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Thiamin Acetate, $C_{12}H_{17}N_4OS^+.C_2H_3O_2^-$

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Abstract

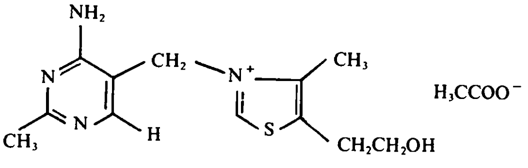
In thiamin acetate crystals, the thiamin cation {3-[(4-amino-2-methyl-5-pyrimidinyl)methyl]-5-(2-hydroxyethyl)-4-methylthiazolium} adopts the usual *F* conformation, with torsion angles C5′—C3,5′—N3—C2 and N3—C3,5′—C5′—C4′ (between the pyridinyl and thiazolium moieties) of 5.6 (7) and −83.5 (6)°, respectively. Hydrogen bonds involving the O5γ—H hydroxyl and N4α′—H_2 amine groups and the N1′ and N3′ pyrimidine atoms interconnect the thiamin cations. The acetate anions are hydrogen bonded to the N4α′—H_2 group and probably also to the C2—H group of the thiazole ring.

Comment

Thiamin (vitamin B_1, Th^+) is an essential dietary component for man and other animals. Its pyrophosphoric acid ester is a coenzyme for several enzyme systems catalysing the decarboxylation of α-keto acids and the transfer of acyl or aldehyde groups (Krampitz, 1969).

Structural studies of Th^+ derivatives in the solid state began in 1962, when the crystal structure of thiamin chloride hydrochloride monohydrate ($ThCl.HCl.H_2O$) was reported (Kraut & Reed, 1962). Since then, several thiamin derivatives have been studied by X-ray diffraction, including both saline compounds containing Th^+ or HTh^{2+} cations and true complexes where a metallic centre is directly bonded to thiamin, usually, though not always, through a pyrimidine N atom (Hu, 1991; Aoki, Yamazaki & Adeyemo, 1991; Jin, Liu, Wei & Wang, 1990; Louloudi, Hadjiliadis, Feng, Sukumar & Bau, 1990).

In this paper we report the crystal structure of thiamin acetate, $ThOOCCH_3$. As far as we know, only one other thiamin salt with an organic anion (thiamin picrolonate; Shin, Pletcher, Blank & Sax, 1977) has been characterized structurally.



$ThOOCCH_3$

Fig. 1 shows an *ORTEP* (Johnson, 1971, and supplementary instructions) diagram of the compound. In general, the values for the pyrimidine and thiazolium rings are in good agreement with those found in other unsubstituted N1′-deprotonated thiamin derivatives (Pletcher, Sax, Sengupta, Chu & Yoo, 1972; Shin, Pletcher, Blank & Sax, 1977), especially with those of thiamin picrolonate dihydrate. Differences from this compound [other than that concerning the C4—C5 distance, which seems likely to have been misprinted in the paper by Shin, Pletcher, Blank & Sax (1977)] arise in the N3′—C4′ and C4′—N4α′ distances (respectively shorter and longer in the acetate) and the angles between the pyrimidine ring and its 4′- and 5′-substitutents (C4′—C5′—C3,5′, C6′—C5′—C3,5′, N3′—C4′—N4α′ and C5′—C4′—N4α′). These differences may be due to the difference between the hydrogen-bond patterns observed in the two compounds (see below). In $ThOOCCH_3$, the thiazolium

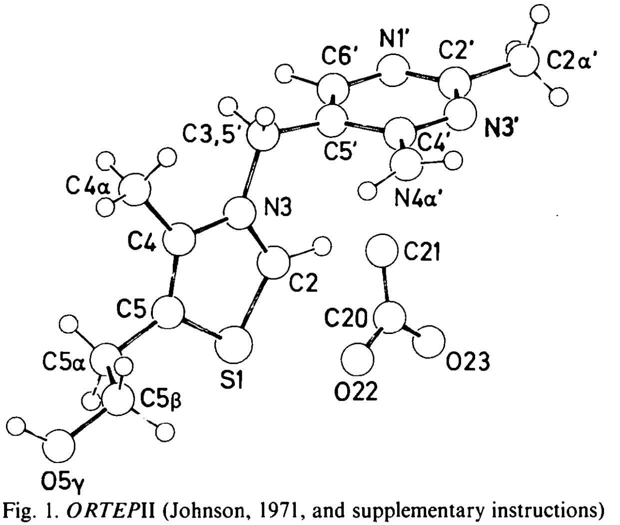


Fig. 1. *ORTEP*II (Johnson, 1971, and supplementary instructions) drawing of the compound.

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and pyrimidine rings are planar ($\chi^2 = 12$ and 8, respectively) and, in the simplified notation of Blank, Rodrigues, Pletcher & Sax (1976), adopt an $F-$ conformation [φ_T (C5′—C3,5′—N3—C2) = − 5.6 (7), φ_P (N3—C3,5′—C5′—C4′) = − 83.5 (6)°], whereas the picrolonate has an $F+$ conformation ($\varphi_T = 6.0$, $\varphi_P = 82.5$°; Shin, Pletcher, Blank & Sax, 1977). The values of the torsion angles S1—C5—C5α—C5β ($\varphi_{5\alpha}$) and C5—C5α—C5β—O5γ ($\varphi_{5\beta}$) are 92.8 (6) and − 175.6 (5)°, respectively.

Table 3 lists the hydrogen bonds detected together with the close contacts around S(1) and various miscellaneous contacts. The hydrogen-bond network is very similar to that observed in thiamin nitrate (Ishida, Tanaka & Inoue, 1984; Turano, Pletcher, Furey & Sax, 1982), in which the unprotonated thiamin cation is also combined with a planar oxoanion. As in thiamin nitrate, the Th^+ cations are interconnected in the lattice by hydrogen bonds involving the exocyclic O5γ—H5γ and N4α'—H4α' bonds and the pyrimidine atoms N1′ and N3′. The acetate anions are hydrogen bonded to the N4α'—H_2 group and probably also to the acidic C2—H2 group. The absolute values of the torsion angles $\varphi_{5\alpha}$ and $\varphi_{5\beta}$, which are the same in both nitrate and acetate, support the notion that the arrangement of the 5-(β-hydroxyethyl) side chain is very dependent on the hydrogen-bonding interactions of O5γ (Shin, Pletcher, Blank & Sax, 1977).

Experimental

The title compound was unexpectedly obtained during our study of the interaction between thiamin and the cadmium(II) cation, as follows: 3.4 g (*ca* 10 mmol) of ThCl.HCl dissolved in 20 ml of water was neutralized with an equimolar amount of aqueous NaOH and then reacted with 3.4 g (*ca* 20 mmol) of $AgNO_3$ dissolved in 3 ml of water; the solid AgCl formed was filtered out and the mother liquor reacted with 1.3 g (*ca* 5 mmol) of solid $Cd(OOCCH_3)_2.2H_2O$; after the resulting clear solution had stood for 3 days in the refrigerator, single crystals appeared, one of which was used in the X-ray measurements.

Crystal data

$C_{12}H_{17}N_4OS^+.C_2H_3O_2^-$
$M_r = 324.40$
Monoclinic
$P2_1/c$
$a = 6.562$ (1) Å
$b = 12.296$ (1) Å
$c = 18.570$ (1) Å
$\beta = 97.620$°
$V = 1485.7$ (2) Å^3
$Z = 4$
$D_x = 1.451$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 5–12$°
$\mu = 0.226$ mm^{-1}
$T = 293$ K
Prism
0.25 × 0.15 × 0.15 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: empirical (Walker & Stuart, 1983)
$T_{\min} = 0.71$, $T_{\max} = 0.99$
3312 measured reflections
2772 independent reflections

1821 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int} = 0.026$
$\theta_{\max} = 26$°
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 15$
$l = -22 \rightarrow 22$
3 standard reflections
frequency: 60 min
intensity variation: none

Refinement

Refinement on F
$R = 0.069$
$wR = 0.075$
$S = 1.59$
1821 reflections
200 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.80$ e Å^{-3}
$\Delta\rho_{\min} = -0.87$ e Å^{-3}
Extinction correction: Zachariasen (1963)
Extinction coefficient: 5.17×10^{-7}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$B_{\rm eq} = (4/3)\sum_i\sum_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$B_{\rm eq}$
S1	0.2259 (2)	0.4185 (1)	0.34221 (8)	2.82 (3)
O22	0.5677 (7)	0.5197 (4)	0.2734 (3)	6.5 (1)
O23	0.8234 (8)	0.5396 (5)	0.2190 (3)	8.4 (1)
O5γ	−0.2460 (7)	0.4157 (4)	0.5205 (2)	5.5 (1)
N1′	0.4308 (7)	0.2410 (4)	0.0510 (2)	3.48 (9)
N3′	0.2030 (7)	0.3900 (4)	0.0206 (2)	3.23 (9)
N3	0.0638 (6)	0.2948 (4)	0.2451 (2)	3.01 (9)
N4α'	−0.0676 (8)	0.4271 (4)	0.0828 (3)	4.5 (1)
C2	0.2133 (9)	0.3672 (5)	0.2584 (3)	3.2 (1)
C2′	0.3651 (8)	0.3281 (4)	0.0112 (3)	2.9 (1)
C4	−0.0460 (8)	0.2768 (5)	0.3030 (3)	3.0 (1)
C4′	0.0951 (8)	0.3641 (4)	0.0742 (3)	2.7 (1)
C5	0.0260 (9)	0.3391 (5)	0.3615 (3)	3.2 (1)
C5′	0.1492 (8)	0.2721 (4)	0.1189 (3)	2.7 (1)
C6′	0.3197 (8)	0.2159 (4)	0.1044 (3)	3.0 (1)
C20	0.6662 (7)	0.4916 (7)	0.2259 (3)	2.29 (9)
C21	0.6130 (7)	0.4144 (4)	0.1858 (2)	2.23 (9)
C2α'	0.4771 (1)	0.3573 (6)	−0.0508 (3)	4.4 (1)
C3,5′	0.0205 (9)	0.2342 (4)	0.1743 (3)	3.1 (1)
C4α	−0.2182 (9)	0.1959 (5)	0.2965 (3)	4.4 (1)
C5α	−0.0393 (9)	0.3382 (5)	0.4366 (3)	3.7 (1)
C5β	−0.2084 (9)	0.4178 (6)	0.4468 (3)	4.1 (1)

Table 2. *Selected geometric parameters* (Å, °)

S1—C2	1.671 (6)	N3—C3,5′	1.505 (7)
S1—C5	1.710 (7)	N4α'—C4′	1.346 (7)
O22—C20	1.211 (7)	C2′—C2α'	1.489 (9)
O23—C20	1.209 (7)	C4—C5	1.361 (7)
O5γ—C5β	1.422 (8)	C4—C4α	1.498 (8)
N1′—C2′	1.340 (7)	C4′—C5′	1.420 (8)
N1′—C6′	1.342 (7)	C5—C5α	1.512 (8)
N3′—C2′	1.339 (8)	C5′—C6′	1.372 (8)
N3′—C4′	1.335 (8)	C5′—C3,5′	1.490 (8)
N3—C2	1.323 (7)	C20—C21	1.228 (7)
N3—C4	1.389 (8)	C5α—C5β	1.510 (9)
C2—S1—C5	92.0 (3)	N4α'—C4′—C5′	122.0 (5)
C2′—N1′—C6′	115.2 (5)	S1—C5—C4	110.4 (4)
C2′—N3′—C4′	118.1 (4)	S1—C5—C5α	121.1 (5)
C2—N3—C4	114.2 (4)	C4—C5—C5α	128.3 (5)
C2—N3—C3,5′	123.1 (5)	C4′—C5′—C6′	115.7 (5)
C4—N3—C3,5′	122.7 (4)	C4′—C5′—C3,5′	122.1 (5)

S1—C2—N3	111.8 (4)	C6′—C5′—C3,5′	122.1 (5)
N1′—C2′—N3′	125.8 (5)	N1′—C6′—C5′	124.5 (5)
N1′—C2′—C2α′	117.6 (5)	O22—C20—O23	118.9 (5)
N3′—C2′—C2α′	116.5 (5)	O22—C20—C21	121.7 (6)
N3—C4—C5	111.5 (5)	O23—C20—C21	119.5 (5)
N3—C4—C4α	120.5 (5)	N3—C3,5′—C5′	113.0 (4)
C5—C4—C4α	128.1 (5)	C5—C5α—C5β	114.5 (5)
N3′—C4′—N4α′	117.3 (5)	O5γ—C5β—C5α	109.6 (5)
N3′—C4′—C5′	120.7 (5)		

Table 3. *Hydrogen bonds and other interatomic close contacts* (Å, °)

Hydrogen bonds

D	H	*A*	*D*···*A*
O5γ	H5γ	N1′^{i}	2.976 (7)
N4α′	H4α′1	O23^{ii}	3.050 (8)
N4α′	H4α′1	N3′^{iii}	3.014 (7)
C2	H2	O22	2.972 (7)

Close contacts around S1

C	S	O	C—S	S···O	C—S···O	C···O
C2	S1	O22	1.671 (6)	2.995 (5)	73.0 (2)	2.972 (7)
C5	S1	O22	1.711 (6)		164.7 (2)	>4
C2	S1	O5γ^{iv}		3.253 (5)	163.4 (2)	>4
C5	S1	O5γ^{iv}			98.4 (2)	3.890 (7)

Miscellaneous contacts

C	H	O	C···O
C3,5′	H3,5′2	O22^{v}	3.809 (7)
C3,5′	H3,5′2	O22^{v}	3.188 (8)

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

The structure was solved by direct methods and subsequent difference Fourier methods. Anisotropic displacement parameters were refined for all non-H atoms. H-atoms were included in the structure-factor calculations, but not refined. Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Data reduction: *SDP-VAX*, Version 3.0 (1986) (Frenz, 1978). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SDP-VAX*. Molecular graphics: *ORTEP*II (Johnson, 1971).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, least-squares-planes data and torsion angles have been deposited with the IUCr (Reference: HA1060). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-Thymin-1-ylethyl Ester of *N-tert*-Butoxycarbonyl-L-tryptophan, $C_{23}H_{28}N_4O_6$

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Abstract

The dihedral angle between the indole and thymine rings is 31°, and little stacking interaction between these rings is observed in the crystalline state. The molecules are linked by three N—H···O hydrogen bonds.

Comment

The title compound, (I), was prepared in order to study the nature of the stacking interaction between nucleic acid bases and tryptophan (Sugiyama, 1984). The absorption and fluorescence spectra of both (I) and 5′-uridylyl-L-tryptophaniate in solution indicated strong stacking interactions between the indole and thymine rings (Sugiyama, 1984). The crystal structure determination of 5′-uridylyl-L-tryptophaniate hydrochloride revealed that the indole ring is stacked on the uracil group of a

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