

## Thiamine tetraphenylborate mono-hydrate: a two-dimensional hydrogen-bonded network with (4,4)-topology

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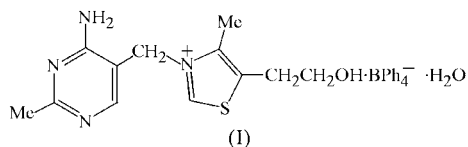
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The title compound, 3-[(4-amino-2-methylpyrimidin-5-yl)-methyl]-5-(2-hydroxyethyl)-4-methylthiazolium tetraphenylborate monohydrate,  $C_{12}H_{17}N_4OS^+ \cdot C_{24}H_{20}B^- \cdot H_2O$ , is a salt in which the thiamine cations are linked by hydrogen bonds into a two-dimensional network having (4,4)-topology. The stacked sheets form channels, which are occupied by the anions; the cations and anions are linked by  $C-H \cdots \pi$ (arene) hydrogen bonds.

### Comment

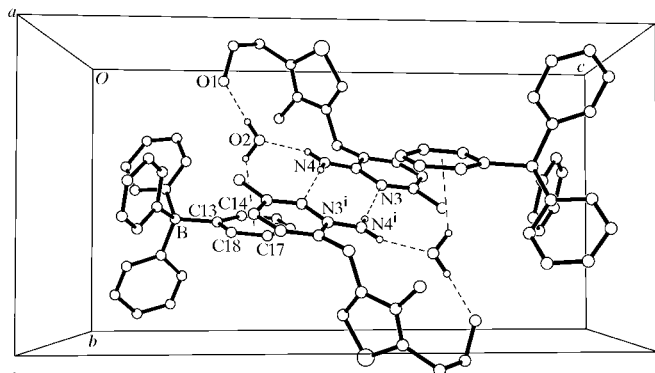
The construction of hydrogen-bonded networks is one of the goals of organic crystal engineering (Etter, 1991; Desiraju, 1995). In the development of new materials for storage, sensors and catalysis, one target is a host framework that traps anionic or neutral guests (Videnova-Adrabińska, 1996; Beatty, 2003; Biradha, 2003). Thiamine (vitamin B<sub>1</sub>), as a naturally occurring cationic host, provides multiple sites that serve as donors or acceptors to form various supramolecular arrays by hydrogen bonding (Aoki *et al.*, 1993; Hu *et al.*, 2001*b*). Structural studies have revealed that the packing features in thiamine–anion systems are closely related to the nature of the anions and the conformation of the thiamine moiety.



The other H atom of the water molecule forms an O—H··· $\pi$ (arene) hydrogen bond (Table 1).

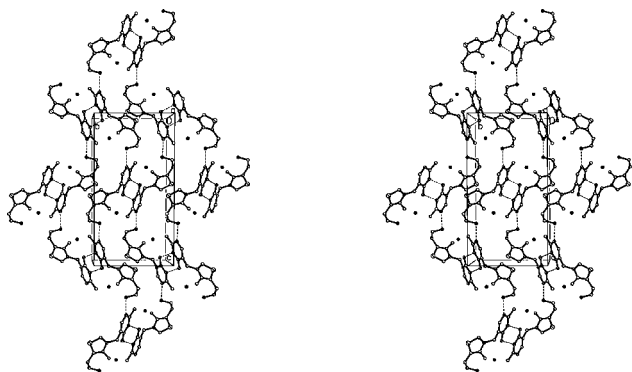
As shown in Table 1, a two-dimensional supramolecular network is constructed using two types of hydrogen bond. Firstly, a base-pairing dimer is formed through a self-complementary pyrimidine–pyrimidine interaction involving a pair of N—H···N hydrogen bonds (Fig. 2); this supramolecular synthon is frequently observed in thiamine structures. Secondly, an O—H···N hydrogen bond is utilized in the assembly of the dimers to complete a two-dimensional sheet parallel to (100) having (4,4)-topology (Batten & Robson, 1998) (Fig. 3). The sheet undulates with a wavelength of *ca* 10.7 Å and a wave height of *ca* 11.5 Å. The thiazolium rings are located in the ridges and troughs of the wave, and the pyrimidine base pairs are located in between the ridges and troughs of the wave. Interestingly, the puckered sheets, which are perpendicular to the *a* axis, are eclipsed such that channels exist along the  $[\bar{1}01]$  direction. The tetraphenylborate anions occupy the channels and are linked to the cationic network *via* C—H··· $\pi$ (arene) hydrogen bonds (Table 1). The C—H···anion interaction is typical of host–guest interactions found in thiamine compounds with the F conformation (Aoki *et al.*, 1988).

It was shown in our previous study (Hu *et al.*, 2003) that there are three types of base-pairing dimers of thiamine,



**Figure 2**

A view of the base-pairing dimer in (I). H atoms, except those taking part in hydrogen bonds, have been omitted for clarity. [Symmetry code: (i)  $1 - x, 1 - y, 1 - z$ .]



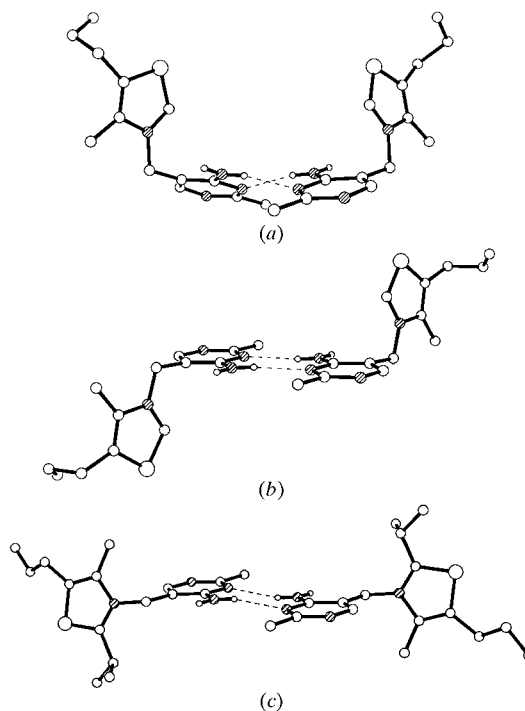
**Figure 3**

A stereoview of the two-dimensional network consisting of hydrogen-bonded thiamine cations, showing the intermolecular connections (dashed lines) and cavities. The anions and H atoms have been omitted.

depending on the molecular conformation, that is, the U and Z forms for dimers in the F conformation and the linear form for dimers in the S conformation (Fig. 4). The two-dimensional hydrogen-bonded motif has been observed for the linear-form dimer in the structure of HET·HgI<sub>4</sub>·H<sub>2</sub>O and for the Z-form dimer in (I), but not for the U form. The difference between HET·HgI<sub>4</sub>·H<sub>2</sub>O and (I) is that an N—H···O hydrogen bond is used to propagate the network in the former, whereas an O—H···N hydrogen bond is used in the latter. Both types of hydrogen bond involve hydroxy O1 atoms. We note that the C3-hydroxyethyl side chain is *trans* with respect to the base-pair plane in both the Z form and the linear form but is *cis* in the U form. The formation of the two-dimensional network is thus closely related to the conformation of the base-pairing dimers of thiamine.

Moreover, the ability of anions to accept hydrogen bonds is also a factor that affects the formation of the two-dimensional network. When the anion is strongly electronegative, it competes for the acceptor sites on thiamine, and thus precludes self-assembly of thiamine molecules in multi-dimensional arrays. In contrast, the existence of weakly electronegative anions, such as [HgI<sub>4</sub>]<sup>2-</sup> and BPh<sub>4</sub><sup>-</sup>, allows facile associations between thiamine molecules leading to two-dimensional structures.

In summary, we have synthesized the first cationic two-dimensional network of thiamine in the F conformation utilizing pyrimidine base pairs as the network nodes. The nature of the anion and the molecular conformation of the



**Figure 4**

Base-pairing dimers of thiamine derivatives in different forms, *viz.* (a) the U form and (b) the Z form for thiamine in the F conformation, and (c) the linear form for HET in the S conformation (N atoms: right hatched; other atoms: circles).

cation play important roles in determining the self-assembly of thiamine cations.

## Experimental

Equimolar quantities of thiamine chloride hydrochloride and sodium tetraphenylborate (purchased from Aldrich) were dissolved in water and acetone, respectively. The solutions were mixed, and the mixture was set aside to afford crystals of (I) suitable for single-crystal X-ray diffraction. Analysis found: C 72.2, H 6.0, N 9.1%;  $C_{36}H_{39}BN_4O_2S$  requires: C 71.8, H 6.5, N 9.3%.

### Crystal data

$C_{12}H_{17}N_4OS^+ \cdot C_{24}H_{20}B^- \cdot H_2O$	$D_x = 1.259 \text{ Mg m}^{-3}$
$M_r = 602.58$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 5012 reflections
$a = 14.6464$ (6) Å	$\theta = 2.4\text{--}26.0^\circ$
$b = 10.6667$ (4) Å	$\mu = 0.14 \text{ mm}^{-1}$
$c = 20.4459$ (8) Å	$T = 187$ (1) K
$\beta = 95.5230$ (10)°	Tablet, colourless
$V = 3179.4$ (2) Å <sup>3</sup>	$0.30 \times 0.24 \times 0.12 \text{ mm}$
$Z = 4$	

### Data collection

Bruker SMART APEX CCD diffractometer	6251 independent reflections
$\varphi$ and $\omega$ scans	5011 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SAINT; Bruker, 2003)	$R_{\text{int}} = 0.026$
$T_{\text{min}} = 0.962$ , $T_{\text{max}} = 0.986$	$\theta_{\text{max}} = 26.0^\circ$
17468 measured reflections	$h = -17 \rightarrow 18$
	$k = -13 \rightarrow 13$
	$l = -19 \rightarrow 25$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.061P)^2 + 1.2737P]$
$R[F^2 > 2\sigma(F^2)] = 0.048$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.123$	$(\Delta/\sigma)_{\text{max}} = 0.004$
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.34 \text{ e \AA}^{-3}$
6251 reflections	$\Delta\rho_{\text{min}} = -0.27 \text{ e \AA}^{-3}$
399 parameters	
H-atom parameters constrained	

**Table 1**

Hydrogen-bond geometry (Å, °).

$Cg_1$  and  $Cg_2$  are the centroids of the C13–C18 and C25–C30 rings, respectively.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N4-H4A \cdots N3^i$	0.88	2.29	3.142 (2)	163
$N4-H4B \cdots O2$	0.88	2.02	2.863 (2)	160
$O1-H1 \cdots N2^{ii}$	0.89	1.86	2.736 (2)	171
$O2-H2A \cdots O1$	0.86	1.92	2.786 (2)	175
$O2-H2B \cdots Cg_1$	0.88	2.69	3.385 (2)	136
$C1-H1A \cdots Cg_2^{iii}$	0.95	2.50	3.252 (2)	137

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

H atoms of the hydroxy group of the C5-hydroxyethyl side chain and of the water molecule were located in difference Fourier maps and were fixed in the refinements. All other H atoms were treated as riding atoms, with C–H distances of 0.98 (CH<sub>3</sub>), 0.99 (CH<sub>2</sub>) or 0.95 Å (CH), and N–H distances of 0.88 Å. All H atoms were assigned isotropic displacement parameters the same as the  $U_{\text{eq}}$  value of their parent non-H atom.

Data collection: SMART (Bruker, 1998); cell refinement: SMART; data reduction: SAINT (Bruker, 2003); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1997); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1390). Services for accessing these data are described at the back of the journal.

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