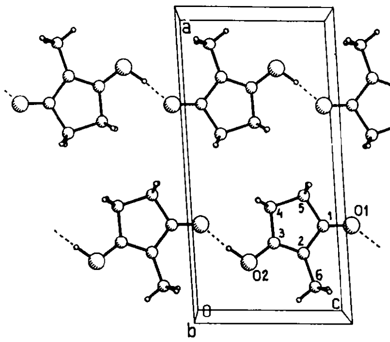

Fig. 2. Arrangement of the MCPD molecules (*PLUTO*, Motherwell, 1976) in the crystal lattice: the chains of MCPD molecules are viewed perpendicular to the *ac* plane and to the plane of the molecules. Hydrogen bonds are represented as dashed lines and only half of the unit-cell contents are included in the direction perpendicular to the drawing to avoid overlaying of the molecules.

pointing towards the O(2)H hydroxyl group. As already mentioned above, the final Fourier map showed a number of peaks, the strongest of which could be assigned to the bonding electrons of each of the C—C bonds and to the disordered H atoms with opposite methyl-group orientation [rotated by 180° about C(2)—C(6)]. These peaks were relatively low, both about 0·16 e Å^{-3}, which was about 0·25 of the electron density corresponding to H(61) or H(62); the distances of these peaks to C(6) were 1·02 and 1·04 Å. One explanation for the appearance of these peaks is that the methyl group is not stable in the structure but can rotate and the opposite orientation is its metastable position which could be detected in this X-ray study due to the relatively high precision of the collected data.

The arrangement of the MCPD molecules in the crystal lattice is presented in Fig 2. The molecules are interconnected into chains along the z axis of the crystal by short hydrogen bonds between the enol hydroxyl H(2) atoms and the carbonyl O(1) atoms. The hydrogen-bond configuration is *anti–syn* [O(1)···O(2) 2·5980 (18), O(1)···H(2) 1·555 (21) Å] and nearly linear [∠O(1)···H(2)—O(2) 174·0 (19)°]. A similar *syn–syn* hydrogen bond of 2·595 (2) Å was observed in dimedone (Semmingsen, 1974), while significantly shorter hydrogen bonds were found in the two forms of CHD: 2·561 (4) Å for the *anti–anti* hydrogen bond in CHD and 2·579 (1) Å for the *syn–anti* hydrogen bond in the 6:1 CHD:benzene inclusion compound (Etter, Urbańczyk-Lipkowska, Jahn & Frye, 1986). Two even shorter independent hydrogen bonds have been observed in the crystals of squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione): 2·553 (1) and 2·554 (1) Å (Semmingsen, Hollander & Koetzle, 1977).

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Structure of Thiamin Hydrochloride Hemisulfate Monohydrate

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Abstract. $C_{12}H_{18}N_4OS^{2+}.Cl^-.\frac{1}{2}SO_4^{2-}.H_2O$, M_r = 367·9, monoclinic, $C2/c$, a = 20·766 (6), b = 11·825 (2), c = 13·367 (2) Å, β = 101·15 (2)°, V = 3220 (1) Å^3, Z = 8, D_x = 1·52 g cm^{-3}, Mo $K\alpha$, λ = 0·71069 Å, μ = 4·45 cm^{-1}, $F(000)$ = 1544, room temperature, R = 0·0405 for 2075 observed reflections for which $I > 3\sigma(I)$. The thiamin cation is found in the usual F conformation. The extensive network of

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interactions between the chloride, sulfate, thiamin and water species includes hydrogen bonds, electrostatic interactions and parallel stacking of pyrimidine bases.

Introduction. In the course of our research on the interaction of metal ions with thiamin, we prepared thiamin chloride hemisulfate monohydrate, (thiamin)Cl$(SO_4)_{0\cdot5}$.H_2O, where thiamin^{2+} is $(C_{12}H_{18}N_4OS)^{2+}$ (Fig. 1).

We report here the structure of this compound and discuss its conformation in relation to the presence of an extensive network of interactions (Cramer, Kirkup & Carrie, 1988).

Experimental.

Preparation of $(Hthiamin)_2Cl_2(SO_4).2H_2O$

The mixing of aqueous solutions of $(Hthiamin)Cl_2$, and Ag_2SO_4 in a 2:1 stoichiometry resulted in the immediate precipitation of AgCl. Filtration of this precipitate followed by evaporation of the solvent to complete dryness resulted in a white powder which was recrystallized from an aqueous solution containing 10% DMF to yield large, colorless, plate-like crystals.

X-ray data collection and reduction

A crystal with maximal dimensions 1·5 × 0·4 × 0·25 mm was inserted in a capillary mounted on a glass fiber, with its longest edge parallel to the glass fiber. Intensity data were collected on a Syntex $P\bar{1}$ four-circle diffractometer with a pulse-height analyser using graphite-monochromatized Mo $K\alpha$ radiation. The unit-cell parameters at 298 K were determined by a least-squares analysis of the angular coordinates of 15 independent reflections with 2θ values from 31·5 to 40·1°. The intensities of three check reflections were measured every 100 reflections throughout data collection. Sharp discontinuities in the output of the detector occurred twice during data collection and based upon the check reflections corrections of up to 40% were subsequently applied to the data. Of the 2779 unique reflections measured (h $-24\rightarrow24$, k $0\rightarrow14$, l $0\rightarrow15$; $3\cdot0 < 2\theta < 50\cdot0°$; $R_{\rm int} = 0\cdot0382$), only 2075 with $I > 3\sigma(I)$ were used in refinement. An absorption correction was performed based on ψ scans (Bruck, 1983) using three reflections with 2θ values of 12·29, 21·76 and 34·44°. The resulting transmission coefficients ranged from 0·86 to 0·98.

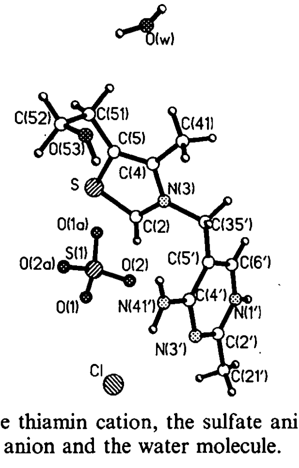

Fig. 1. Plot of the thiamin cation, the sulfate anion, the chloride anion and the water molecule.

Solution and refinement of the structure

The space group $C2/c$, which is consistent with observed systematic absences, was assumed and confirmed by satisfactory refinement. The structure was solved using *MULTAN* (Main *et al.*, 1980) with which the sulfate group and 16 of the 18 atoms constituting the thiamin skeleton were located. Isotropic refinement of these positions using *SHELX* (Sheldrick, 1976) led to the location of the two remaining thiamin C atoms, Cl and O(W) in successive Fourier maps. Two cycles of anisotropic refinement lowered R from 0·15 to 0·07. Subsequent refinement resulted eventually in the location of all H atoms. With all H-atom thermal parameters refined isotropically, the final error index was $R = 0\cdot0405$ (unit weights) for 2075 reflections and 285 parameters (overdetermination ratio = 7·3). Positional parameters for non-H atoms are given in Table 1.* $\Delta/\sigma_{\rm max} = 0\cdot2$; $\Delta\rho_{\rm max} = 0\cdot4$ e Å^{-3}. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Discussion. The sulfate ion is located on a twofold axis so that the unit cell is composed of eight thiamins, eight chlorides, four sulfates and eight water molecules (Fig. 2). Interactions between these components include an extensive network of hydrogen bonds and electrostatic interactions (Table 2) and parallel stacking of pyrimidine bases.

The arrangement of the atoms and molecules forming the crystal can be conveniently described by reference to a projection of the structure along the b axis. Thiamin units form columns along this axis, and along each column the thiamins are arranged in centrosymmetric pairs held together through a strong stacking interaction of the pyrimidine bases (the mean separation of the pyrimidine planes is 3·18 Å). These columns are linked to each other along the a–c direction through crossed O(53)—S electrostatic con-

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* Lists of anisotropic thermal parameters, H-atom parameters, distances involving H atoms, and the observed and calculated structure amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52038 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional and equivalent isotropic thermal parameters in* (Hthiamin)Cl$(SO_4)_{0·5}.H_2O$

	x	y	z	U_{eq}*(Å^2)
S	0·3457 (1)	0·2148 (1)	0·2162 (1)	0·0345
C(2)	0·3932 (2)	0·2459 (3)	0·1316 (2)	0·030
N(3)	0·3645 (1)	0·3183 (2)	0·0621 (2)	0·026
C(4)	0·3027 (2)	0·3539 (3)	0·0740 (2)	0·028
C(5)	0·2846 (2)	0·3035 (3)	0·1556 (2)	0·030
C(51)	0·2238 (2)	0·3264 (4)	0·1972 (3)	0·040
C(52)	0·2338 (2)	0·4234 (4)	0·2750 (3)	0·052
O(53)	0.2474 (2)	0·5272 (3)	0·2323 (3)	0·059
C(41)	0·2655 (2)	0·4378 (4)	0·0028 (3)	0·036
C(35′)	0·3964 (2)	0·3654 (3)	−0·0207 (3)	0·032
C(5′)	0·4646 (2)	0·3238 (3)	−0·0147 (2)	0·028
C(6′)	0·4790 (2)	0·2484 (3)	−0·0841 (3)	0·031
N(1′)	0·5411 (1)	0·2141 (3)	−0·0805 (2)	0·033
C(2′)	0·5906 (2)	0·2570 (3)	−0·0108 (3)	0·033
N(3′)	0·5811 (1)	0·3320 (2)	0·0578 (2)	0·031
C(4′)	0·5186 (2)	0·3651 (3)	0·0581 (2)	0·029
C(21′)	0·6581 (2)	0·2167 (4)	−0·0121 (4)	0·046
N(41′)	0·5110 (2)	0·4392 (3)	0·1296 (2)	0·036
S(1)	$\frac{1}{2}$	0·0163 (1)	$\frac{1}{4}$	0·0314
O(1)	0·5565 (1)	−0·0562 (3)	0·2842 (3)	0·080
O(2)	0·5149 (2)	0·0855 (3)	0·1683 (2)	0·080
Cl	0·611 (2)	0·5697 (1)	0·2985 (1)	0·0381
O(*W*)	0·0923 (2)	0·4650 (3)	0·0336 (3)	0·061

* Defined as one-third the trace of the orthogonalized U_{ij} tensor.

Table 2. *Possible hydrogen-bonding interactions* (*A*—H···*B*) *and other short contacts in* (Hthiamin)Cl$(SO_4)_{0·5}.H_2O$

A	*B*	Equivalent position of *B*	*A*—*B* (Å)
Hydrogen bonds			
N(1′)	O(1)	*x*, −*y*, 0·5+*z*	2·661 (5)
C(6′)	O(*W*)	*x*, *y*, *z*	3·066 (5)
O(*W*)	O(2)	*x*, *y*, *z*	3·205 (5)
N(41′)	Cl	*x*, *y*, *z*	3·156 (3)
N(41′)	Cl	1−*x*, *y*, 0·5−*z*	3·262 (4)
O(53)	Cl	1−*x*, *y*, 0·5−*z*	3·092 (4)
C(2)	O(2)	1−*x*, *y*, 0·5−*z*	3·122 (5)
C(2)	O(*W*)	*x*, *y*, *z*	3·383 (5)
O(*W*)	O(2)	1−*x*, −*y*, −*z*	2·996 (5)
Other short contacts			
O(53)	S	0·5−*x*, 0.5+*y*, 0·5−1	3·106 (4)
O(2)	S	1−*x*, *y*, 0·5−*z*	3·372 (4)
Cl	N(1′)	*x*, −1+*y*, *z*	3·486 (5)
O(*W*)	N(1′)	1−*x*, −*y*, −*z*	3·392 (5)

tacts and are separated along the *c* direction by columns of sulfate ions (Fig. 3). These crossed contacts are formed between the O(53) and S positions of each molecule and their electrostatic counterparts on the two nearest molecules, resulting in a succession of O(53)—S and S—O(53) interactions along the *b* axis. It is interesting to note that the short intramolecular contact between S and O(53) observed in several thiamin structures (Pletcher, Sax, Yoo, Chu & Wood, 1977; Pletcher, Wood, Blank, Shin & Sax, 1977; Cramer, Maynard & Ibers, 1981; Pletcher, Sax, Yoo, Chu & Power, 1974) is observed here as an intermolecular contact of which it is the first example. The O(53)—S distance of 3·106 (4) Å is slightly longer than similar distances reported in other thiamin derivatives, which range from 2·88 to 3·06 Å (Cramer, Maynard & Ibers, 1981; Pletcher, Sax, Yoo, Chu & Wood, 1977; Pletcher, Wood, Blank, Shin & Sax, 1977). The values of the torsion angles (Shin, Pletcher, Blank & Sax, 1977) $\varphi_{5\alpha} = 83·1$ and $\varphi_{5\beta} = 63·0°$ are an indication of the large flexibility of this side chain (Shin, Pletcher, Blank & Sax, 1977).

Interactions between sulfate anions and thiamin cations include O(1)—N(1′) and O(2)—C(2) hydrogen bonds and O(2)—S electrostatic contacts (Fig. 3). The water molecule acts as a hydrogen-bond donor towards the sulfate O(2) atom while also interacting with thiamin units (Fig. 3 and Table 2). Finally the chloride anion makes several short contacts with thiamin atoms (Table 2). In particular, it forms a bridge between the two thiamin rings through dipolar contacts with the thiazolium moiety and a hydrogen bond with the pyrimidine exocyclic N(41′) atom. The presence of this chloride can be compared to the previously discussed (Cramer, Kirkup & Carrie, 1988; Archibong, Adeyemo, Aoki & Yamazaki, 1988) presence of polychlorometalloanions $(M^{n+}Cl_x)^{(x-n)-}$ in other thiamin structures. These anions, simultaneously involved in hydrogen bonding with the amino group of the

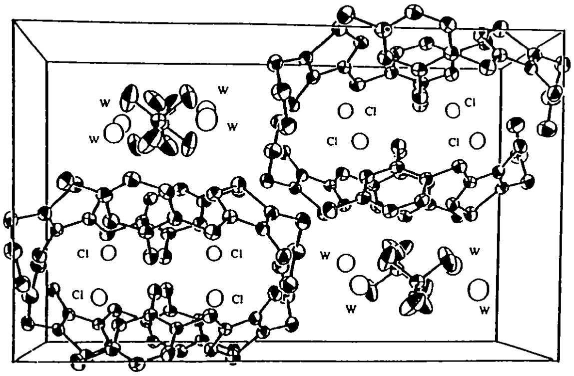

Fig. 2. Unit-cell contents.

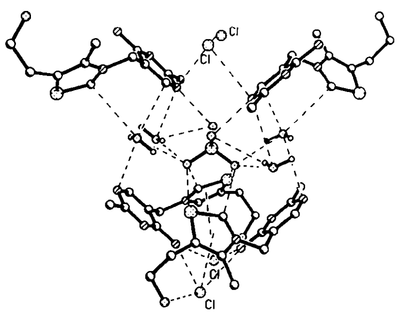

Fig. 3. View nearly perpendicular to the C_2 axis of a sulfate anion interacting with four thiamin cations. Short contacts indicated by broken lines.

Table 3. *Bond distances* (Å) *and angles* (°) *in* (Hthiamin)Cl$(SO_4)_{0\cdot5}.H_2O$

S—C(2)	1·679 (4)	C(4′)—C(5′)	1·422 (4)
C(2)—N(3)	1·318 (4)	C(5′)—C(6′)	1·361 (4)
N(3)—C(4)	1·388 (4)	N(1′)—C(6′)	1·343 (4)
S—C(5)	1·723 (3)	N(1′)—C(2′)	1·345 (4)
C(4)—C(5)	1·358 (4)	C(2′)—N(3′)	1·317 (4)
C(5)—C(51)	1·500 (6)	N(3′)—C(4′)	1·355 (4)
C(51)—C)52)	1·535 (6)	C(2′)—C(21′)	1·485 (6)
C(52)—O(53)	1·405 (6)	C(4′)—N(41′)	1·328 (4)
C(4)—C(41)	1·484 (4)	S(1)—O(1)	1·454 (3)
N(3)—C(35′)	1·502 (4)	S(1)—O(2)	1·445 (4)
C(5′)—C(35′)	1·487 (4)		
C(5)—S—C(2)	91·4 (1)	C(4′)—C(5′)—C(35′)	122·7 (3)
N(3)—C(2)—S	111·9 (3)	C(4′)—C(5′)—C(6′)	116·3 (3)
C(4)—N(3)—C(2)	114·7 (3)	N(1′)—C(6′)—C(5′)	120·6 (3)
C(35′)—N(3)—C(2)	123·7 (3)	C(2′)—N(1′)—C(6′)	120·7 (3)
C(35′)—N(3)—C(4)	121·5 (3)	N(3′)—C(2′)—N(1′)	122·6 (3)
C(5)—C(4)—N(3)	111·4 (3)	C(21′)—C(2′)—N(1′)	117·9 (3)
C(41)—C(4)—N(3)	120·5 (3)	C(21′)—C(2′)—N(3′)	119·5 (3)
C(41)—C(4)—C(5)	128·1 (3)	C(4′)—N(3′)—C(2′)	118·0 (3)
C(4)—C(5)—S	110·6 (3)	N(3′)—C(4′)—C(5′)	121·8 (3)
C(51)—C(5)—S	122·2 (3)	N(41′)—C(4′)—C(5′)	122·1 (3)
C(51)—C(5)—C(4)	127·0 (3)	N(41′)—C(4′)—N(3′)	116·1 (3)
C(52)—C(51)—C(5)	111·9 (3)	O(2)—S(1)—O(1)	107·1 (2)
O(53)—C(52)—C(51)	112·9 (3)	O(1)—S(1)—O(1)	107·8 (2)
C(6′)—C(5′)—C(35′)	120·9 (3)	O(2)—S(1)—O(2)	111·9 (2)

pyrimidine moiety and electrostatic contacts with the thiazolium ring have been thought to constitute a determinant factor of the conformation of the molecule. In our case, the bridging interaction of this chloride results in torsion angles (Pletcher & Sax, 1972) $\varphi_T = 1{\cdot}30°$ and $\varphi_P = 76{\cdot}2°$, corresponding to the common *F* conformation (Shin, Pletcher, Blank & Sax, 1977).

Bond distances and bond angles (Table 3) within the thiamin unit are in accordance with those obtained in other thiamin structures in which the N(1′) position is protonated (Cramer, Maynard & Ibers, 1981). Both thiazolium and pyrimidine rings of the thiamin moiety are planar as shown by least-squares calculations (maximal deviations: 0·018 Å for the pyrimidine plane and 0·005 Å for the thiazolium plane). Bond distances and bond angles within the sulfate anion (Table 3) are comparable with those observed in other structures (Lanfredi, Pellinghelli & Tiripicchio, 1974; Weber, 1974). The slightly larger bond length obtained for S(1)—O(1) can be attributed to the strong O—N(1′) hydrogen bonds between this O and a neighboring pyrimidine. The geometry about the S atom is tetrahedral as indicated by the O—S—O angles which range from 107·1 (2) to 111·9 (2)°, similar to those reported previously (Lanfredi, Pellinghelli & Tiripicchio, 1974; Weber, 1974).

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Structures of Aminopyrazole Derivatives

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Abstract. (I): 1-Amino-3-phenylpyrazole, $C_9H_9N_3$, $M_r = 159{\cdot}2$, monoclinic, $P2_1/n$, $a = 18{\cdot}729$ (1), $b = 5{\cdot}742$ (2), $c = 15{\cdot}807$ (2) Å, $\beta = 104{\cdot}39$ (1)°, $U = 1646{\cdot}7$ (7) Å^3, $Z = 8$, $D_x = 1{\cdot}285$ Mg m^{-3}, λ(Cu $K\alpha_1$) = 1·5405 Å, $\mu = 0{\cdot}658$ mm^{-1}, $F(000) = 672$, $T = 293$ K, final $R = 0{\cdot}053$ for 2715 observed reflexions.

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