

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

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

Crystal data

$\text{C}_5\text{H}_{11}\text{N}_3^+ \cdot 2\text{Cl}^-$

$M_r = 184.07$

Monoclinic, $P2_1$

Hall symbol: $P\ 2_1yb$

$a = 4.4358\ (2)\ \text{\AA}$

$b = 12.6281\ (4)\ \text{\AA}$

$c = 7.5588\ (3)\ \text{\AA}$

$\beta = 91.910\ (1)^\circ$

$V = 423.18\ (3)\ \text{\AA}^3$

$Z = 2$

$F(000) = 192$

$D_x = 1.445\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2786 reflections

$\theta = 2.7\text{--}27.5^\circ$

$\mu = 0.70\ \text{mm}^{-1}$

$T = 150\ \text{K}$

Prism, colourless

$0.43 \times 0.32 \times 0.09\ \text{mm}$

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 $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 3.1^\circ$

$h = -5 \rightarrow 5$

$k = -16 \rightarrow 13$

$l = -9 \rightarrow 9$

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 $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.22\ \text{e \AA}^{-3}$

$\Delta\rho_{\min} = -0.17\ \text{e \AA}^{-3}$

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 (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|-------------|---------------|--------------|----------------------------------|
| 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 (\AA^2)

| | 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, °)

| | | | |
|-------------|--------------|-------------|--------------|
| 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, °)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|-----------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N1—H1A \cdots Cl1 ⁱ | 0.92 (3) | 2.19 (3) | 3.1071 (17) | 171 (2) |
| N1—H1B \cdots Cl1 | 0.95 (3) | 2.34 (3) | 3.1930 (17) | 150 (2) |
| N1—H1C \cdots Cl2 ⁱ | 0.89 (3) | 2.44 (3) | 3.1768 (16) | 141 (2) |
| N6—H6 \cdots Cl2 ⁱⁱ | 0.88 (3) | 2.28 (3) | 3.1046 (16) | 157 (2) |
| N8—H8 \cdots Cl2 ⁱⁱⁱ | 0.84 (3) | 2.28 (3) | 3.1157 (15) | 169 (3) |

Symmetry codes: (i) $x+1, y, z$; (ii) $-x+2, y-1/2, -z+1$; (iii) $x, y, z+1$.