

Hydrogen bonding in cytosinium dihydrogen phosphite

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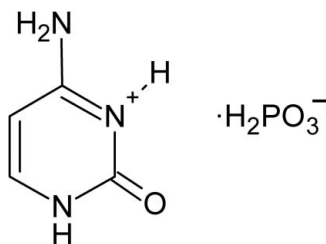
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.035; wR factor = 0.084; data-to-parameter ratio = 13.4.

In the title compound, $\text{C}_4\text{H}_8\text{N}_3\text{O}_4\text{P}^+\cdot\text{H}_2\text{PO}_3^-$, the cytosine molecule is monoprotonated and the phosphoric acid is in the monoionized state. Strong hydrogen bonds, dominated by $\text{N}-\text{H}\cdots\text{O}$ interactions, are responsible for cohesion between the organic and inorganic layers and maintain the stability of this structure.

Related literature

For general background, see: Jeffrey & Saenger (1991); Kabanos *et al.* (1992); Weber & Craven (1990); Sivanesan *et al.* (2000). For hydrogen bonds, see: Blessing (1986); Masse & Levy (1991). For related structures, see: Bendheif *et al.* (2003); Bouchouit *et al.* (2005); Benali-Cherif, Abouimrane *et al.* (2002); Benali-Cherif *et al.* (2007); Benali-Cherif, Benguedouar *et al.* (2002); Bendjeddou *et al.* (2003); Cherouana, Benali-Cherif & Bendjeddou (2003); Cherouana, Bouchouit *et al.* (2003); Messai *et al.* (2009).



Experimental

Crystal data

$\text{C}_4\text{H}_8\text{N}_3\text{O}^+\cdot\text{H}_2\text{PO}_3^-$
 $M_r = 193.10$
 Triclinic, $P1$
 $a = 4.5625$ (3) Å
 $b = 6.4739$ (4) Å

$c = 6.5933$ (6) Å
 $\alpha = 92.934$ (4)°
 $\beta = 91.236$ (4)°
 $\gamma = 98.627$ (5)°
 $V = 192.21$ (2) Å³

$Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 0.34$ mm⁻¹

$T = 293$ K
 $0.1 \times 0.1 \times 0.1$ mm

Data collection

Nonius KappaCCD diffractometer
 Absorption correction: none
 1500 measured reflections

1500 independent reflections
 1430 reflections with $I > 2\sigma(I)$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.084$
 $S = 1.13$
 1500 reflections
 112 parameters
 4 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.25$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.33$ e Å⁻³
 Absolute structure: Flack (1983), 580 with Friedel pairs
 Flack parameter: 0.06 (10)

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1}\cdots\text{O2}^{\text{i}}$	0.86	1.86	2.713 (3)	170
$\text{O1}-\text{H1A}\cdots\text{O3}^{\text{ii}}$	0.82	1.75	2.542 (3)	163
$\text{N3}-\text{H3}\cdots\text{O3}^{\text{iii}}$	0.86	1.94	2.797 (3)	175
$\text{N8}-\text{H7}\cdots\text{O2}^{\text{iii}}$	0.86	1.89	2.750 (3)	178
$\text{N8}-\text{H8}\cdots\text{O1}^{\text{ii}}$	0.86	2.29	3.034 (3)	145
$\text{N8}-\text{H8}\cdots\text{O3}^{\text{ii}}$	0.86	2.44	3.153 (3)	141

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

Data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GW2061).

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Acta Cryst. (2009). E65, o1147–o1148 [doi:10.1107/S1600536809014020]

Hydrogen bonding in cytosinium dihydrogen phosphite

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S1. Comment

Studies of metal ion–nucleic acid interactions are of great current interest, since metal ions play a crucial role in the structure and function of nucleic acid and genetic information transfer (Kabanos *et al.*, 1992). Cytosine (6-amino-pyrimidin-2-one) is one of the pyrimidines found in deoxyribonucleic acids. It has been the subject of several investigations with the aim of studying the electrostatic properties of its monohydrate form (Weber & Craven, 1990), the relative stabilities of its tautomeric forms and its hydration effects and hydrogen bonding (Sivanesan *et al.*, 2000).

In several crystal structures of purines and pyrimidines with inorganic anions, the structural cohesion is assured by strong hydrogen bonds, as was observed in guaninium sulfate monohydrate (Cherouana, Benali-Cherif & Bendjeddou, 2003) and adeninium perchlorate (Bendjeddou *et al.*, 2003). The potential importance of hydrogen bonding in the structure and function of biomolecules has been well established (Jeffrey & Saenger, 1991); in particular, N—H \cdots O hydrogen bonds are most predominant in determining the formation of secondary structure elements in proteins, base-pairing in nucleic acids and their biomolecular interactions. This structure analysis of cytosinium hydrogenphosphite (I) was undertaken as part of a more general investigation into the nature of hydrogen bonding between organic bases or amino acids and inorganic acids in their crystalline forms (Messai *et al.*, 2009; Benali-Cherif, Abouimrane *et al.*, 2002; Benali-Cherif, Benguedouar *et al.*, 2002; Benali-Cherif *et al.*, 2007).

The asymmetric unit contains one protonated cytosine rings and one hydrogenphosphite anion (Fig. 1). The main feature of the alkyl or aryl ammonium hydrogenphosphite is that the anionic subnetwork is built up through short strong hydrogen bonds (Blessing, 1986) and the organic cations are bonded to the phosphite layers by weaker hydrogen bonds (Masse & Levy, 1991) forming a two-dimensional network of hydrogen bonds (Fig. 2).

The inorganic moiety is a network of H₂P O₃⁻ tetrahedra, connected by short and strong hydrogen bonds. Inside these chains each H₂P O₃⁻ group is connected to its two adjacent neighbours by strong hydrogen bonds (O5—H2 \cdots O3) to build a two-dimensional network along the *c* direction. Some similarities may be observed between the present atomic arrangement and the corresponding hydrogenphosphites investigated earlier (Bendheif *et al.*, 2003). cytosine is monoprotonated at atom N3. Some base stacking is retained and hydrogen bonding between cytosine rings, as found cytosinium nitrate (Cherouana, Bouchouit *et al.*, 2003), and cytosinium oxalate monohydrate (Bouchouit *et al.*, 2005) are observed. The pyrimidine ring bond distances are, in general, not significantly different from those found in cytosine or cytosine monohydrate. Each ring is linked to three nitrate anions by strong N—H \cdots O hydrogen bonds *via* atoms N1, N3 and N8. The shortest hydrogen bond is observed between the protonated atom N3 of pyrimidine and atom O3 of hydrogenphosphite.

S2. Experimental

The title compound (I) was crystallized from a 1:1 aqueous solution of cytosine [4-aminopyrimidine-2(1*H*)-one] and phosphorous acid. Yellow crystals grew after a few days, at room temperature and were manually separated for single-

crystal X-ray analysis.

S3. Refinement

The title compound crystallizes in the non centrosymmetric space group P_1 . All non-H atoms were refined with anisotropic atomic displacement parameters. All H atoms were located in Fourier maps; and treated as riding on their parent atoms, with C—H = 0.93 Å, N—H = 0.86 Å, O—H = 0.82 Å, P—H = 1.30 Å, $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C,N,P})$ and $U_{\text{iso}} = 1.5U_{\text{eq}}(\text{O})$.

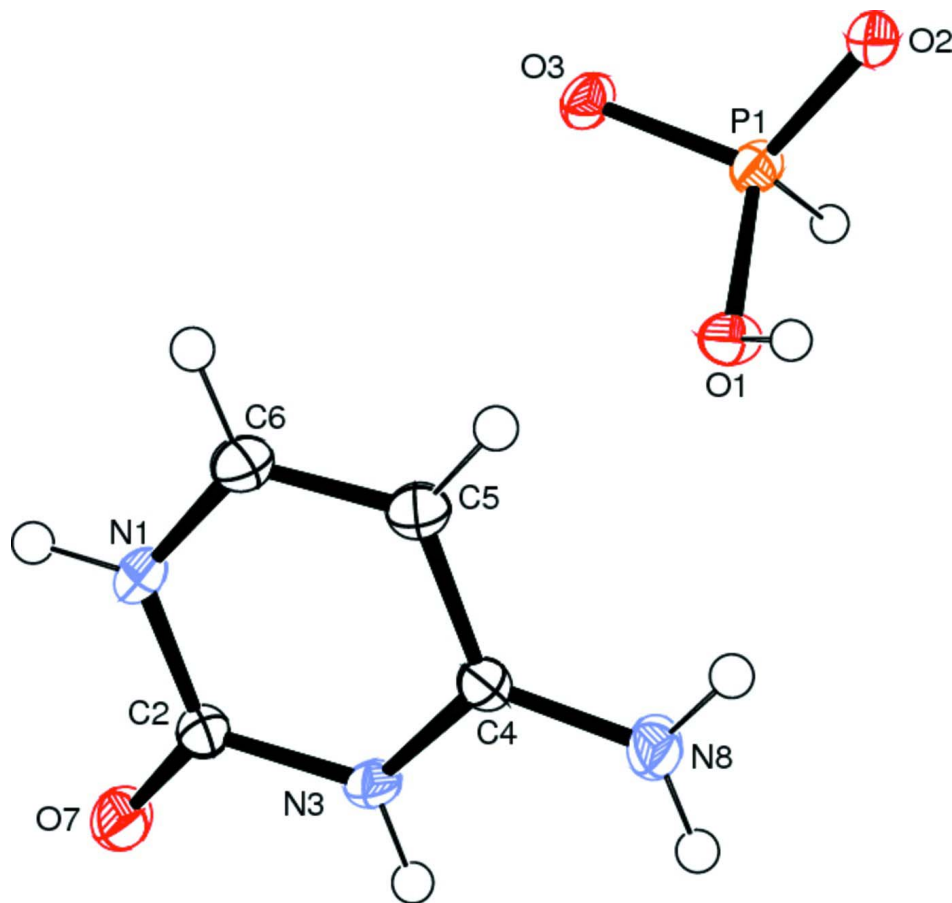
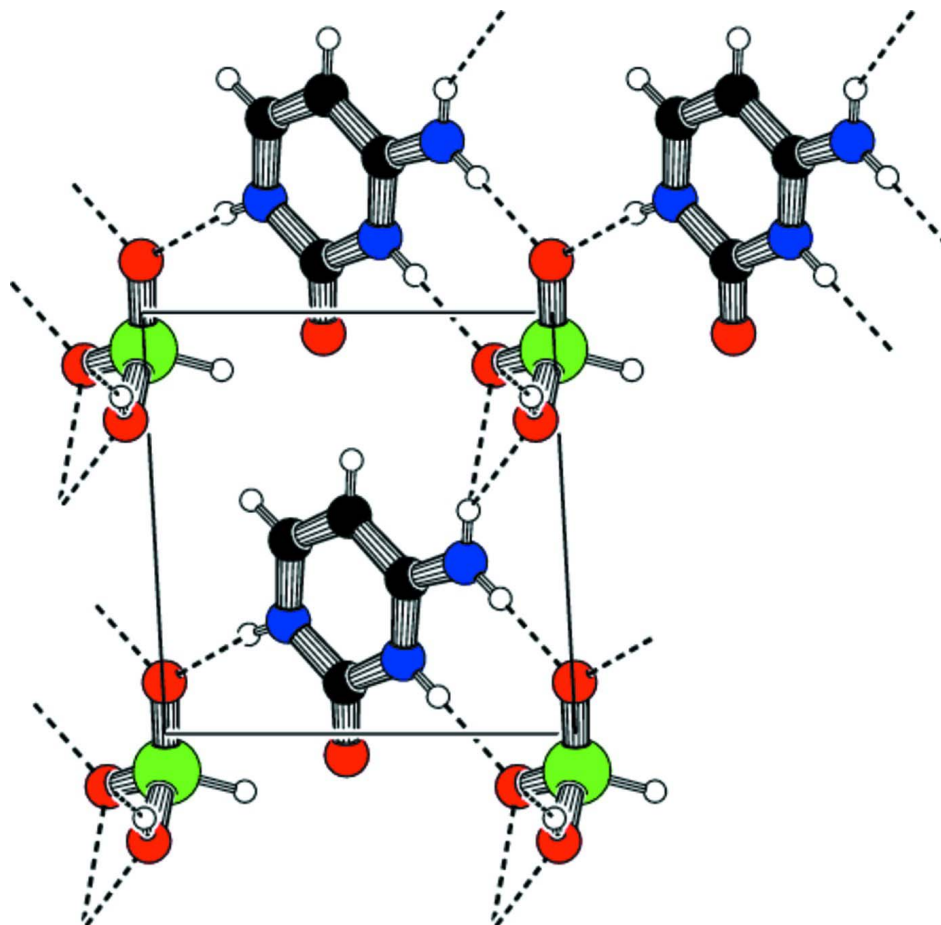


Figure 1

ORTEP view of asymmetric unit.

**Figure 2**

PLUTON view down *a* axis, showing alternate layers of cations and anions stabilized by N—H···O hydrogen bonds.

Cytosinium dihydrogen phosphite

Crystal data

$C_4H_6N_3O^+ \cdot H_2PO_3^-$

$M_r = 193.10$

Triclinic, *P*1

Hall symbol: P 1

$a = 4.5625$ (3) Å

$b = 6.4739$ (4) Å

$c = 6.5933$ (6) Å

$\alpha = 92.934$ (4)°

$\beta = 91.236$ (4)°

$\gamma = 98.627$ (5)°

$V = 192.21$ (2) Å³

$Z = 1$

$F(000) = 100$

$D_x = 1.668$ Mg m⁻³

Mo *K*α radiation, $\lambda = 0.71073$ Å

Cell parameters from 739 reflections

$\theta = 0.7$ – 27.9 °

$\mu = 0.34$ mm⁻¹

$T = 293$ K

Cubic, yellow

$0.1 \times 0.1 \times 0.1$ mm

Data collection

Nonius KappaCCD

diffractometer

Radiation source: fine-focus sealed tube

Horizontally mounted graphite crystal

monochromator

Detector resolution: 9 pixels mm⁻¹

CCD rotation images, thick slices scans

1500 measured reflections

1500 independent reflections

1430 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.000$
 $\theta_{\text{max}} = 28.0^\circ$, $\theta_{\text{min}} = 3.2^\circ$
 $h = -6 \rightarrow 5$

$k = -8 \rightarrow 8$
 $l = -8 \rightarrow 8$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.084$
 $S = 1.13$
 1500 reflections
 112 parameters
 4 restraints
 Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map

Hydrogen site location: difference Fourier map
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0447P)^2 + 0.0402P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.25 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.33 \text{ e } \text{\AA}^{-3}$
 Absolute structure: Flack (1983), with how
 many Friedel pairs?
 Absolute structure parameter: 0.06 (10)

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
O7	0.3049 (5)	0.5610 (3)	1.0498 (3)	0.0265 (5)
N1	0.3442 (5)	0.6856 (3)	0.7331 (4)	0.0213 (5)
H1	0.2420	0.7833	0.7642	0.026*
N3	0.5864 (5)	0.4107 (3)	0.8218 (3)	0.0183 (5)
H3	0.6371	0.3301	0.9118	0.022*
N8	0.8625 (5)	0.2462 (4)	0.5932 (4)	0.0236 (5)
H7	0.9227	0.1652	0.6793	0.028*
H8	0.9180	0.2312	0.4701	0.028*
C2	0.4021 (5)	0.5545 (4)	0.8791 (4)	0.0177 (5)
C4	0.6911 (5)	0.3898 (4)	0.6323 (4)	0.0178 (5)
C5	0.6099 (6)	0.5224 (4)	0.4837 (4)	0.0232 (6)
H5	0.6711	0.5094	0.3507	0.028*
C6	0.4412 (6)	0.6684 (4)	0.5406 (4)	0.0228 (6)
H6	0.3901	0.7593	0.4457	0.027*
P1	-0.06174 (7)	0.00189 (6)	0.08872 (6)	0.01852 (18)
O1	0.1928 (4)	0.0549 (3)	0.2547 (3)	0.0209 (4)
H1A	0.3538	0.0628	0.2004	0.031*
O2	0.0527 (4)	-0.0044 (3)	-0.1225 (3)	0.0222 (4)
O3	-0.2857 (4)	0.1487 (3)	0.1256 (3)	0.0214 (4)
H9	-0.172 (6)	-0.1857 (19)	0.137 (5)	0.026*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O7	0.0323 (11)	0.0300 (11)	0.0203 (11)	0.0138 (8)	0.0056 (9)	0.0032 (8)
N1	0.0274 (12)	0.0176 (11)	0.0212 (13)	0.0108 (9)	-0.0016 (10)	0.0023 (9)
N3	0.0231 (11)	0.0198 (11)	0.0138 (11)	0.0079 (9)	-0.0004 (9)	0.0043 (8)
N8	0.0343 (13)	0.0234 (11)	0.0163 (11)	0.0134 (9)	0.0058 (10)	0.0031 (9)
C2	0.0175 (13)	0.0174 (13)	0.0181 (15)	0.0036 (10)	-0.0010 (10)	-0.0007 (10)
C4	0.0218 (13)	0.0166 (12)	0.0150 (13)	0.0034 (10)	-0.0016 (11)	-0.0005 (10)
C5	0.0327 (14)	0.0224 (13)	0.0165 (13)	0.0094 (11)	0.0002 (12)	0.0042 (10)
C6	0.0308 (15)	0.0188 (13)	0.0193 (15)	0.0056 (11)	-0.0032 (11)	0.0033 (10)
P1	0.0176 (3)	0.0189 (3)	0.0200 (4)	0.0051 (2)	0.0016 (2)	0.0033 (2)
O1	0.0142 (8)	0.0330 (10)	0.0170 (10)	0.0066 (7)	0.0028 (7)	0.0039 (7)
O2	0.0271 (10)	0.0250 (10)	0.0174 (10)	0.0129 (8)	0.0018 (8)	0.0008 (8)
O3	0.0175 (9)	0.0255 (10)	0.0235 (11)	0.0098 (7)	0.0024 (8)	0.0032 (8)

Geometric parameters (Å, °)

O7—C2	1.220 (3)	C4—C5	1.414 (4)
N1—C6	1.358 (4)	C5—C6	1.349 (4)
N1—C2	1.362 (4)	C5—H5	0.9300
N1—H1	0.8600	C6—H6	0.9300
N3—C4	1.354 (3)	P1—O2	1.498 (2)
N3—C2	1.389 (3)	P1—O3	1.5114 (18)
N3—H3	0.8600	P1—O1	1.5655 (18)
N8—C4	1.321 (3)	P1—H9	1.301 (16)
N8—H7	0.8601	O1—H1A	0.8200
N8—H8	0.8600		
C6—N1—C2	122.8 (2)	N3—C4—C5	118.4 (2)
C6—N1—H1	118.6	C6—C5—C4	118.1 (3)
C2—N1—H1	118.6	C6—C5—H5	121.0
C4—N3—C2	123.8 (2)	C4—C5—H5	121.0
C4—N3—H3	118.1	C5—C6—N1	121.5 (2)
C2—N3—H3	118.1	C5—C6—H6	119.2
C4—N8—H7	126.0	N1—C6—H6	119.2
C4—N8—H8	117.2	O2—P1—O3	114.99 (10)
H7—N8—H8	116.8	O2—P1—O1	112.60 (10)
O7—C2—N1	123.7 (2)	O3—P1—O1	108.41 (11)
O7—C2—N3	121.1 (2)	O2—P1—H9	110.0 (14)
N1—C2—N3	115.2 (2)	O3—P1—H9	109.9 (13)
N8—C4—N3	119.0 (2)	O1—P1—H9	99.9 (14)
N8—C4—C5	122.7 (3)	P1—O1—H1A	109.5
C6—N1—C2—O7	-176.3 (2)	C2—N3—C4—C5	0.3 (4)
C6—N1—C2—N3	4.5 (3)	N8—C4—C5—C6	-178.0 (3)
C4—N3—C2—O7	177.1 (2)	N3—C4—C5—C6	2.4 (4)
C4—N3—C2—N1	-3.7 (3)	C4—C5—C6—N1	-1.7 (4)

C2—N3—C4—N8

-179.2 (2)

C2—N1—C6—C5

-2.0 (4)

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—H1 \cdots O2 ⁱ	0.86	1.86	2.713 (3)	170
O1—H1A \cdots O3 ⁱⁱ	0.82	1.75	2.542 (3)	163
N3—H3 \cdots O3 ⁱⁱⁱ	0.86	1.94	2.797 (3)	175
N8—H7 \cdots O2 ⁱⁱⁱ	0.86	1.89	2.750 (3)	178
N8—H8 \cdots O1 ⁱⁱ	0.86	2.29	3.034 (3)	145
N8—H8 \cdots O3 ⁱⁱ	0.86	2.44	3.153 (3)	141

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