

1-Carboxymethyl-2-ethyl-4-methyl-1*H*-imidazol-3-ium chloride monohydrate

Chuan-Qing Chen,^a Shi-Neng Luo,^{b*} Jian-Guo Lin,^b Ling Qiu^b and Yong-Mei Xia^a

^aSchool of Chemical and Materials Engineering, Jiangnan University, Wuxi 214122, People's Republic of China, and ^bThe Key Laboratory of Nuclear Medicine, Ministry of Health, Jiangsu Institute of Nuclear Medicine, Wuxi, 214063, People's Republic of China

Correspondence e-mail: shineng914@yahoo.com.cn

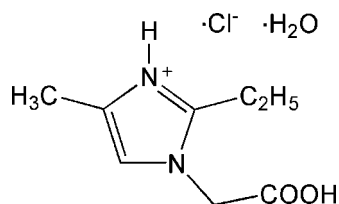
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Key indicators: single-crystal X-ray study; $T = 93$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.036; wR factor = 0.099; data-to-parameter ratio = 17.5.

In the title compound, $\text{C}_8\text{H}_{13}\text{N}_2\text{O}_2^+\cdot\text{Cl}^-\cdot\text{H}_2\text{O}$, the methyl C atom of the ethyl group is slightly out of the imidazole plane, with an N—C(ring)—C—C torsion angle of -15.1 (2)°. In the crystal structure, there are strong intermolecular hydrogen-bonding interactions between the solvent water molecule, the free chloride anion and the organic cation, resulting in a two-dimensional supramolecular network in the *ab* plane.

Related literature

The title compound is a vital intermediate in the synthesis of bisphosphonic acid, *i.e.* 2-(2-ethyl-4-methyl-1*H*-imidazol-1-yl)-1-hydroxyethane-1,1-diylidiphosphonic acid; for a general background on bisphosphonates, see: Dawson (2003); Vasireddy *et al.* (2003). For related structures, see: Gao *et al.* (2004); Barczynski *et al.* (2008). For the synthesis, see: Zederenko *et al.* (1994).



Experimental

Crystal data

$\text{C}_8\text{H}_{13}\text{N}_2\text{O}_2^+\cdot\text{Cl}^-\cdot\text{H}_2\text{O}$
 $M_r = 222.67$

Monoclinic, $P2_1/n$

$a = 11.077$ (2) Å

$b = 8.4542$ (18) Å

$c = 11.938$ (3) Å

$\beta = 90.265$ (3)°

$V = 1117.9$ (4) Å³

$Z = 4$

Mo $K\alpha$ radiation

$\mu = 0.33$ mm⁻¹

$T = 93$ K

$0.40 \times 0.40 \times 0.35$ mm

Data collection

Rigaku SPIDER diffractometer

Absorption correction: multi-scan

(RAPID-AUTO; Rigaku, 2004)

$T_{\min} = 0.880$, $T_{\max} = 0.894$

8869 measured reflections

2532 independent reflections

2203 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.031$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.099$

$S = 1.00$

2532 reflections

145 parameters

1 restraint

H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{\text{max}} = 0.29$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.20$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1N}\cdots\text{Cl1}$	0.881 (17)	2.300 (18)	3.1635 (14)	166.6 (15)
$\text{O3}-\text{H3A}\cdots\text{Cl1}$	0.91 (2)	2.20 (2)	3.1062 (14)	177 (2)
$\text{O1}-\text{H1O}\cdots\text{O3}^{\text{i}}$	0.96 (2)	1.60 (2)	2.5557 (16)	170 (2)
$\text{O3}-\text{H3B}\cdots\text{Cl1}^{\text{ii}}$	0.96 (2)	2.14 (2)	3.0860 (14)	168.2 (19)

Symmetry codes: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$.

Data collection: RAPID-AUTO (Rigaku, 2004); cell refinement: RAPID-AUTO; data reduction: RAPID-AUTO; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2205).

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supplementary materials

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1-Carboxymethyl-2-ethyl-4-methyl-1*H*-imidazol-3-ium chloride monohydrate

C.-Q. Chen, S.-N. Luo, J.-G. Lin, L. Qiu and Y.-M. Xia

Comment

Bisphosphonates with an imidazole ring, namely zoledronate, are effective bone-specific palliative treatments that reduce tumor-induced skeletal complications. With this idea in mind, we intend to synthesis one of the third-generation bisphosphonate compound, 2-(2-ethyl-4-methyl-1*H*-imidazol-1-yl)-1-*H*-hydroxyethane-1,1- bisphosphonic acid, which is potentially used for treatment of patients. As a vital intermediate compound for the stepwise reactions of the bisphosphonic acid, the synthesis and crystal structure of the title compound has been reported herein.

In the title compound (I) (Fig. 1), $C_8H_{13}N_2O_2^+.Cl^- \cdot H_2O$, all the carbon atoms (C4, C5 and C7) linked to the imidazole ring are almost coplanar with the imidazole ring. The ethyl is slightly out of the imidazole plane with an N1—C3(ring)—C5—C6 torsion angle of $-15.116(211)^\circ$. While the 1-substituted acetic acid group is approximately perpendicular to the imidazole ring [dihedral angle = $77.438(111)^\circ$]. There are strong intermolecular hydrogen interactions between the free water molecule (O3), the free chloride anion (Cl1), and the O1 and N1 from the organic cation (Table 1). And the crystal structure is stabilized by these strong hydrogen bond interactions to form two-dimensional supramolecular network along *ab* plane (Table 1 and Fig. 2).

Experimental

The title compound (I) was synthesized according to previous literature (Zederenko *et al.*, 1994). After reaction, a white powder was obtained (yield 65%). Mp 170–171 °C. Then, compound (I) was recrystallized from acetone solvent; colourless block-shaped crystals were formed after several days (yield 61%). Analysis calculated for $C_8H_{15}ClN_2O_3$: C 43.15, H 6.79, N 12.58%; found: C 43.01, H 6.96, N 12.45%.

Figures

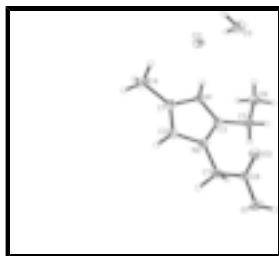


Fig. 1. The molecular structure of (I), with atom labels and 30% probability displacement ellipsoids for non-H atoms.

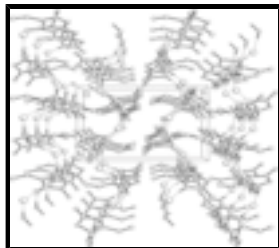


Fig. 2. Perspective view of the supramolecular network built from strong intermolecular hydrogen bonds (dashed lines). H atoms not involved in hydrogen bonds have been omitted.

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Crystal data

$C_8H_{13}N_2O_2^+ \cdot Cl^- \cdot H_2O$

$M_r = 222.67$

Monoclinic, $P2_1/n$

Hall symbol: $-P\ 2yn$

$a = 11.077\ (2)\ \text{\AA}$

$b = 8.4542\ (18)\ \text{\AA}$

$c = 11.938\ (3)\ \text{\AA}$

$\beta = 90.265\ (3)^\circ$

$V = 1117.9\ (4)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 472$

$D_x = 1.323\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 3544 reflections

$\theta = 3.0\text{--}27.5^\circ$

$\mu = 0.33\ \text{mm}^{-1}$

$T = 93\ \text{K}$

Block, colorless

$0.40 \times 0.40 \times 0.35\ \text{mm}$

Data collection

Rigaku SPIDER
diffractometer

Radiation source: Rotating Anode

Monochromator: graphite

$T = 93\ \text{K}$

ω scans

Absorption correction: multi-scan
(RAPID-AUTO; Rigaku, 2004)

$T_{\min} = 0.880$, $T_{\max} = 0.894$

8869 measured reflections

2532 independent reflections

2203 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.031$

$\theta_{\max} = 27.5^\circ$

$\theta_{\min} = 3.0^\circ$

$h = -13 \rightarrow 14$

$k = -10 \rightarrow 10$

$l = -15 \rightarrow 14$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.099$

$S = 1.00$

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

$w = 1/[\sigma^2(F_o^2) + (0.0582P)^2 + 0.06P]$

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

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

2532 reflections $\Delta\rho_{\max} = 0.29 \text{ e } \text{\AA}^{-3}$
 145 parameters $\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$
 1 restraint Extinction correction: none
 Primary atom site location: structure-invariant direct methods

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.19761 (3)	0.57092 (4)	0.31835 (3)	0.02509 (14)
O1	0.88525 (10)	0.95264 (13)	0.14174 (10)	0.0295 (3)
O2	0.79630 (9)	0.72040 (13)	0.17923 (9)	0.0273 (3)
O3	0.40590 (10)	0.32662 (16)	0.33959 (12)	0.0382 (3)
N1	0.42391 (11)	0.70595 (14)	0.18900 (10)	0.0184 (3)
N2	0.57147 (10)	0.84373 (14)	0.12622 (10)	0.0184 (3)
C1	0.42085 (12)	0.68984 (18)	0.07348 (12)	0.0210 (3)
C2	0.51409 (12)	0.77535 (17)	0.03442 (12)	0.0211 (3)
H2	0.5366	0.7869	-0.0418	0.025*
C3	0.51465 (12)	0.79974 (16)	0.21927 (12)	0.0178 (3)
C4	0.32597 (14)	0.5958 (2)	0.01537 (14)	0.0292 (4)
H4A	0.3426	0.5934	-0.0652	0.035*
H4B	0.2469	0.6445	0.0281	0.035*
H4C	0.3258	0.4877	0.0449	0.035*
C5	0.54916 (13)	0.84647 (19)	0.33464 (12)	0.0234 (3)
H5A	0.5677	0.9610	0.3355	0.028*
H5B	0.6236	0.7891	0.3562	0.028*
C6	0.45261 (15)	0.8131 (2)	0.42068 (13)	0.0304 (4)
H6A	0.3789	0.8710	0.4008	0.037*
H6B	0.4809	0.8473	0.4947	0.037*
H6C	0.4355	0.6994	0.4222	0.037*
C7	0.67760 (12)	0.94450 (17)	0.12097 (12)	0.0202 (3)
H7A	0.6672	1.0345	0.1731	0.024*
H7B	0.6849	0.9879	0.0443	0.024*
C8	0.79233 (12)	0.85727 (18)	0.15091 (12)	0.0205 (3)
H1N	0.3693 (15)	0.667 (2)	0.2348 (14)	0.027 (4)*
H1O	0.961 (2)	0.900 (3)	0.1558 (18)	0.060 (7)*

supplementary materials

H3A	0.344 (2)	0.397 (3)	0.336 (2)	0.077 (8)*
H3B	0.385 (2)	0.243 (3)	0.289 (2)	0.067 (7)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0190 (2)	0.0276 (2)	0.0287 (2)	-0.00309 (14)	0.00545 (15)	-0.00028 (14)
O1	0.0168 (5)	0.0245 (6)	0.0472 (7)	-0.0020 (5)	0.0009 (5)	0.0008 (5)
O2	0.0199 (5)	0.0236 (6)	0.0384 (6)	0.0035 (4)	0.0019 (5)	0.0087 (5)
O3	0.0206 (6)	0.0333 (7)	0.0605 (9)	0.0012 (5)	-0.0053 (6)	-0.0059 (6)
N1	0.0141 (6)	0.0215 (6)	0.0196 (6)	-0.0007 (5)	0.0018 (5)	-0.0005 (5)
N2	0.0139 (6)	0.0212 (6)	0.0202 (6)	0.0015 (5)	0.0002 (5)	0.0007 (5)
C1	0.0162 (7)	0.0250 (8)	0.0220 (7)	0.0033 (6)	-0.0002 (6)	-0.0028 (6)
C2	0.0178 (7)	0.0276 (8)	0.0178 (7)	0.0040 (6)	0.0004 (5)	-0.0008 (6)
C3	0.0139 (6)	0.0179 (7)	0.0217 (7)	0.0029 (5)	0.0018 (5)	-0.0005 (5)
C4	0.0202 (8)	0.0392 (10)	0.0281 (8)	-0.0016 (7)	-0.0013 (6)	-0.0088 (7)
C5	0.0236 (8)	0.0269 (8)	0.0197 (7)	-0.0040 (6)	-0.0004 (6)	-0.0027 (6)
C6	0.0303 (9)	0.0381 (10)	0.0229 (8)	-0.0054 (7)	0.0031 (7)	-0.0040 (7)
C7	0.0165 (7)	0.0195 (7)	0.0247 (7)	-0.0007 (6)	0.0021 (6)	0.0018 (5)
C8	0.0173 (7)	0.0232 (8)	0.0211 (7)	-0.0001 (6)	0.0021 (6)	-0.0003 (6)

Geometric parameters (\AA , $^\circ$)

O1—C8	1.3125 (18)	C3—C5	1.481 (2)
O1—H1O	0.96 (2)	C4—H4A	0.9800
O2—C8	1.2063 (18)	C4—H4B	0.9800
O3—H3A	0.91 (2)	C4—H4C	0.9800
O3—H3B	0.96 (2)	C5—C6	1.513 (2)
N1—C3	1.3290 (18)	C5—H5A	0.9900
N1—C1	1.3860 (18)	C5—H5B	0.9900
N1—H1N	0.881 (17)	C6—H6A	0.9800
N2—C3	1.3322 (18)	C6—H6B	0.9800
N2—C2	1.3903 (18)	C6—H6C	0.9800
N2—C7	1.4534 (18)	C7—C8	1.5109 (19)
C1—C2	1.346 (2)	C7—H7A	0.9900
C1—C4	1.487 (2)	C7—H7B	0.9900
C2—H2	0.9500		
C8—O1—H1O	112.3 (13)	H4B—C4—H4C	109.5
H3A—O3—H3B	106.1 (16)	C3—C5—C6	113.66 (12)
C3—N1—C1	110.13 (12)	C3—C5—H5A	108.8
C3—N1—H1N	125.1 (11)	C6—C5—H5A	108.8
C1—N1—H1N	124.5 (11)	C3—C5—H5B	108.8
C3—N2—C2	108.97 (12)	C6—C5—H5B	108.8
C3—N2—C7	125.80 (12)	H5A—C5—H5B	107.7
C2—N2—C7	125.22 (12)	C5—C6—H6A	109.5
C2—C1—N1	106.06 (12)	C5—C6—H6B	109.5
C2—C1—C4	131.87 (14)	H6A—C6—H6B	109.5
N1—C1—C4	122.06 (13)	C5—C6—H6C	109.5

C1—C2—N2	107.40 (13)	H6A—C6—H6C	109.5
C1—C2—H2	126.3	H6B—C6—H6C	109.5
N2—C2—H2	126.3	N2—C7—C8	112.54 (12)
N1—C3—N2	107.43 (12)	N2—C7—H7A	109.1
N1—C3—C5	127.13 (13)	C8—C7—H7A	109.1
N2—C3—C5	125.44 (13)	N2—C7—H7B	109.1
C1—C4—H4A	109.5	C8—C7—H7B	109.1
C1—C4—H4B	109.5	H7A—C7—H7B	107.8
H4A—C4—H4B	109.5	O2—C8—O1	125.81 (14)
C1—C4—H4C	109.5	O2—C8—C7	124.34 (13)
H4A—C4—H4C	109.5	O1—C8—C7	109.85 (13)
C3—N1—C1—C2	0.88 (16)	C7—N2—C3—N1	-178.83 (12)
C3—N1—C1—C4	-177.84 (13)	C2—N2—C3—C5	179.31 (13)
N1—C1—C2—N2	-0.76 (16)	C7—N2—C3—C5	0.3 (2)
C4—C1—C2—N2	177.78 (15)	N1—C3—C5—C6	-15.1 (2)
C3—N2—C2—C1	0.40 (16)	N2—C3—C5—C6	165.88 (14)
C7—N2—C2—C1	179.39 (13)	C3—N2—C7—C8	77.86 (17)
C1—N1—C3—N2	-0.63 (16)	C2—N2—C7—C8	-100.96 (15)
C1—N1—C3—C5	-179.78 (14)	N2—C7—C8—O2	-2.0 (2)
C2—N2—C3—N1	0.14 (15)	N2—C7—C8—O1	178.25 (12)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1N...C11	0.881 (17)	2.300 (18)	3.1635 (14)	166.6 (15)
O3—H3A...C11	0.91 (2)	2.20 (2)	3.1062 (14)	177 (2)
O1—H1O...O3 ⁱ	0.96 (2)	1.60 (2)	2.5557 (16)	170 (2)
O3—H3B...C11 ⁱⁱ	0.96 (2)	2.14 (2)	3.0860 (14)	168.2 (19)

Symmetry codes: (i) $-x+3/2, y+1/2, -z+1/2$; (ii) $-x+1/2, y-1/2, -z+1/2$.

Fig. 1

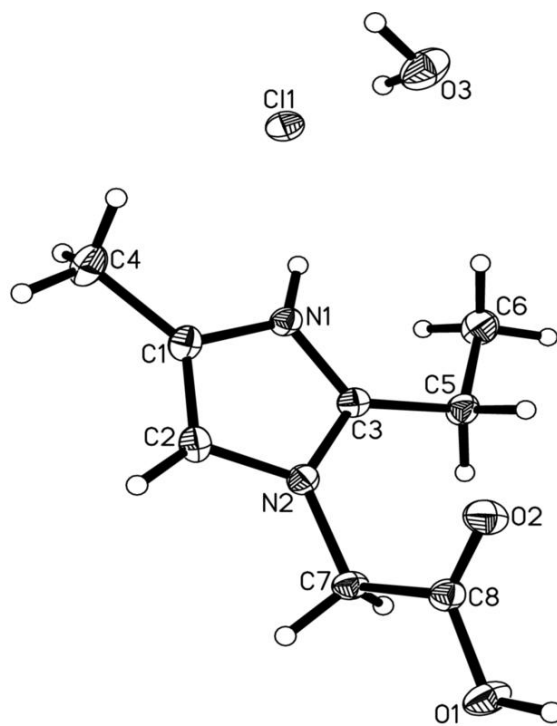


Fig. 2

