The partly saturated pyrimidine-2-thione ring assumes a rather flattened envelope conformation [Cremer & Pople's (1975) puckering parameters if the atomic sequence is chosen from N(1) through C(2)··· to C(8a): $Q = 0.114$ (2) Å, $\varphi = 171.2$ (10), $\theta = 70.4$ (9)°] with C(4) on the flap to which the phenyl ring is bound pseudoaxially [C(9)–C(4)–N(3)–C(2) $= 110.3$ (3)°]. The planar thiourea moiety is characterized by the C–S and C–N multiple bonds similar to those found in other structures. The relevant difference between the lengths of C(2)–N(1) and C(2)–N(3) multiple bonds [$\Delta = 0.035$ (2) Å] can be attributed to the difference in the hybridization of the adjacent carbon atoms C(8a)–sp^2 vs C(4)–sp^3. The carbo ring of the quinazoline skeleton due to the three sp^3 C atoms possesses a slightly distorted [puckering parameters if the atomic sequence is chosen from C(4a) through C(5)··· to C(8a): $Q = 0.471$ (2) Å, $\varphi = 316.9$ (3), $\theta = 130.3$ (2)°] half-chair shape. C(6) with the highest out-of-plane displacement [0.317 (2) Å] from the least-squares plane of the ring bears the methyl substituent in an equatorial position [C(15)–C(6)–C(7)–C(8) = -177.0 (3)°].

In the crystal lattice centre-of-symmetry-related pairs of molecules form dimer associates with the hydrogen-bond parameters

	$D \cdots A$ (Å)	$H \cdots A$ (Å)	$DH \cdots A$ (°)
N(3)–H(3)$\cdots$S($1-x, -y, -z$)	3.362 (3)	2.40 (2)	159 (1).

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Structures of Thiamine Hexafluorophosphate Monohydrate, Thiaminium Diperchlorate, Thiaminium Bis(hexafluorophosphate) Tetrahydrate, and Thiaminemonophosphate Hexafluorophosphate Dihydrate

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Abstract. $C_{12}H_{17}N_4OS^+.PF_6^-.H_2O$ (1), $M_r = 428.336$, monoclinic, $P2_1/n$, $a = 12.968$ (2), $b = 11.381$ (2), $c = 12.335$ (3) Å, $\beta = 92.71$ (2)°, $V = 1818.5$ (6) Å^3, $Z = 4$, $D_x = 1.564$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 3.28$ cm^{-1}, $F(000) = 880$, $T = 293$ K, $R = 0.047$ for 2522 reflections; $C_{12}H_{18}N_4OS^{2+}.2ClO_4^-$ (2), $M_r = 465.265$, monoclinic, $P2_1/n$, $a = 18.728$ (5), $b = 7.683$ (1), $c = 13.968$ (3) Å, $\beta = 101.87$ (2)°, $V = 1966.9$ (7) Å^3, $Z = 4$, $D_x = 1.571$ g cm^{-3}, μ(Mo $K\alpha$) $= 4.82$ cm^{-1}, $F(000) = 960$, $T = 293$ K, $R = 0.064$ for 2771 reflections; $C_{12}H_{18}N_4OS^{2+}.2PF_6^-.4H_2O$ (3), $M_r = 628.351$, monoclinic, $P2_1/a$, $a = 11.198$ (2), $b = 26.659$ (7), $c = 8.407$ (2) Å, $\beta = 90.03$ (2)°, $V = 2510.0$ (9) Å^3, $Z = 4$, $D_x = 1.663$ g cm^{-3}, μ(Mo $K\alpha$) $= 3.65$ cm^{-1}, $F(000) = 1280$, $T = 293$ K, $R = 0.060$ for 2190 reflections; $C_{12}H_{18}N_4O_4PS^+.PF_6^-.2H_2O$ (4), $M_r = 526.330$, triclinic, $P\bar{1}$, $a = 11.633$ (1), $b = 11.255$ (2), $c = 8.441$ (2) Å, $\alpha = 78.80$ (2), $\beta = 94.90$ (1), $\gamma = 103.63$ (1)°, $V = 1052.7$ (3) Å^3, $Z = 2$, $D_x = 1.679$ g cm^{-3}, μ(Mo $K\alpha$) = 3.84 cm^{-1}, $F(000) = 540$, $T = 293$ K, $R = 0.045$ for 3092 reflections. In each compound, the thiamine moiety that adopts the F conformation holds a monovalent anion in a position in which the anion interacts with the thiazolium ring *via* a hydrogen bond with the acidic C(2)H and an electrostatic interaction with the positively charged S(1) atom, and it further contacts, possibly electrostatically, with the pyrimidine (or pyrimidinium) ring.

Table 1. *Experimental details*

Compound	(1)	(2)	(3)	(4)
Crystal size (mm)	0·64 × 0·39 × 0·48	0·35 × 0·27 × 0·25	0·51 × 0·39 × 0·17	0·54 × 0·48 × 0·35
Crystal shape	Columnar	Columnar	Plate	Columnar
2θ range measured (°)	3·0–55·0	3·0–50·0	3·0–45·0	3·0–50·0
Scan mode	ω scan for 2θ ≤ 30°	ω scan for 2θ ≤ 30°	ω scan for 2θ ≤ 30°	ω scan for 2θ ≤ 30°
	ω–2θ scan for 2θ > 30°	ω–2θ scan for 2θ > 30°	ω–2θ scan for 2θ > 30°	ω–2θ scan for 2θ > 30°
Scan range (°)	1·2 + 0·5tanθ	1·2 + 0·5tanθ	1·2 + 0·5tanθ	1·5 + 0·5tanθ
Unique data measured	4191	3751	3289	3702
Unique data used $[F_o > 3\sigma(F_o)]$	2522	2771	2190	3092
Scan speed (2θ) (° min⁻¹)	4·0	4·0	4·0	4·0
Background counting (s)	5	5	5	5
Transmission factors*	0·98–1·02	0·97–1·02	0·95–1·07	0·93–1·13
Final number of variables	347	316	325	392
Weighting scheme w	$w = 1\cdot0$ for $F_o \le 50\cdot0$	$w = 1\cdot0$ for $F_o \le 50\cdot0$	$w = 1\cdot0$ for $F_o \le 50\cdot0$	$w = 1\cdot0$
	$w^{1/2}=50\cdot0/F_o$ for $F_o > 50\cdot0$	$w^{1/2}=50\cdot0/F_o$ for $F_o>50\cdot0$	$w^{1/2}=50\cdot0/F_o$ for $F_o>50\cdot0$	
R	0·047	0·064	0·060	0·045
wR	0·046	0·060	0·066	0·049
S	0·98	1·17	1·85	0·97
$(\Delta/\sigma)_{max}$	0·25	0·43	0·39	0·23
$(\Delta\rho)_{max}$ (e Å⁻³)	0·60	0·28	0·39	0·49

* Normalized to an average of unity.

Introduction. Thiamine (vitamin B_1), as its pyrophosphate ester, is a cofactor for a number of metabolic enzymes catalyzing the decarboxylation of α-keto acids and the transfer of aldehyde or acyl groups (Krampitz, 1969). Previously, we presented tentatively a substrate fixation model in which the carboxylate group of a substrate forms a hydrogen bond with the acidic C(2)H and electrostatic interactions with both the positively charged S(1) atom and the pyrimidine ring that assumes the *F* conformation (Aoki & Yamazaki, 1985). This prompted us to undertake a further X-ray investigation to examine the general significance of such interactions. We report here the crystal structures of thiamine hexafluorophosphate monohydrate (1), thiaminium diperchlorate (2), thiaminium bis(hexafluorophosphate) tetrahydrate (3), and thiaminemonophosphate hexafluorophosphate dihydrate (4). (1) is isomorphous to thiamine perchlorate monohydrate (Koziol, Palenik & Palenik, 1987).

Experimental. The hexafluorophosphate salts were prepared from NH_4PF_6 and thiamine.NO_3 for (1), thiamine.Cl.HCl for (3) and thiaminemonophosphate.Cl for (4) in aqueous solution each with 2:1 molar ratio, and the perchlorate salt (2) was from $Mg(ClO_4)_2$ and thiamine.Cl.HCl with 2:1 molar ratio.

The crystals for (1) and (2) were mounted on glass fibers and those for (3) and (4) were sealed in glass capillaries together with a small quantity of mother liquor. Cell parameters were determined on a Rigaku AFC-5 four-circle diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0\cdot71073$ Å) from 20 high-order reflections [24 < 2θ < 34° for (1), 22 < 2θ < 34° for (2), 22 < 2θ < 32° for (3), and 23 < 2θ < 34° for (4)]. Details of the data collection together with structure refinement are summarized in Table 1. Throughout the data collection the intensities of the three standard reflections were monitored every 100

Table 2. *Fractional atomic coordinates and equivalent isotropic temperature factors with e.s.d.'s in parentheses for thiamine.*$PF_6.H_2O$ (1)

$$B_{eq} = \tfrac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å²)
N(1')	0·4391 (2)	−0·1669 (2)	0·0739 (2)	3·0
C(2')	0·3968 (2)	−0·2424 (3)	0·0018 (3)	3·1
N(3')	0·3292 (2)	−0·2155 (2)	−0·0797 (2)	2·9
C(4')	0·2978 (2)	−0·1027 (3)	−0·0892 (2)	2·5
C(5')	0·3365 (2)	−0·0168 (3)	−0·0156 (2)	2·3
C(6')	0·4067 (2)	−0·0548 (3)	0·0630 (2)	2·7
C(2'a)	0·4279 (3)	−0·3689 (3)	0·0124 (4)	5·3
N(4'a)	0·2287 (2)	−0·0783 (3)	−0·1707 (2)	3·6
C(3,5')	0·3069 (2)	0·1102 (3)	−0·0210 (3)	2·6
S(1)	0·05234 (7)	0·11343 (7)	0·14210 (8)	3·4
C(2)	0·1522 (2)	0·0555 (3)	0·0792 (3)	2·9
N(3)	0·2078 (2)	0·1355 (2)	0·0319 (2)	2·2
C(4)	0·1707 (2)	0·2496 (3)	0·0425 (2)	2·5
C(5)	0·0856 (2)	0·2535 (3)	0·1022 (2)	2·5
C(4a)	0·2249 (3)	0·3513 (3)	−0·0054 (3)	4·1
C(5a)	0·0301 (3)	0·3627 (3)	0·1356 (3)	3·3
C(5β)	−0·0783 (3)	0·3439 (3)	0·1742 (3)	3·7
O(5γ)	−0·0816 (2)	0·2626 (2)	0·2614 (2)	3·3
O(W)	0·1537 (2)	0·1490 (3)	−0·2286 (2)	5·6
P(1)	0·11775 (8)	−0·28076 (9)	0·19053 (8)	3·9
F(1)*	0·2190 (3)	−0·2140 (4)	0·1721 (4)	7·8
F(2)	0·0491 (2)	−0·1783 (3)	0·1383 (3)	9·0
F(3)*	0·0166 (3)	−0·3566 (3)	0·1980 (4)	6·8
F(4)	0·1820 (2)	−0·3826 (3)	0·2480 (3)	7·7
F(5)*	0·0984 (4)	−0·2243 (4)	0·3008 (3)	8·9
F(6)*	0·1366 (4)	−0·3527 (4)	0·0819 (3)	8·7
F(1)'*	0·2022 (7)	−0·1856 (9)	0·2368 (8)	8·2
F(3)'*	0·0387 (10)	−0·3558 (9)	0·1267 (9)	9·5
F(5)'*	0·0459 (11)	−0·2989 (13)	0·2875 (10)	13·2
F(6)'*	0·1642 (9)	−0·2528 (11)	0·0816 (7)	9·0

* Disordered F atoms; occupancy factors: 0·7 for F(1), F(3), F(5), and F(6) and 0·3 for F(1)', F(3)', F(5)', and F(6)'.

measurements; a maximum variation in intensity of less than 2% was noted for (2). Intensities were corrected for Lp effects but not for absorption because of the small variations in intensity of an axial reflection (at χ ~ 90°) with the spindle angle φ.

The structures were solved by *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by block-diagonal least-squares methods minimizing the function $\Sigma w(F_o - |F_c|)^2$. Anions in (1),

Table 3. *Fractional atomic coordinates and equivalent isotropic temperature factors with e.s.d.'s in parentheses for thiaminium.*$(ClO_4)_2$ (2)

$$B_{eq} = \tfrac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
N(1')	0·3252 (2)	0·8227 (5)	1·0003 (2)	4·1
C(2')	0·3798 (2)	0·7466 (6)	1·0642 (3)	3·9
N(3')	0·4459 (2)	0·7319 (5)	1·0466 (2)	4·0
C(4')	0·4580 (2)	0·7910 (5)	0·9596 (3)	3·4
C(5')	0·4010 (2)	0·8633 (5)	0·8878 (3)	3·1
C(6')	0·3348 (2)	0·8778 (6)	0·9124 (3)	3·7
C(2'α)	0·3631 (3)	0·6722 (7)	1·1556 (3)	5·6
N(4'α)	0·5255 (2)	0·7752 (5)	0·9465 (2)	4·5
C(3,5')	0·4108 (2)	0·9288 (6)	0·7898 (3)	3·5
S(1)	0·40403 (8)	0·4918 (2)	0·64150 (8)	5·1
C(2)	0·4109 (2)	0·6194 (6)	0·7396 (3)	4·2
N(3)	0·4091 (2)	0·7855 (4)	0·7167 (2)	3·2
C(4)	0·4029 (2)	0·8174 (6)	0·6169 (3)	3·6
C(5)	0·3994 (2)	0·6686 (6)	0·5651 (3)	3·9
C(4α)	0·3986 (3)	1·0000 (7)	0·5797 (3)	5·3
C(5α)	0·3897 (3)	0·6437 (7)	0·4566 (3)	5·0
C(5β)	0·3157 (3)	0·5666 (7)	0·4117 (3)	5·2
O(5γ)	0·3072 (2)	0·3981 (4)	0·4494 (2)	5·1
Cl(1)	0·30009 (6)	0·3566 (2)	0·87789 (8)	4·6
O(1)*	0·3671 (4)	0·4315 (11)	0·9192 (6)	8·1
O(2)*	0·3200 (10)	0·290 (2)	0·7873 (8)	17·1
O(3)*	0·2938 (6)	0·274 (2)	0·9665 (7)	11·8
O(4)*	0·2628 (3)	0·5053 (7)	0·8385 (5)	12·0
O(1)'*	0·3713 (3)	0·3111 (9)	0·8593 (5)	5·7
O(2)'*	0·3057 (10)	0·411 (2)	0·9733 (10)	18·6
O(3)'*	0·2544 (5)	0·235 (2)	0·8216 (7)	10·3
Cl(2)	0·61247 (7)	0·8626 (2)	0·71867 (9)	5·6
O(5)*	0·6754 (3)	0·8796 (10)	0·6880 (5)	9·7
O(6)*	0·5616 (3)	1·0030 (10)	0·6770 (5)	9·7
O(7)*	0·6200 (4)	0·8844 (10)	0·8188 (4)	9·3
O(8)*	0·5782 (4)	0·7020 (9)	0·6926 (6)	11·1
O(5)'*	0·6746 (7)	0·984 (2)	0·6992 (9)	7·2
O(6)'*	0·5702 (7)	0·953 (2)	0·7643 (9)	7·5
O(7)'*	0·6634 (14)	0·739 (3)	0·781 (2)	15·8
O(8)'*	0·5825 (6)	0·789 (2)	0·6304 (8)	7·2

* Disordered O atoms; occupancy factors: 0·6 for O(1), O(2), and O(3) and 0·4 for O(1)', O(2)', and O(3)', and 0·7 for O(5)–O(8) and 0·3 for O(5)'–O(8)'.

Table 4. *Fractional atomic coordinates and equivalent isotropic temperature factors with e.s.d.'s in parentheses for thiaminium.*$(PF_6)_2.4H_2O$ (3)

$$B_{eq} = \tfrac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
N(1')	0·1407 (4)	0·1296 (2)	0·4124 (6)	3·6
C(2')	0·1909 (6)	0·1453 (2)	0·2753 (8)	3·8
N(3')	0·1296 (4)	0·1500 (2)	0·1434 (6)	3·9
C(4')	0·0120 (5)	0·1367 (2)	0·1454 (7)	3·3
C(5')	−0·0423 (5)	0·1162 (2)	0·2845 (7)	3·0
C(6')	0·0259 (5)	0·1141 (2)	0·4164 (7)	3·5
C(2'α)	0·3207 (6)	0·1574 (3)	0·2777 (10)	5·5
N(4'α)	−0·0473 (5)	0·1445 (2)	0·0111 (6)	4·6
C(3,5')	−0·1686 (5)	0·0980 (2)	0·2850 (8)	3·4
S(1)	−0·1277 (1)	−0·04363 (7)	0·1710 (2)	3·9
C(2)	−0·0876 (5)	0·0147 (2)	0·2126 (7)	3·2
N(3)	−0·1787 (4)	0·0449 (2)	0·2344 (5)	2·7
C(4)	−0·2897 (5)	0·0210 (2)	0·2163 (7)	3·1
C(5)	−0·2769 (5)	−0·0278 (2)	0·1795 (7)	3·3
C(4α)	−0·4023 (5)	0·0505 (3)	0·2363 (9)	4·4
C(5α)	−0·3707 (5)	−0·0669 (3)	0·1520 (8)	4·0
C(5β)	−0·3833 (6)	−0·1028 (3)	0·2906 (9)	4·7
O(5γ)	−0·2760 (4)	−0·1303 (2)	0·3159 (6)	5·0
O(W1)	−0·3002 (5)	0·1402 (2)	−0·0524 (7)	7·6
O(W2)	−0·0374 (7)	0·1921 (3)	−0·2955 (8)	10·8
O(W3)	−0·2219 (8)	0·2879 (3)	−0·1115 (8)	10·5
O(W4)	−0·4455 (8)	0·2259 (3)	−0·0047 (9)	10·9
P(1)	0·2462 (1)	−0·01674 (7)	0·2887 (2)	3·9
F(1)	0·2018 (5)	0·0353 (2)	0·2200 (6)	7·0
F(2)	0·1554 (4)	−0·0422 (2)	0·1675 (6)	7·0
F(3)	0·3338 (4)	0·0101 (3)	0·4056 (6)	9·0
F(4)	0·2867 (5)	−0·0688 (2)	0·3540 (7)	9·6
F(5)	0·1435 (4)	−0·0127 (2)	0·4186 (5)	7·9
F(6)	0·3460 (3)	−0·0203 (2)	0·1571 (5)	6·7
P(2)	0·1466 (2)	0·28686 (8)	0·4589 (3)	5·4
F(7)	0·0670 (6)	0·2511 (2)	0·3580 (9)	11·5
F(8)	0·0458 (8)	0·2902 (3)	0·5823 (10)	15·1
F(9)	0·2307 (8)	0·3220 (3)	0·5540 (10)	14·0
F(10)	0·2468 (6)	0·2843 (3)	0·3329 (10)	13·2
F(11)	0·0967 (5)	0·3336 (2)	0·3708 (9)	10·2
F(12)	0·1973 (6)	0·2391 (2)	0·5447 (7)	9·5

(2) and (4) were disordered each in two positions. The types of disorder were: rotation around the F(2)–P(1)–F(4) vector in (1), one rotating around the Cl(1)–O(4) vector and the other rotating around the Cl(2) atom in (2), and rotation around the F(5)–P(1)–F(6) vector in (4); the occupancy factors were estimated on the basis of the values of temperature factors. All H atoms were located from difference Fourier maps, except for six attached to three water molecules, O(W2), O(W3) and O(W4) in (3), and except for three, one bonded to phosphate O(5δ3) and two to a water O(W2) in (4). Thermal parameters of all nonhydrogen atoms including disordered anions were refined anisotropically. The H-atom positions and their isotropic thermal parameters were included in the structure-factor calculations in the final cycles of the refinements, where these parameters were refined for (1) and (4) but fixed for (2) and (3) ($B = 5\cdot0$ Å^2). The weighting schemes were of the type suggested by Hughes (1941) for (1)–(3) and unit weight for (4); no systematic variation was observed in an analysis of $\Sigma w(F_o - |F_c|)^2$ as a function of either F_o or $(\sin\theta)/\lambda$ for each case. Final atomic parameters with their e.s.d.'s

are listed in Tables 2–5.* Neutral atomic scattering factors and anomalous-dispersion corrections for Cl, S and P were taken from *International Tables for X-ray Crystallography* (1974). All calculations were performed with the *UNICS*III program system (Sakurai & Kobayashi, 1979) on a FACOM 380 computer.

Discussion. Bond distances and angles of thiamine molecules in (1)–(4) are listed in Table 6. Molecular structures of (1)–(4) are shown in Figs. 1(*a*)–1(*d*), respectively, and their crystal-packing arrangements are in Figs. 2(*a*)–2(*d*).

There are many structural features common to these four structures. The thiamine moiety assumes the F conformation: $\varphi_T = C(5')–C(3,5')–N(3)–C(2) = 0\cdot4$ (4) (1), $-10\cdot4$ (5) (2), $9\cdot0$ (8) (3), and $9\cdot0$ (5)° (4),

Table 5. *Fractional atomic coordinates and equivalent isotropic temperature factors with e.s.d.'s in parentheses for thiaminemonophosphate.*$PF_6.2H_2O$ (4)

$$B_{eq} = \tfrac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
N(1')	0·3523 (3)	−0·0340 (3)	0·0965 (3)	2·5
C(2')	0·3717 (3)	−0·1055 (3)	0·2381 (4)	2·5
N(3')	0·3666 (3)	−0·0724 (3)	0·3784 (3)	2·5
C(4')	0·3418 (3)	0·0390 (3)	0·3820 (4)	2·4
C(5')	0·3206 (3)	0·1185 (3)	0·2348 (4)	2·5
C(6')	0·3263 (3)	0·0776 (3)	0·0944 (4)	2·6
C(2'α)	0·4010 (4)	−0·2269 (4)	0·2357 (5)	3·9
N(4'α)	0·3378 (3)	0·0654 (3)	0·5269 (4)	3·1
C(3,5')	0·2959 (3)	0·2440 (3)	0·2304 (5)	2·8
S(1)	−0·04482 (9)	0·15396 (9)	0·3089 (1)	3·3
C(2)	0·0887 (3)	0·1325 (3)	0·2815 (5)	2·9
N(3)	0·1717 (3)	0·2354 (3)	0·2682 (3)	2·4
C(4)	0·1296 (3)	0·3394 (3)	0·2821 (4)	2·6
C(5)	0·0127 (3)	0·3105 (3)	0·3060 (4)	2·8
C(4α)	0·2134 (4)	0·4636 (4)	0·2702 (6)	4·1
C(5α)	−0·0655 (4)	0·3937 (4)	0·3303 (5)	3·6
C(5β)	−0·1571 (4)	0·4079 (4)	0·1956 (6)	4·2
O(5γ)	−0·2271 (3)	0·2864 (3)	0·1811 (5)	5·3
P(5δ)	−0·36490 (8)	0·24680 (8)	0·1947 (1)	2·4
O(5δ1)	−0·3926 (2)	0·1133 (2)	0·1741 (3)	2·8
O(5δ2)	−0·4218 (3)	0·3375 (3)	0·0853 (3)	3·8
O(5δ3)	−0·3919 (4)	0·2559 (3)	0·3698 (3)	5·7
O(W1)	0·3136 (3)	0·2854 (4)	0·6263 (5)	6·3
O(W2)	0·4485 (4)	0·4380 (4)	0·8284 (5)	8·6
P(1)	−0·0056 (1)	−0·2155 (1)	0·1949 (1)	3·5
F(1)*	0·1021 (3)	−0·1827 (4)	0·3178 (4)	6·8
F(2)*	−0·0679 (4)	−0·1239 (3)	0·2649 (5)	6·7
F(3)*	−0·1178 (4)	−0·2377 (4)	0·0773 (5)	7·3
F(4)*	0·0499 (4)	−0·3062 (3)	0·1271 (5)	7·6
F(5)	0·0637 (3)	−0·1038 (3)	0·0699 (4)	6·5
F(6)	−0·0749 (2)	−0·3260 (2)	0·3250 (3)	4·7
F(1)'*	0·006 (2)	−0·137 (1)	0·318 (2)	11·1
F(2)'*	−0·106 (2)	−0·160 (2)	0·132 (3)	11·5
F(3)'*	−0·048 (2)	−0·295 (2)	0·064 (2)	10·6
F(4)'*	0·106 (1)	−0·273 (2)	0·268 (3)	10·0

* Disordered F atoms; occupancy factors: 0·8 for F(1)–F(4) and 0·2 for F(1)'–F(4)'.

Table 6. *Bond lengths* (Å) *and angles* (°) *of the thiamine or the thiaminemonophosphate molecules in thiamine.*$PF_6.H_2O$ (1), *thiaminium.*$(ClO_4)_2$ (2), *thiaminium.*$(PF_6)_2.4H_2O$ (3), *and thiaminemonophosphate.*$PF_6.2H_2O$ (4) *with e.s.d.'s in parentheses*

	(1)	(2)	(3)	(4)
N(1')–C(2')	1·336 (4)	1·346 (5)	1·351 (8)	1·339 (4)
C(2')–N(3')	1·338 (4)	1·316 (6)	1·309 (8)	1·319 (5)
N(3')–C(4')	1·351 (4)	1·358 (5)	1·364 (8)	1·357 (5)
C(4')–C(5')	1·411 (4)	1·419 (5)	1·427 (8)	1·423 (5)
C(5')–C(6')	1·368 (4)	1·358 (6)	1·347 (9)	1·364 (4)
C(6')–N(1')	1·349 (4)	1·345 (5)	1·351 (8)	1·357 (5)
C(2')–C(2'α)	1·500 (5)	1·490 (7)	1·489 (9)	1·488 (6)
C(4')–N(4'α)	1·342 (4)	1·319 (6)	1·326 (8)	1·321 (5)
C(5')–C(3,5')	1·496 (4)	1·504 (5)	1·496 (8)	1·500 (6)
C(3,5')–N(3)	1·496 (4)	1·497 (5)	1·481 (8)	1·483 (5)
S(1)–C(2)	1·676 (3)	1·668 (4)	1·657 (6)	1·669 (4)
C(2)–N(3)	1·315 (4)	1·315 (6)	1·312 (7)	1·314 (4)
N(3)–C(4)	1·393 (4)	1·396 (5)	1·406 (7)	1·399 (5)
C(4)–C(5)	1·355 (4)	1·347 (6)	1·344 (9)	1·345 (5)
C(5)–S(1)	1·729 (3)	1·719 (5)	1·725 (6)	1·727 (4)
C(4)–C(4α)	1·491 (5)	1·493 (7)	1·496 (9)	1·495 (5)
C(5)–C(5α)	1·505 (5)	1·500 (6)	1·497 (9)	1·501 (6)
C(5α)–C(5β)	1·519 (5)	1·519 (7)	1·515 (10)	1·502 (6)
C(5β)–O(5γ)	1·421 (4)	1·418 (6)	1·424 (8)	1·439 (5)
O(5γ)–P(5δ)				1·567 (3)
P(5δ)–O(5δ1)				1·502 (3)
P(5δ)–O(5δ2)				1·477 (3)
P(5δ)–O(5δ3)				1·564 (3)
N(1')–C(2')–N(3')	126·0 (3)	122·0 (4)	122·3 (6)	122·8 (4)
C(2')–N(3')–C(4')	117·8 (3)	118·3 (3)	118·1 (5)	119·6 (3)
N(3')–C(4')–C(5')	120·4 (3)	121·6 (4)	121·4 (5)	119·9 (3)
C(4')–C(5')–C(6')	116·2 (3)	116·5 (4)	116·7 (5)	117·3 (4)
C(5')–C(6')–N(1')	124·4 (3)	120·4 (3)	120·4 (6)	120·8 (3)
C(6')–N(1')–C(2')	115·2 (3)	121·1 (4)	120·9 (5)	119·7 (3)
N(1')–C(2')–C(2'α)	117·3 (3)	118·0 (4)	117·6 (6)	118·2 (3)
N(3')–C(2')–C(2'α)	116·7 (3)	120·0 (4)	120·2 (6)	119·0 (3)
N(3')–C(4')–N(4'α)	116·7 (3)	115·7 (3)	115·6 (5)	116·1 (3)
C(5')–C(4')–N(4'α)	122·9 (3)	122·7 (4)	123·0 (6)	124·1 (4)
C(4')–C(5')–C(3,5')	123·9 (3)	124·1 (4)	122·0 (5)	122·5 (3)
C(6')–C(5')–C(3,5')	119·9 (3)	119·4 (3)	121·3 (6)	120·2 (3)
C(5')–C(3,5')–N(3)	113·0 (2)	112·6 (3)	112·4 (5)	112·0 (3)
C(3,5')–N(3)–C(2)	124·1 (3)	123·5 (3)	124·6 (5)	124·1 (3)
C(3,5')–N(3)–C(4)	121·9 (2)	122·5 (3)	122·1 (5)	122·6 (3)
S(1)–C(2)–N(3)	112·6 (2)	112·2 (3)	113·3 (4)	113·1 (3)
C(2)–N(3)–C(4)	113·9 (3)	114·0 (3)	113·2 (5)	113·2 (3)
N(3)–C(4)–C(5)	112·0 (3)	111·9 (4)	111·7 (5)	112·1 (3)
C(4)–C(5)–S(1)	110·2 (2)	110·2 (3)	110·5 (4)	110·6 (3)
C(5)–S(1)–C(2)	91·3 (2)	91·8 (2)	91·3 (3)	91·0 (2)
N(3)–C(4)–C(4α)	121·0 (3)	120·0 (4)	119·6 (5)	119·7 (3)
C(5)–C(4)–C(4α)	127·0 (3)	128·1 (4)	128·7 (6)	128·3 (4)
S(1)–C(5)–C(5α)	123·7 (2)	120·4 (4)	120·2 (5)	120·6 (3)
C(4)–C(5)–C(5α)	126·0 (3)	129·3 (4)	129·3 (6)	128·8 (3)
C(5)–C(5α)–C(5β)	115·6 (3)	112·2 (4)	112·7 (6)	113·1 (4)
C(5α)–C(5β)–O(5γ)	113·0 (3)	111·5 (4)	111·2 (6)	108·5 (3)
C(5β)–O(5γ)–P(5δ)				124·3 (3)
O(5γ)–P(5δ)–O(5δ1)				102·9 (2)
O(5γ)–P(5δ)–O(5δ2)				110·2 (2)
O(5γ)–P(5δ)–O(5δ3)				106·9 (2)
O(5δ1)–P(5δ)–O(5δ2)				120·2 (2)
O(5δ1)–P(5δ)–O(5δ3)				110·2 (2)
O(5δ2)–P(5δ)–O(5δ3)				105·8 (2)

and φ_P = N(3)–C(3,5')–C(5')–C(4') = 83·2 (3) (1), 81·5 (5) (2), 87·1 (7) (3), and 78·8 (4)° (4). The C(5) hydroxyethyl or phosphate ester side chain folds back towards the thiazolium moiety to make a close contact between O(5γ) and S(1), where the O(5γ) lone pair is directed towards the positively charged S(1): O(5γ)··· S(1) = 2·882 (2) (1), 3·001 (3) (2), 3·096 (5) (3), and 2·892 (3) Å (4) [sum of van der Waals radii for O···S = 3·32 Å (Bondi, 1964)]; $\varphi_{5\alpha}$ = S(1)–C(5)–C(5α)–C(5β) = −20·0 (4) (1), 66·5 (5) (2), 73·5 (7) (3), and −66·1 (4)° (4), and $\varphi_{5\beta}$ = C(5)–C(5α)–(5β)–O(5γ) = 55·7 (4) (1), −62·6 (5) (2), −62·5 (7) (3), and 57·3 (5)° (4), and $\varphi_{5\gamma}$ = C(5α)–C(5β)–O(5γ)–P(5δ) = 122·5 (3)° (4). An anion attaches, in most cases bifunctionally, to the thiazolium ring *via* a hydrogen bond with the C(2)H and an electrostatic interaction with the S(1): F(1)···H(C2) = 2·50 (3) Å, C(2)–H··· F(1) = 149 (3)°, F(2)···H(C2) = 2·48 (3) Å, C(2)– H···F(2) = 120 (2)° (a bifurcated hydrogen bond) for (1); O(1)···H(C2) = 2·31 Å, C(2)–H···O(1) = 141°, O(1)'···H(C2) = 2·45 Å, C(2)–H···O(1)' = 121°, and O(2)···S(1) = 3·22 (2) Å for (2); F(1)···H(C2) = 2·27 Å, C(2)–H···F(1) = 159°, and F(2)···S(2) = 3·170 (4) Å for (3); and F(1)···H(C2) = 2·65 (4) Å,

C(2)–H···F(1) = 158 (3)°, F(2)···H(C2) = 2·57 (4) Å, C(2)–H···F(2) = 112 (3)° (a bifurcated hydrogen bond), F(1)'···H(C2) = 2·24 (4) Å, C(2)– H···F(1)' = 129 (3)°, and F(2)···S(1) = 3·167 (4) Å for (4) [sum of van der Waals radii (Bondi, 1964) = 2·67 Å for F···H, 2·72 Å for O···H, and 3·27 Å for F···S]. Furthermore, this anion makes a close contact with the pyrimidine ring of the same molecule: F(1)···N(1') = 3·198 (5), F(1)···C(2') = 3·208 (6) Å for (1), O(1)···C(2') = 3·134 (10), O(1)··· N(3') = 3·097 (9), O(1)···C(4') = 3·233 (9) Å for (2),

F(1)···N(1') = 3·067 (7), F(1)···C(2') = 2·973 (8), F(1)···N(3') = 3·227 (7) Å for (3), and F(1)···C(2') = 3·145 (5), F(1)···N(3') = 3·074 (4) Å for (4) [sum of van der Waals radii (Bondi, 1964) = 3·24 Å for F···aromatic ring and 3·29 Å for O···aromatic ring]. Though a limited accuracy of the atomic coordinates, partly due to the disordering of anions, precludes a detailed comparison, the closest F···pyrimidine contact is shorter for the cationic pyrimidine in (3) or (4) (see below) than for the neutral one in (1) (see below), suggesting an electrostatic interaction between them. This anion also takes part in an electrostatic interaction with the thiazolium moiety of the neighboring molecule(s) by lying on it, in most cases the closest contact being with the cationic quarternary nitrogen N(3): F(4)···N(3) = 3·015 (4) Å (1), O(3)'···N(3) = 3·024 (10) Å (2), F(5)···N(3) = 3·067 (6) Å on one side and F(6)···C(4) and F(6)···C(5) = 3·201 (7) Å on the other side (3), and F(1')···S(1) = 3·12 (1) Å on one side and F(3)···N(3) = 2·927 (5) Å on the other side

(4). Another anion of the two independent ones in (2) and (3) also engages in an electrostatic stacking interaction, with the thiazolium ring [O(6)'···N(3) = 3·22 (1) Å] in (2) or with the pyrimidinium ring [F(12)···N(1') = 3·189 (7) Å] in (3).

Major differences include the following. Protonation at the pyrimidine N(1') site occurs in (2), (3) and (4), while it does not in (1). Consistent with a previous observation (Cramer, Maynard & Ibers, 1981), the N(1') protonation affects mainly the C(4')—N(4'α) bond length and the C(2')—N(1')—C(6') angle: there is a decrease in bond length of ca 0·02 Å and an increase in bond angle of ca 4° in the protonated thiamines. There are pyrimidine base–base stacking interactions [with average spacing of 3·11 Å] but no base–base hydrogen-bonding interactions in (1), while there is neither base–base stacking nor interbase hydrogen bonding in (2), (3) and (4).

The most interesting structural feature is the host–guest-like thiamine–anion complexation: a thiamine
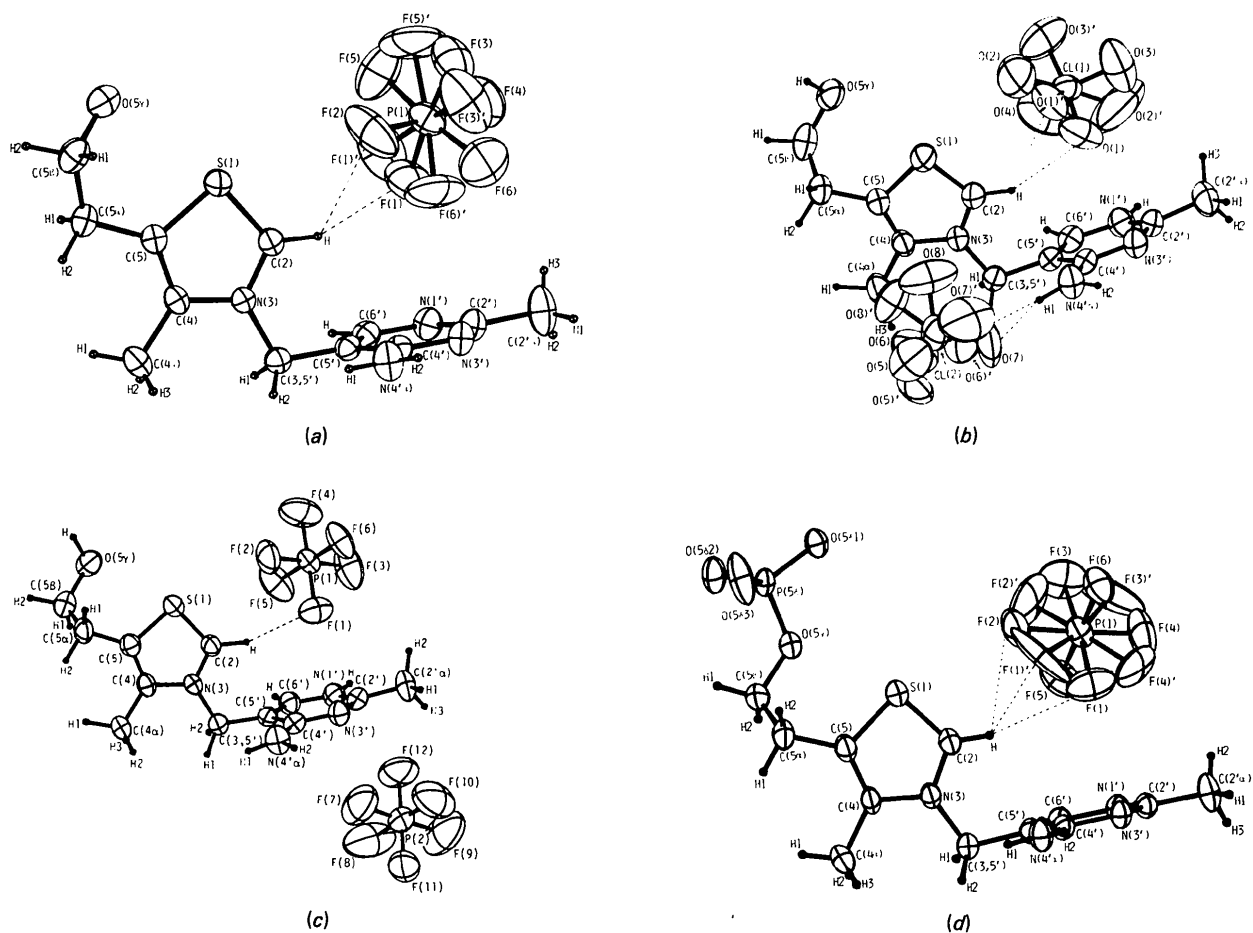

Fig. 1. Molecular structures of (a) (1), (b) (2), (c) (3) and (d) (4), where broken lines denote hydrogen bonds. Anions in (1), (2) and (4) are disordered into two positions; unprimed atoms occupy the major sites while primed (') atoms occupy the minor sites. Water molecules in (1), (3) and (4) are omitted.

'host' captures an anion 'guest' in an 'anion hole' near the C(2) site through three types of interactions; that is, a C(2)H···anion hydrogen bond, an S(1)···anion and a pyrimidine–anion electrostatic interaction. A literature survey, in which we calculated these interactions when they have not been noticed, has revealed that the same type of thiamine–anion interactions are also formed with other anions or anionic groups such as phosphate (Karle & Britts, 1966; Aoki & Yamazaki, 1985), nitrate (Aoki & Yamazaki, 1980; Turano, Pletcher, Furey & Sax, 1982; Ishida, Tanaka & Inoue, 1984; Yang, Pletcher, Rose, Yoo, Furey, Wang & Sax, 1987), picrolonate (Shin, Pletcher, Blank & Sax, 1977),

sulfonate (Shin & Lah, 1987), or PtCl$_3^-$ (Cramer, Kirkup & Carrie, 1988). Therefore, widespread occurrence of such thiamine–anion interactions may allow us to expect that an anionic α-ketocarboxylate substrate such as pyruvate could be incorporated into the vicinity of the catalytic C(2) site in the enzyme system in a manner similar to that observed here.

Another noticeable thiamine–anion interaction is a thiazolium–anion stacking. We can also expect that such an electrostatic interaction may be involved in the coenzyme binding processes to the apoenzyme, for example, with the carboxylate side chain of aspartic acid or glutamic acid residues.
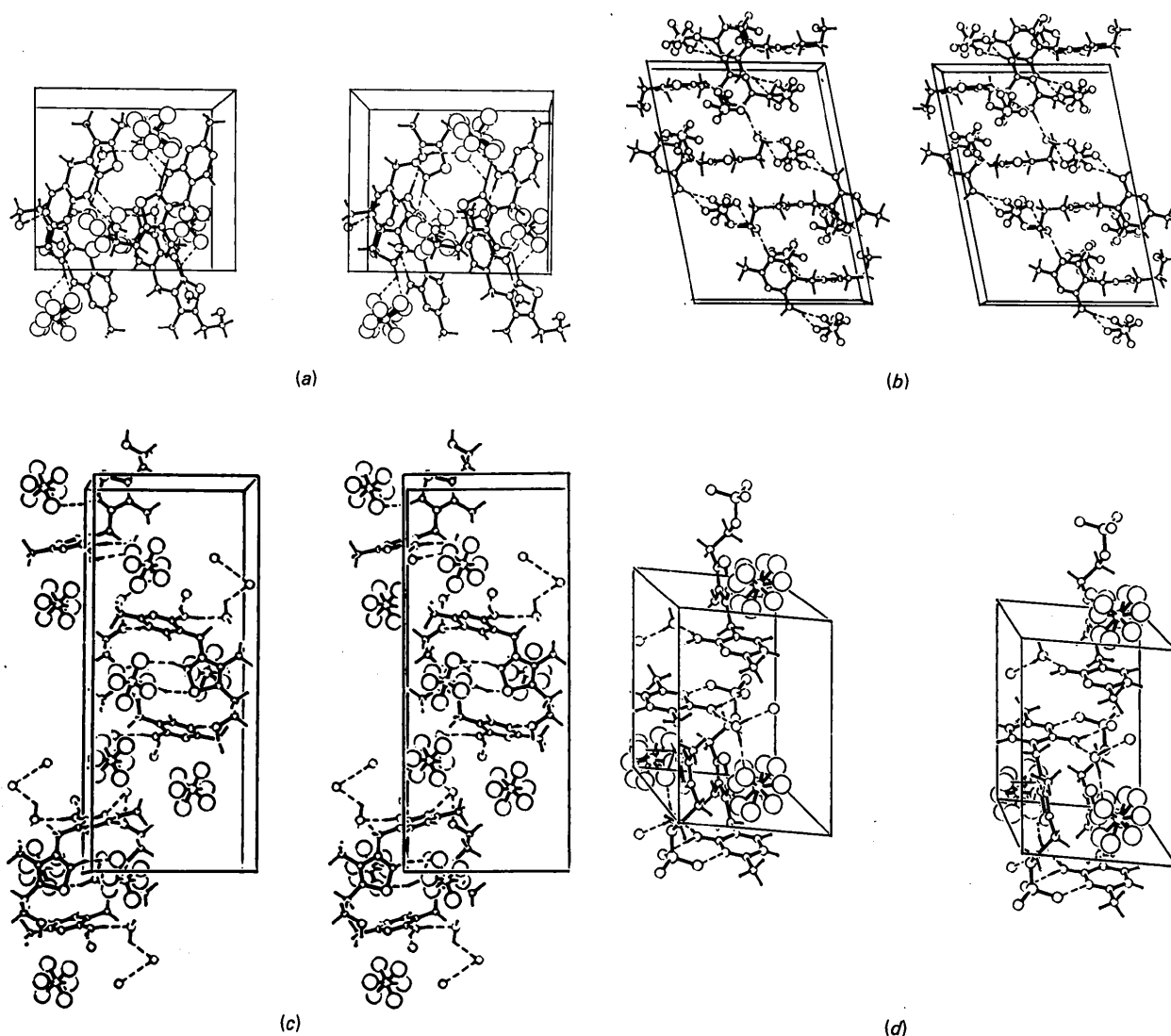

(a)

(b)

(c)

(d)

Fig. 2. Crystal-packing arrangements of (a) (1) viewed down the c axis with the a axis horizontal and the b axis vertical, (b) (2) viewed down the b axis with the c axis horizontal and the a axis vertical, (c) (3) viewed down the c axis with the a axis horizontal and the b axis vertical, and (d) (4) viewed down the b axis with the c axis horizontal and the a axis vertical. Broken lines denote hydrogen bonds.

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Structure of (2R*,8R*)-2-[α-(Thiocarbamoylthio)benzyl]indan-1-one

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Abstract. $C_{17}H_{15}NOS_2$, $M_r = 313.44$, monoclinic, $C2/c$, $a = 20.710(2)$, $b = 9.268(2)$, $c = 17.303(1)$ Å, $\beta = 114.11(1)°$, $V = 3031.5(9)$ Å^3, $Z = 8$, $D_x = 1.37$ Mg m^{-3}, $\lambda(\text{Cu } K\bar{\alpha}) = 1.54184$ Å, $\mu = 3.1$ mm^{-1}, $F(000) = 1312$, $T = 296(1)$ K, $R = 0.041$ for 2289 observed reflections. Only X-ray analysis could reveal the structure of the title compound obtained by the reaction of 2-benzylideneindanone with dithiocarbamic acid. It has been shown to be the diastereomer in which the chiral centres have the stereochemistry: 2R*,8R* (and/or 2S*,8S* as indicated by the asterisks).

Introduction. Continuing our earlier studies on the reactions of α,β-unsaturated carbonyl compounds with thiocarbonic acid derivatives (Argay, Kálmán, Perjési & Szabó, 1987; Perjési, Földesi, Szabó, Zschunke & Mák, 1987; Perjési, Szabó, Batta & Földesi, 1987) the reaction of 2-benzylideneindanone (1) with dithiocarbamic acid has been investigated. In this reaction stereohomogeneous 2-[α-(thiocarbamoylthio)benzyl]-indan-1-one (2) was formed as depicted in the reaction scheme. However, no spectroscopic answer could be

given as to which of the two possible diastereomers was formed. Consequently, an X-ray analysis of (2) (melted at 407–410 K) has been performed.

(1)   (2)
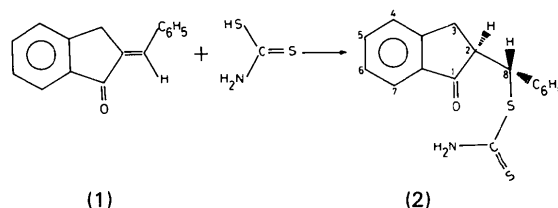
Experimental. Crystal *ca* 0.11 × 0.25 × 0.40 mm was mounted on a CAD-4 diffractometer equipped with graphite monochromator. Cell constants were refined by least-squares fit for 25 centred reflections collected in the range of $25 \le \theta \le 35°$. Systematic absences *hkl*: $h + k = 2n + 1$, *h0l*: $l = 2n + 1$, *0k0*: $k = 2n + 1$ permit space groups Cc and $C2/c$ of which $C2/c$ was substantiated by refinement. Scan range $0.017 \le (\sin\theta)/\lambda \le 0.626$ Å^{-1}, $\omega/2\theta$ scan. A total of 3260 reflections was collected with *h*: 0 to 25, *k*: −11 to 0 and *l*: −21 to 21, of which 2780 were unique, non-zero and not systematically absent. In the refinement,

† Deceased on June 14, 1987.