and Cl(2)–C(12) are anticlinal with respect to the O(5)–C(11) bond, while both these bonds are synclinal in chloramphenicol (Chatterjee *et al.*, 1979; Ravindra Acharya *et al.*, 1979) and bromamphenicol (Dunitz, 1952).

A projection of the molecular packing of the thiamphenicol molecule viewed down the *a* axis is shown in Fig. 2. The structure is found to be stabilized by intermolecular hydrogen bonds of the type N–H···O and O–H···O. The proton attached to the amide N takes part in hydrogen bonding with O(4), resulting in an infinite chain extended along the **a** direction. The other two available protons attached to the two hydroxy oxygens, O(3) and O(4), are involved in hydrogen bonding to a sulfonyl oxygen, O(2), of a screw-related molecule and to one of the hydroxy oxygens, O(3), of a translation-related molecule respectively. The geometrical details of the hydrogen bonding with their symmetry code are as follows:

A–H···*B*	*A*–H(Å)	*A*···*B*(Å)	H···*B*(Å)	∠*A*–H···*B*(°)
O(4)–H(41)···O(3^{i})	0·83 (12)	2·989 (5)	2·17 (12)	170 (12)
N–H(1)···O(4^{ii})	0·86 (6)	2·892 (5)	2·13 (6)	148 (6)
O(3)–H(31)···O(2^{iii})	0·82 (5)	2·892 (5)	2·07 (5)	171 (5)

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

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Acta Cryst. (1987). C**43**, 1555–1557

Structure of Thiamin Perchlorate Monohydrate

By A. E. Kozioł,* R. C. Palenik and G. J. Palenik†

Center for Molecular Structure, Chemistry Department, University of Florida, Gainesville, Florida 32611, *USA*

(*Received* 11 *October* 1986; *accepted* 10 *February* 1987)

Abstract. 3-[(4-Amino-2-methyl-5-pyrimidinyl)methyl]-5-(2-hydroxyethyl)-4-methylthiazolium perchlorate monohydrate, $C_{12}H_{17}N_4OS^+.ClO_4^-.H_2O$, $M_r = 382·83$, monoclinic, $P2_1/n$, $a = 11·968$ (3), $b = 11·234$ (2), $c = 12·965$ (3) Å, $\beta = 92·98$ (2)°, $V = 1740·8$ (6) Å^3, $Z = 4$, $D_x = 1·461$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 3·8$ cm^{-1}, $F(000) = 800$, $T = 300$ K. Final $R = 0·089$ for 2082 reflections with $F_o \geq 3\sigma(F_o)$. The dimensions of the thiamin cation are not significantly different from the average values observed in other thiamin derivatives. The torsion angles in the thiamin cation are $\varphi_T = 2·3$ (8), $\varphi_P = 83·2$ (7), $\varphi_{5\alpha} = -17·8$ (8) and $\varphi_{5\beta} = 54·3$ (8)°. The φ_T and φ_P angles are consistent with the F conformation. A comparison with other thiamin derivatives suggests that $\varphi_{5\alpha}$ and $\varphi_{5\beta}$ are dependent on crystal packing and/or hydrogen bonding. The perchlorate anion has high thermal motion as is usually the case.

Introduction. Thiamin pyrophosphate is a coenzyme in a number of important biological processes. The

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* Present address: Department of Crystallography, Institute of Chemistry, M. Curie – Sklodowska University, 20–031 Lublin, Poland.

† To whom correspondence should be addressed.

0108-2701/87/081555-03$01.50

question of the involvement of metal ions in the enzymatic reactions has been of continuing interest. Although a number of thiamin salts containing metal complexes as cations or anions have been prepared, in only three cases [Aoki & Yamazaki (1985), Cramer, Maynard & Evangelista (1984), and Cramer, Maynard & Ibers (1981)], has the metal ion been bonded to N(1′) [N(16)] of the pyrimidine ring. In one other case (Aoki & Yamazaki, 1980), the metal ion was coordinated to the O atoms of the pyrophosphate group. In an attempt to prepare metal complexes of thiamin we chose perchlorate as the cation because of its poor coordinating ability. Furthermore, we used nonaqueous solvents to avoid hydrated metal ions. The reaction of thiamin perchlorate in methanol with magnesium perchlorate in a minimum of tetrahydrofuran gave colorless crystals which proved to be thiamin perchlorate, one of the starting materials. Since the structure of thiamin perchlorate had not been reported, we determined the structure for a comparison of the thiamin conformation with those of the other salts.

Experimental. The colorless crystals were obtained from a methanol–tetrahydrofuran solution. A crystal 0·24 × 0·27 × 0·48 mm was sealed in a glass capillary and used for the data collection on a Nicolet $R3m$ diffractometer. Lattice cell parameters were obtained from a least-squares fit of 25 reflections in the 2θ range of 4·8 to 26·5°. Intensities were measured at room temperature using graphite-monochromatized Mo $K\alpha$ radiation, the θ–2θ scan technique and a variable scan speed 2·0–29·3°min^{-1}. Two standard reflections ($\bar{3}22$, $\bar{3}05$), monitored every 98 reflections, showed the intensity variation <5%. Of 2599 unique reflections collected in the 2θ range 1–45°, 2082 were observed [$F > 3\sigma(F)$] and their *hkl* range was 0–13, 0–12, ±14. No absorption corrections were applied. The Cl atom was located using the Patterson function; the remaining atoms found by Fourier syntheses. All H atoms were found in difference maps. The non-H atoms were refined anisotropically and H atoms having fixed parameters were included in the structure-factor calculations. The final refinement on F of 389 parameters, using 2082 reflections, converged to $R = 0{\cdot}089$, $wR = 0{\cdot}069$ [$w = 1/\sigma^2(F_o)$], $S = 5{\cdot}59$. The maximum shift/e.s.d. in the last cycle was 0·3 and the mean was 0·03. The residual density in the difference map was in the range −0·73 to 0·92 e Å^{-3}. The highest peaks were in the region near the Cl atom. The relatively high R value is not uncommon for organic perchlorates, see for example Owen (1983) or Trueblood, Knobler, Lawrence & Stevens (1982), and is usually accompanied by high thermal parameters. A more elaborate model for the thermal motion and/or disorder in the ClO_4^- ion would certainly lower the R value. However, since the ClO_4^- anion was not of intrinsic structural interest, we did not feel that further refinement was merited. All calculations were carried out using the programs, scattering factors and other data in the *DESKTOP SHELXTL* system (Sheldrick, 1986). Positional and equivalent isotropic thermal parameters of non-H atoms are given in Table 1 and Table 2 gives the bond distances.*

Discussion. Crystals of thiamin perchlorate monohydrate consist of the thiamin cation, perchlorate ions and a water molecule hydrogen-bonded together. The incorporation of the water was unexpected because of the nonaqueous solvents used in the synthesis. Although the corresponding chloride salt is also a

Table 1. *Atomic coordinates* (×10^4) *and equivalent isotropic thermal parameters* (Å^2 ×10^3)

	x	y	z	U_{eq}*
Cl	3115 (2)	2281 (2)	3747 (2)	64 (1)
O(1)	3921 (7)	2916 (9)	4236 (9)	206 (6)
O(2)	2871 (14)	2978 (11)	2971 (12)	301 (10)
O(3)	2349 (13)	2099 (16)	4306 (10)	369 (12)
O(4)	3276 (13)	1233 (8)	3339 (11)	277 (9)
O*w*	2175 (4)	−1571 (5)	8572 (4)	67 (2)
S(1)	−1464 (2)	−1156 (2)	9509 (1)	46 (1)
C(2)	−893 (6)	−590 (6)	8452 (5)	38 (2)
N(3)	−403 (4)	−1408 (4)	7914 (4)	29 (2)
C(4)	−477 (5)	−2554 (6)	8331 (5)	33 (2)
C(5)	−1019 (5)	−2574 (6)	9202 (5)	33 (2)
C(6)	−1281 (6)	−3664 (6)	9817 (5)	43 (3)
C(7)	−1655 (6)	−3442 (7)	10899 (5)	49 (3)
O(8)	−2573 (4)	−2659 (4)	10917 (3)	42 (2)
C(9)	52 (6)	−3577 (6)	7812 (6)	53 (3)
C(10)	127 (5)	−1168 (6)	6924 (5)	35 (2)
C(11)	87 (5)	112 (5)	6621 (4)	27 (2)
C(12)	863 (5)	963 (6)	6997 (4)	33 (2)
N(12)	1693 (5)	705 (5)	7708 (4)	46 (2)
N(13)	801 (4)	2093 (5)	6669 (4)	38 (2)
C(14)	−38 (6)	2383 (6)	5986 (5)	38 (2)
C(15)	−108 (7)	3656 (7)	5646 (7)	71 (3)
N(16)	−803 (5)	1638 (5)	5582 (4)	40 (2)
C(17)	−724 (5)	510 (6)	5912 (5)	36 (2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Bond lengths* (Å)

Cl–O(1)	1·334 (10)	Cl–O(2)	1·296 (14)
Cl–O(3)	1·216 (16)	Cl–O(4)	1·308 (11)
S(1)–C(2)	1·686 (7)	S(1)–C(5)	1·732 (7)
C(2)–N(3)	1·311 (8)	N(3)–C(4)	1·401 (8)
N(3)–C(10)	1·486 (8)	C(4)–C(5)	1·332 (9)
C(4)–C(9)	1·488 (10)	C(5)–C(6)	1·503 (9)
C(6)–C(7)	1·516 (10)	C(7)–O(8)	1·409 (8)
C(10)–C(11)	1·491 (9)	C(11)–C(12)	1·402 (9)
C(11)–C(17)	1·376 (8)	C(12)–N(12)	1·351 (8)
C(12)–N(13)	1·340 (8)	N(13)–C(14)	1·344 (8)
C(14)–C(15)	1·498 (10)	C(14)–N(16)	1·327 (9)
N(16)–C(17)	1·339 (9)		

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* Tables of bond angles, hydrogen-bond dimensions, anisotropic thermal parameters, H-atom parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43877 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

monohydrate (Pletcher, Sax, Sengupta, Chu & Yoo, 1972), the nitrate salt is anhydrous (Ishida, Tanaka & Inoue, 1984).

The cation and atomic numbering are shown in Fig. 1. The dihedral angle between the pyrimidine and thiazolium ring planes is 84·5 (8)° which falls within the range (70·9 to 104·0°) observed in various thiamin derivatives. The value for the chloride salt is 77·2° and for the nitrate 84·7°. The thiamin cation has the *F* conformation as defined by Pletcher, Sax, Turano & Chang (1982). The torsion angles are $\varphi_T = 2{\cdot}3$ (8), $\varphi_P = 83{\cdot}2$ (7), $\varphi_{5\alpha} = 17{\cdot}8$ (8) and $\varphi_{5\beta} = 54{\cdot}3°$. The φ_T and φ_P angles are appropriate for the *F* conformation. The $\varphi_{5\alpha}$ value deviates significantly from the average value of 76·4° given by Pletcher *et al.* (1982). A somewhat similar situation was observed in the nitrate salt (Ishida *et al.*, 1984), where φ_T of 5·9 (5), φ_P of 83·1 (4), and $\varphi_{5\alpha}$ of −92·8 (4)° were appropriate for the *F* conformation but the $\varphi_{5\beta}$ value of 175·7 (3)° was significantly different from 70°. Since in the perchlorate, the nitrate, and the chloride salts, the hydroxyethyl side chain is involved in hydrogen bonding, the conformation of this side chain probably reflects crystal-packing requirements. Consequently, average values for the $\varphi_{5\alpha}$ and $\varphi_{5\beta}$ torsion angles are meaningless.

The distances in the thiamin cation are similar to those of the 29 other thiamin derivatives found in the Cambridge Structural Database (1986). The S(1)—C(5) distance of 1·732 (7) Å is always longer than S(1)—C(2) of 1·686 (7) Å. C(4)—C(5), 1·332 (9) Å, is essentially a localized double bond. The bonds involving N(3) in the ring, N(3)—C(2) of 1·311 (8) Å and N(3)—C(4) of 1·401 (8) Å, show some delocalization while the N(3)—C(10) bond of 1·486 (8) Å is in essence a single bond. In summary, there is very little delocalization in the thiazolium ring. The distances in the pyrimidine ring are also close to the average values.

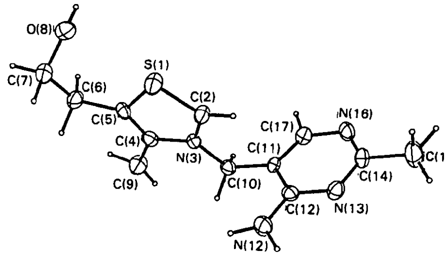

Fig. 1. A view of the thiaminium cation showing the atomic numbering and the thermal ellipsoids.

We thank the NSF for contributing to the purchase of the diffractometer, the Center for Instructional Research Computing Activities, University of Florida, for a grant of computer time and the Department of Chemistry for a Postdoctoral Fellowship (AEK).

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Acta Cryst. (1987). C**43**, 1557–1560

Structure of 2-(2,3-Dihydro-1,3-dimethylbenzimidazol-2-yl)phenol

By André L. Beauchamp,* France Montgrain and James D. Wuest*

Département de Chimie, Université de Montréal, Montréal, Québec H3C 3J7, Canada

(*Received* 6 *February* 1987; *accepted* 3 *March* 1987)

Abstract. $C_{15}H_{16}N_2O$, $M_r = 240{\cdot}31$, monoclinic, $P2_1/c$, $a = 8{\cdot}853$ (3), $b = 10{\cdot}731$ (3), $c = 13{\cdot}729$ (4) Å, $\beta = 94{\cdot}81$ (3)°, $V = 1299{\cdot}7$ Å^3, $Z = 4$, $D_x = 1{\cdot}228$ Mg m^{-3}, λ(Mo $K\bar{\alpha}$) = 0·71069 Å (graphite monochromator), μ(Mo $K\alpha$) = 0·073 mm^{-1}, $F(000) = 512$, $T = 295$ K, final $R = 0{\cdot}032$ for 1352 nonzero reflections. The five-membered ring assumes an envelope conformation in which the N lone pairs and

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* Authors to whom correspondence should be addressed.