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Thiaminium chloride perchlorate

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In the title compound, $C_{12}H_{18}N_4OS^{2+}\cdot Cl^-\cdot ClO_4^-$, the thiaminium cations form ‘head-to-tail’ N—H···O hydrogen-bonded dimers about inversion centres. N—H···Cl and O—H···Cl hydrogen bonds further stabilize the structure, forming a one-dimensional chain running along the diagonal of the *ac* plane. Both anions are located adjacent to ‘anion holes’ in the thiaminium cation. The perchlorate anions show rotational disorder about a Cl—O bond.

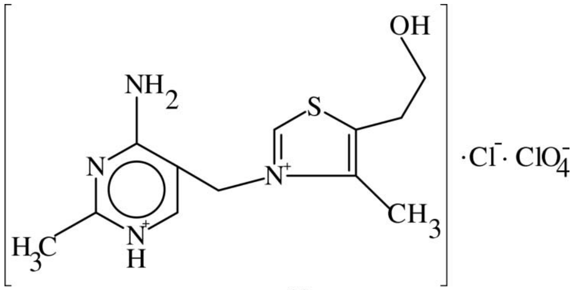
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
Disorder in solvent or counterion
R factor = 0.029
wR factor = 0.082
Data-to-parameter ratio = 12.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Thiamine (vitamin B1) deficiency leads to an number of medical problems, including wet beri-beri and heart failure, and hence vitamin B1 supplements are commonly administered (Suter, 2004). Thiamine, in the form of pyrophosphate cocarboxylase, is the coenzyme for many reactions, including the oxidative decarboxylation of pyruvic acid (Breslow, 1958). Derivatives of thiamine disulfides are also used as therapeutic provitamins, due to their high absorptivity in the gastro-intestinal tract (Suzuoki *et al.*, 1965). Protonation on one of the N atoms of monovalent thiamine (Th^+) leads to a divalent cation with a protonated pyrimidine ring and a monovalent thiazolium ring. Numerous crystal structures of mono- and divalent thiamine cations with a variety of anions have been reported previously (Kraut & Reed, 1962; Ishida *et al.*, 1984; Shin & Chun, 1987; Kozioł *et al.*, 1987; Aoki *et al.*, 1988; Cramer & Carrie, 1989; Casas *et al.*, 1994).



(I)

The title compound, (I), crystallizes with a divalent thiaminium cation, and chloride and perchlorate anions in the asymmetric unit (Fig. 1). The pyrimidine ring is protonated at N1, with C—N bond distances and the C—N—C bond angle being typical for a protonated N atom (Hu *et al.*, 2000). The planar pyridimine and thiazolium rings are inclined to one another at a dihedral angle of 71.8 (1)°. Two conformation angles about the C7 methylene group [φ_T (C5—C7—N8—C12) and φ_P (C4—C5—C7—N8)] define three possible forms of thiamine, namely F, S and V (Shin *et al.*, 1977). Our

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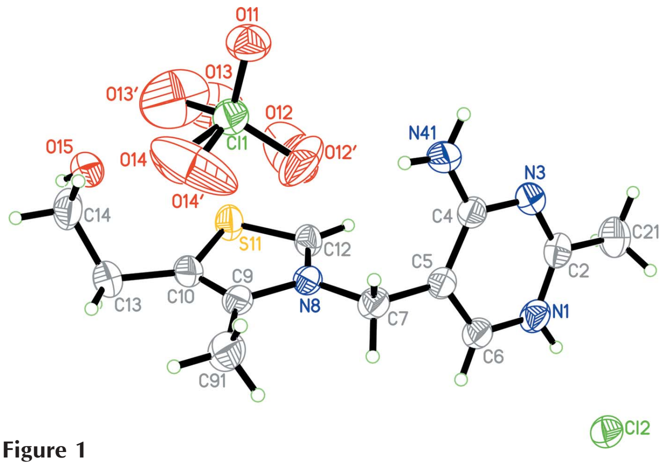

Figure 1
The molecular structure of compound (I), with the atom-numbering scheme and 50% probability displacement ellipsoids. Both disorder components are shown.

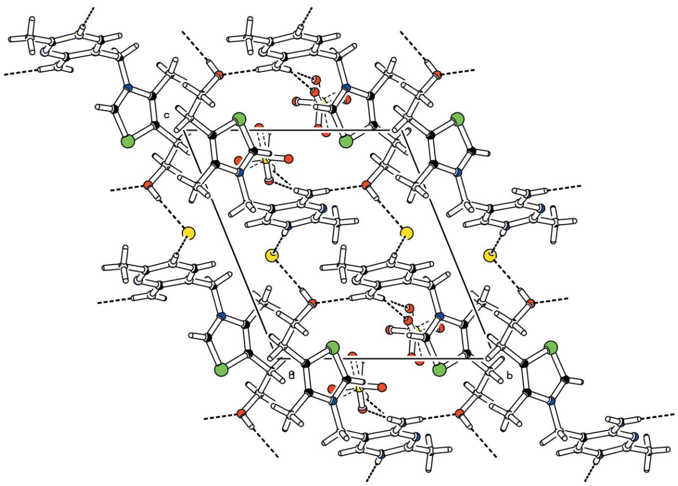

Figure 2
A packing diagram of (I), viewed down the *a* axis. Hydrogen bonds are drawn as dashed lines.

statistical analysis using the Cambridge Structural Database (Version 5.26 of November 2004; Allen, 2002) indicates that the F form occurs frequently when atom C12 in the thiazolium ring carries no substituents. In (I), the thiamine is in the preferred F conformation, with φ_T = −8.6 (3)° and φ_P = 79.2 (2)°, close to the ideal values ($\varphi_T = 0°$ and $\varphi_P = \pm 90°$). The conformation of the 5-(β-hydroxyethyl) side chain is also described by the two torsion angles $\varphi_{5\alpha}$ (S11—C10—C13—C14) and $\varphi_{5\beta}$ (C10—C13—C14—O15) (Table 1), which result in a close contact between the electronegative atom O15 and the electropositive atom S11 of 2.921 (2) Å, a common structural feature of thiamine compounds (Shin *et al.*, 1977), causing the hydroxyethyl side-chain to fold back towards the thaizolium ring.

Stabilization in the crystal structure of (I) results from interactions between adjacent thiaminium cations, both directly with themselves and through the anions. This occurs through a range of classical and non-classical hydrogen-bonding interactions (Table 2), augmented by a weak S···O interaction [S1···O11(−*x* + 1, −*y* + 1, −*z* + 2) 3.117 (2) Å] and electrostatic interactions. In the title compound, however, classical hydrogen bonding dominates. 'Head-to-tail' dimers form around inversion centres through N41—H41*A*···O15 hydrogen bonds (Fig. 3), to form a closed hydrogen-bonding network in the *bc* plane. This results in a cavity of approximate dimensions 5.52 × 5.24 Å running along the *a* axis. In addition, N41—H41*B*···O interactions link the perchlorate anion to the cation in a location described as anion hole II (Hu *et al.*, 2000). Further strong N1—H1···Cl2 and O15—H15···Cl2 hydrogen bonds complete the network, forming infinite chains along the diagonal of the *ac* plane. C12—H12···O interactions are also of interest because of the importance of the acidic atom H12 in hydroxyethylthiamine pyrophosphate reactions (Krampitz, 1969). Weak intermolecular C12—H12···O11/O13 bifurcated hydrogen bonds lock an alternative perchlorate into 'anion hole I', characteristic of thiamine systems in the F conformation (Hu *et al.*, 2001), with a final weak C6—H6···Cl2 interaction designating the Cl⁻ anion to 'anion hole III' (Hu *et al.*, 2000).

Experimental

The title compound was crystallized from a liquid mixture of thiamine chloride and perchloric acid in the stoichiometric ratio of 1:1 at room temperature by the technique of slow evaporation. CAUTION: Although no problems were encountered in this work, perchlorate compounds are potentially explosive. They should be prepared in small amounts and handled with care.

Crystal data

$C_{12}H_{18}N_4OS^{2+}\cdot Cl^-\cdot ClO_4^-$
M_r = 401.26
Triclinic, $P\overline{1}$
a = 8.076 (3) Å
b = 10.896 (4) Å
c = 11.594 (5) Å
α = 107.61 (3)°
β = 97.39 (3)°
γ = 111.30 (3)°
V = 872.7 (7) Å^3
Z = 2
D_x = 1.527 Mg m^{-3}
D_m = 1.514 Mg m^{-3}
D_m measured by flotation, using a mixture of xylene and carbon tetrachloride
Mo *Kα* radiation
Cell parameters from 25 reflections
θ = 10.2–14.1°
μ = 0.52 mm^{-1}
T = 293 (2) K
Block, colourless
0.21 × 0.19 × 0.16 mm

Data collection

Nonius MACH3 four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.902, T_{max} = 0.926
3775 measured reflections
3065 independent reflections
2474 reflections with $I > 2\sigma(I)$
R_{int} = 0.011
θ_{max} = 25.0°
h = −1 → 9
k = −12 → 12
l = −13 → 13
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.082
S = 1.02
3065 reflections
248 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0416P)^2 + 0.338P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.341 (3)	N1—C6	1.346 (3)
C2—N1—C6	120.67 (18)		
C4—C5—C7—N8	79.2 (2)	S11—C10—C13—C14	−56.3 (3)
C5—C7—N8—C12	−8.6 (3)	C10—C13—C14—O15	61.2 (3)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl2	0.86	2.24	3.100 (2)	176
N41—H41*A*···O15^{i}	0.86	2.01	2.854 (3)	168
N41—H41*B*···O12	0.86	2.19	3.048 (8)	172
N41—H41*B*···O12′	0.86	2.13	2.955 (12)	161
O15—H15···Cl2^{ii}	0.82 (3)	2.24 (3)	3.056 (2)	174 (3)
C12—H12···O11^{i}	0.93	2.78	3.229 (3)	111
C12—H12···O13^{i}	0.93	2.84	3.273 (7)	110
C6—H6···Cl2^{iii}	0.93	2.85	3.687 (3)	151

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

The H atom on atom O15 of the hydroxyethyl substituent in the thiaminium cation was located and refined isotropically. All other H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93–0.97 Å and N—H = 0.86 Å, and U_{iso}(H) = 1.2–1.5U_{eq}(parent atom). The perchlorate anion shows rotational disorder around the axis of the Cl1—O11 bond, which leads to occupancy factors of 0.63 (2) and 0.37 (6) for O12/O13/O14 and O12′/O13′/O14′, respectively.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997).

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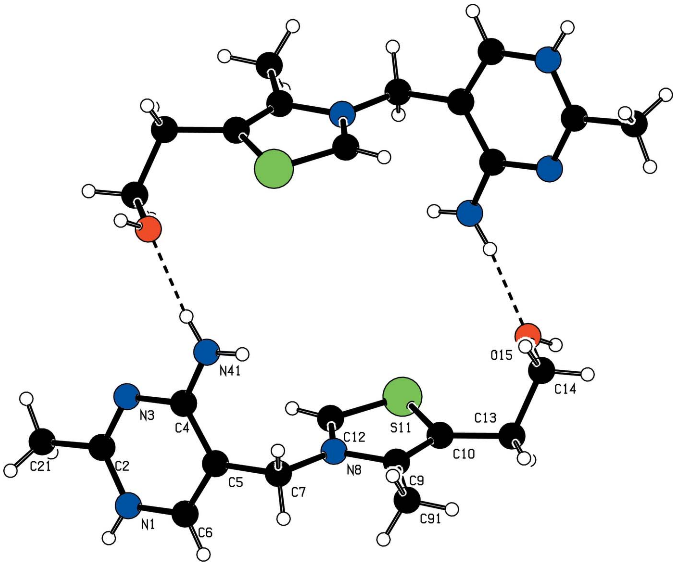

Figure 3
The inversion-generated closed hydrogen-bonding loop formed by the cations. Hydrogen bonds are drawn as dashed lines.

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