and are comparable with those given by Glen, Silverton & Hoard (1962). All oxygen atoms in the ligand are coordinated to the alkali metal ions. Three of the coordination sites are used by a chelated ligand and the rest by carboxylate oxygen atoms of four adjoining ligands (Fig. 1).

Table 8. *Coordination distances in* NaHOXY *and* KHOXY

	NaHOXY	KHOXY
M^+–O(1)	2·398 (3) Å	2·740 (2) Å
M^+–O(2)	2·742 (3)	2·805 (2)
M^+–O(4)	2·468 (3)	2·708 (2)
M^+–O(3^{iii})	2·773 (3)	2·770 (2)
M^+–O(4^{iv})	2·378 (3)	2·695 (2)
M^+–O(2^{ii})	2·407 (3)	2·756 (2)
M^+–O(5^{v})	2·720 (3)	2·921 (2)

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Guanidinium 5,5-Diethylbarbiturate Dihydrate

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$[CH_6N_3]^+[C_8H_{11}N_2O_3]^-.2H_2O$: M.W. 274·3: triclinic, $P\bar{1}$: $a=12·984(5)$, $b=7·134(3)$, $c=9·110(4)$Å, $\alpha=92·92(2)$, $\beta=104·00(2)$, $\gamma=114·73(2)$°:25°C: $D_{\text{meas}}=1·26$, $D_{\text{calc}}=1·25$ g cm^{-3} for Z=2. The two covalent and two hydrogen bonds at the barbiturate deprotonated nitrogen atom are tetrahedrally disposed. The crystal structure has features in common with that of calcium barbital trihydrate.

Introduction

The salt (Fig. 1) was prepared by addition of one equivalent of 5,5-diethylbarbituric acid (hereafter called barbital) to a fresh solution of guanidine in ethanol. The ethanol was evaporated and the dihydrate was recrystallized from water.

The lattice parameters* and intensity data were measured on a computer-controlled four-circle diffractometer using graphite monochromated Mo$K\alpha$ radiation ($\lambda=0·7107$ Å). The crystal was a transparent prism ($0·25\times0·35\times0·40$ mm) mounted with **c** along the diffractometer φ axis. Intensities were scanned in the $\theta/2\theta$ mode at 1° in 2θ per 60 s, with 10 s background counts at the scan limits. Of the 2757 non-symmetry-related reflections with $2\theta\le 50°$, 868 were found to have an integrated intensity less than 2σ. These were assigned an intensity of $\sigma(I)$. No corrections were made for X-ray absorption.

The phase problem was solved by direct methods, using the symbolic addition procedure. The atomic par-

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* The transformation matrix $(0,-1,0/0,0,1/-1,-1,0)$ gives the reduced cell with parameters 7·134, 9·110, 11·914 Å, 73·29, 81·79, 87·71°. The reduced cell was not used in this crystal structure determination.

Table 1. *Atomic parameters*

The positional parameters are fractions of unit-cell translations. Thermal parameters are given according to the expression $T=\exp\left(-\sum\sum\beta_{ij}h_ih_j\right)$. E.s.d.'s given in parentheses refer to the least significant digit in the parameter values.

(*a*) Barbital anion

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(2)	0·92753 (13)	0·5533 (3)	0·62858 (15)	0·00809 (14)	0·0429 (5)	0·0075 (2)	0·0131 (2)	0·00152 (12)	0·0019 (2)
O(4)	0·61103 (12)	0·6559 (2)	0·40745 (16)	0·00622 (12)	0·0356 (5)	0·0123 (2)	0·0101 (2)	0·00157 (13)	−0·0015 (3)
O(6)	0·83509 (13)	0·5160 (2)	0·11823 (15)	0·00907 (14)	0·0353 (5)	0·0078 (2)	0·0103 (2)	0·00358 (13)	0·0015 (2)
N(1)	0·87767 (14)	0·5363 (3)	0·37307 (17)	0·00568 (13)	0·0286 (5)	0·0077 (2)	0·0084 (2)	0·00185 (13)	0·0008 (3)
N(3)	0·76740 (14)	0·6059 (3)	0·52362 (17)	0·00553 (13)	0·0249 (5)	0·0075 (2)	0·0067 (2)	0·00188 (13)	0·0003 (2)
C(2)	0·85829 (16)	0·5653 (3)	0·51431 (20)	0·00525 (15)	0·0221 (6)	0·0075 (2)	0·0059 (2)	0·00179 (16)	0·0000 (3)
C(4)	0·69283 (15)	0·6156 (3)	0·39620 (20)	0·00458 (15)	0·0175 (5)	0·0090 (3)	0·0045 (2)	0·00164 (16)	−0·0005 (3)
C(5)	0·70444 (16)	0·5798 (3)	0·23567 (20)	0·00583 (16)	0·0197 (5)	0·0075 (2)	0·0060 (2)	0·00148 (16)	0·0012 (3)
C(6)	0·81060 (16)	0·5427 (3)	0·23628 (20)	0·00563 (16)	0·0180 (5)	0·0072 (2)	0·0046 (2)	0·00184 (16)	0·0002 (3)
C(7)	0·7172 (2)	0·7754 (4)	0·1622 (3)	0·0108 (2)	0·0301 (7)	0·0137 (3)	0·0118 (4)	0·0047 (2)	0·0075 (4)
C(8)	0·8223 (3)	0·9732 (5)	0·2502 (4)	0·0128 (3)	0·0249 (8)	0·0264 (6)	0·0083 (4)	0·0078 (4)	0·0105 (6)
C(9)	0·5928 (2)	0·3872 (4)	0·1412 (2)	0·0061 (2)	0·0311 (7)	0·0107 (3)	0·0060 (3)	−0·0001 (2)	−0·0052 (4)
C(10)	0·5752 (2)	0·1867 (4)	0·2028 (4)	0·0094 (3)	0·0220 (7)	0·0257 (6)	0·0018 (3)	0·0035 (3)	−0·0030 (5)

(*b*) Guanidinium cation and water oxygen atoms

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
*G*N(1)	0·6723 (2)	−0·0013 (3)	0·6391 (2)	0·0099 (2)	0·0366 (7)	0·0141 (3)	0·0122 (3)	−0·0005 (2)	−0·0064 (4)
*G*N(2)	0·7847 (2)	0·2010 (3)	0·8710 (2)	0·0102 (2)	0·0302 (6)	0·0121 (3)	0·0102 (3)	0·0011 (2)	−0·0026 (3)
*G*N(3)	0·8249 (2)	−0·0551 (3)	0·7802 (2)	0·0111 (2)	0·0348 (7)	0·0136 (3)	0·0130 (3)	−0·0008 (2)	−0·0049 (3)
*G*C(1)	0·7609 (2)	0·0482 (3)	0·7631 (2)	0·0079 (2)	0·0241 (6)	0·0102 (3)	0·0069 (3)	0·0019 (2)	−0·0016 (3)
W(1)	0·9824 (2)	0·7403 (3)	0·9369 (2)	0·0094 (2)	0·0296 (5)	0·0103 (2)	0·0058 (2)	0·0033 (2)	0·0001 (3)
W(2)	0·3888 (2)	−0·3415 (3)	0·3046 (2)	0·0084 (2)	0·0406 (7)	0·0204 (3)	0·0123 (3)	0·0054 (2)	0·0127 (4)

(*c*) Hydrogen atoms

Isotropic thermal parameters are listed in Å^2 units.

	x	y	z	B		x	y	z	B
H(1)	0·941 (2)	0·521 (4)	0·374 (3)	4·2 (5)	*G*H(11)	0·637 (2)	0·075 (4)	0·629 (3)	3·9 (6)
H(71)	0·643 (2)	0·786 (3)	0·153 (3)	4·0 (5)	*G*H(12)	0·653 (2)	−0·102 (3)	0·578 (2)	3·2 (5)
H(72)	0·724 (2)	0·756 (4)	0·061 (3)	4·5 (6)	*G*H(21)	0·853 (2)	0·240 (4)	0·943 (3)	4·8 (6)
H(81)	0·829 (3)	1·097 (5)	0·205 (3)	6·6 (7)	*G*H(22)	0·739 (2)	0·263 (4)	0·852 (3)	4·4 (6)
H(82)	0·899 (3)	0·972 (5)	0·278 (4)	7·3 (8)	*G*H(31)	0·810 (2)	−0·152 (4)	0·708 (3)	4·1 (5)
H(83)	0·821 (3)	0·993 (5)	0·360 (4)	7·6 (8)	*G*H(32)	0·875 (2)	−0·030 (4)	0·856 (3)	3·9 (5)
H(91)	0·523 (2)	0·414 (4)	0·140 (3)	4·5 (5)	*W*H(11)	0·934 (3)	0·667 (5)	0·979 (3)	5·8 (8)
H(92)	0·599 (2)	0·372 (4)	0·035 (3)	5·3 (6)	*W*H(12)	0·957 (2)	0·680 (4)	0·849 (3)	5·2 (7)
H(101)	0·571 (3)	0·196 (6)	0·311 (4)	8·8 (9)	*W*H(21)	0·449 (3)	−0·353 (4)	0·317 (3)	6·1 (8)
H(102)	0·500 (3)	0·075 (5)	0·142 (3)	6·9 (7)	*W*H(22)	0·349 (3)	−0·432 (5)	0·347 (4)	7·5 (8)
H(103)	0·641 (3)	0·153 (5)	0·204 (4)	7·8 (9)					

ameters (Table 1) were refined by full-matrix least-squares methods, minimizing $\sum \Delta F^2/\sigma^2(F)$ with $\sigma^2(F) = 0{\cdot}66 - 0{\cdot}10|F| + 0{\cdot}0043|F|^2$. The variances in all structure amplitudes, including the unobservably weak, were assumed to be given by this expression. The final value of $R = \sum \Delta F/\sum F_{\text{meas}}$ with $\Delta F = |F_{\text{meas}}| - |F_{\text{calc}}|$ is 0·044. The list of $|F_{\text{meas}}|$ and $|F_{\text{calc}}|$ is available.†

Discussion

The nature of the molecular and ionic interactions in guanidinium 5,5-diethylbarbiturate dihydrate are of interest because they may be illustrative of the association of weakly acidic barbiturate drugs with the strongly basic arginine residues of proteins. The molecular structures of the component ions are similar to those observed in guanidinium chloride (Haas, Harris & Mills, 1965), sodium barbital (Berking & Craven, 1971) and calcium barbital trihydrate (Berking, 1972). The guanidinium C–N bond lengths are 1·311, 1·315, 1·307, the bond angles N–C–N are 120·1, 120·2 and 119·8°, and the carbon and nitrogen atoms are coplanar within 0·003 Å. Guanidinium N–H distances are in the range 0·78 to 0·89 Å. The barbiturate bond lengths and angles (Table 2) are all within the range observed for corresponding values tabulated by Berking (1972) for five independent barbital anions, except for the ethyl C–C bond lengths which are slightly shorter (0·01 Å). The oxopyrimidine ring is almost planar and thus resembles ion II in Berking's (1972) Fig. 2. The water molecule O–H distances range from 0·79 to 0·82 Å and the H–O–H angles are 104 and 105°.

The crystal structure is shown in Fig. 2 and the hydrogen bonding arrangements about the guanidinium and barbital ions are shown in Figs. 3 and 4.

All guanidinium N–H groups are hydrogen bonded except one, which forms a weaker interaction (H···O distance, 2·46 Å) with water molecule *W*(2). Each guanidinium cation forms two hydrogen bonds with the same barbital anion, and three other hydrogen bonds to water molecules. The barbiturate NH group forms NH···O(2) hydrogen bonded dimers across a crystallographic center of symmetry, similar to those formed by all four independent anions in calcium barbital trihydrate. In the latter structure, water molecules link dimers of anions I and IV by means of N(3)···HOH···O(2) hydrogen bonds to form chains. In anions II and III the deprotonated nitrogen atom N(3) interacts with Ca cations. In the guanidinium salt these features are combined, with the barbital N(3)

Table 2. *Interatomic distances and angles*

The atomic nomenclature (Fig. 1) is the same as in Berking (1972). E.s.d.'s are 0·003 Å in ring bonds, 0·004 Å in ethyl group bonds, 0·03 Å in bonds involving hydrogen atoms, 0·2° in bond angles.

(*a*) Bond lengths and angles in the barbital anion

N(1)–C(2)	1·390 Å	C(6)–N(1)–C(2)	125·4°
C(2)–N(3)	1·345	N(1)–C(2)–N(3)	120·6
N(3)–C(4)	1·342	C(2)–N(3)–C(4)	120·4
C(4)–C(5)	1·525	N(3)–C(4)–C(5)	123·0
C(5)–C(6)	1·505	C(4)–C(5)–C(6)	113·1
C(6)–N(1)	1·348	C(5)–C(6)–N(1)	117·4
C(2)–O(2)	1·229	N(1)–C(2)–O(2)	117·3
C(4)–O(4)	1·233	N(3)–C(2)–O(2)	122·1
C(6)–O(6)	1·220	N(3)–C(4)–O(4)	119·4
C(5)–C(7)	1·532	C(5)–C(4)–O(4)	117·7
C(5)–C(9)	1·535	C(5)–C(6)–O(6)	121·9
C(7)–C(8)	1·502	N(1)–C(6)–O(6)	120·6
C(9)–C(10)	1·502	C(4)–C(5)–C(7)	108·3
N(1)–H(1)	0·87	C(4)–C(5)–C(9)	108·7
C——H	0·95–1·01	C(6)–C(5)–C(7)	108·0
		C(6)–C(5)–C(9)	108·3
		C(7)–C(5)–C(9)	110·6
		C(5)–C(7)–C(8)	114·2
		C(5)–C(9)–C(10)	114·1

(*b*) Hydrogen bond distances

N(1)—O(2)	2·85 Å	*W*(2)—N(3)	2·94 Å
W(1)—O(2)	2·84	*G*N(3)–N(3)	3·00
W(2)—O(4)	2·81	*G*N(1)–*W*(2)	2·93
*G*N(1)–O(4)	2·86	*G*N(2)–*W*(1)	2·94
W(1)—O(6)	2·85	*G*N(2)–*W*(2)	2·98

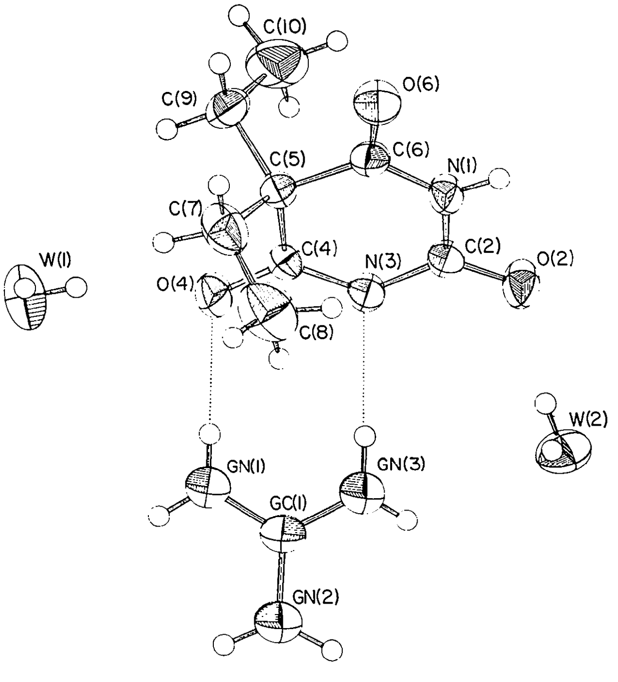

Fig. 1. Molecular structure and atomic nomenclature for guanidinium 5,5-diethylbarbiturate dihydrate. Non-hydrogen atoms are represented as ellipsoids with 50% probability of enclosing the atoms, as determined from anisotropic temperature factors.

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† The table of structure factors has been deposited with with the National Lending Library, England, as Supplementary Publication No. SUP 30081. Copies may be obtained through the Executive Secretary, I.U.Cr., 13 White Friars, Chester, CH1 1NZ, England.

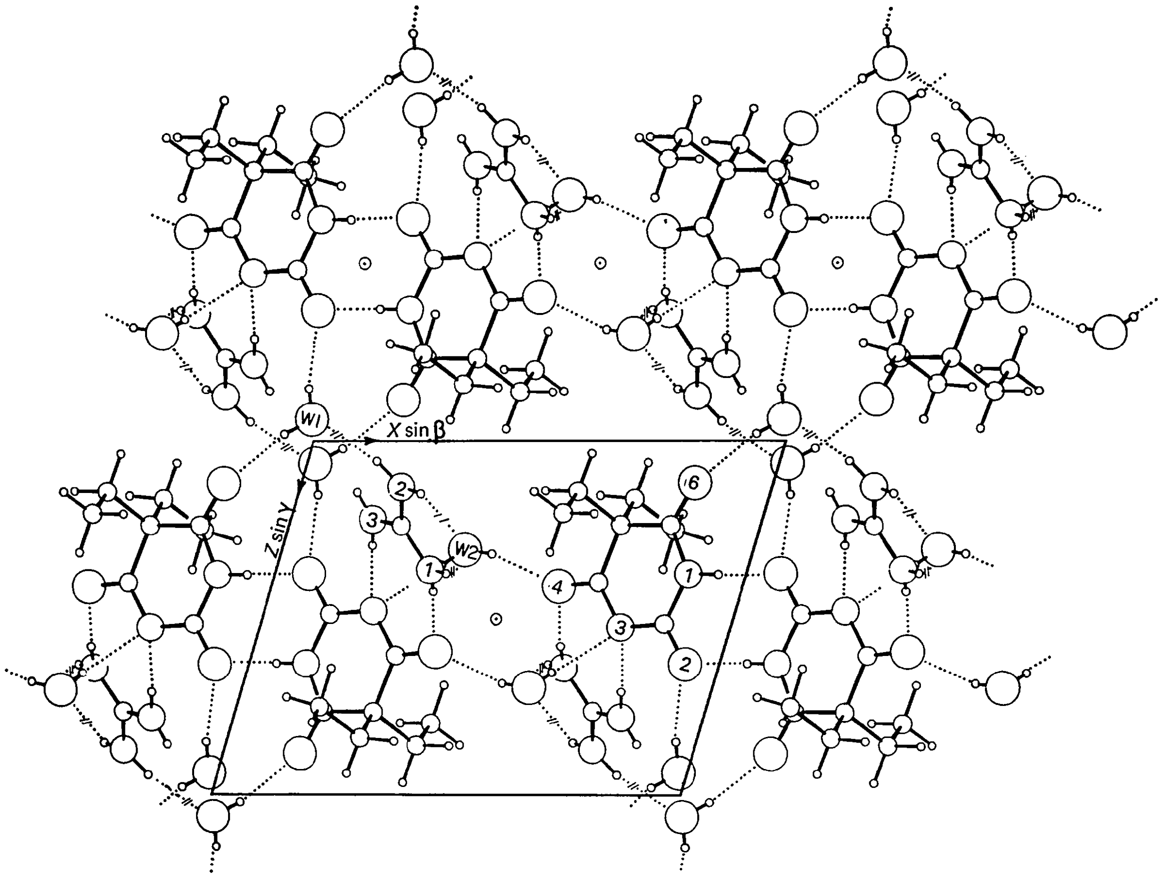

Fig. 2. The crystal structure of guanidinium 5,5-diethylbarbiturate dihydrate, projected down the *b* axis. Circles of decreasing size represent oxygen, nitrogen, carbon and hydrogen atoms, respectively. Hydrogen bonds are shown as dotted lines.

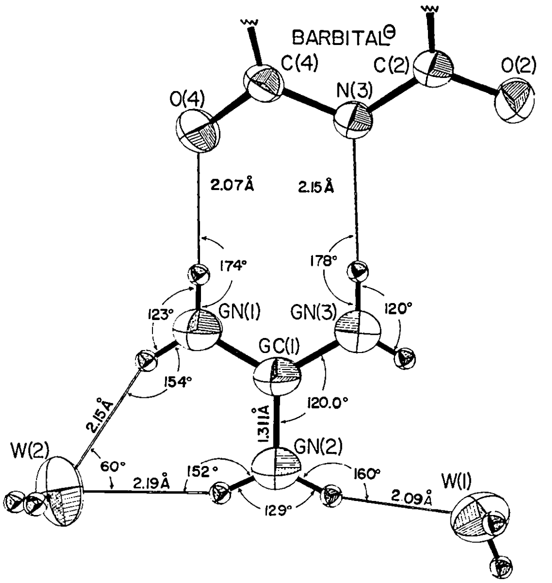

Fig. 3. The hydrogen bonding of the guanidinium cation [see also Table 2(*b*)].

hydrogen bonded both in a water bridge and with the guanidinium cation. In Fig. 4, the guanidinium ion is below the plane of the barbital ring and water *W*(2) is above, so that the two hydrogen bonds and the two covalent bonds at N(3) are tetrahedrally disposed.

Thus, the two crystal structures of the hydrated calcium and guanidinium salts of barbital are more closely related to each other than to the anhydrous potassium and sodium salts. In the latter (Berking & Craven, 1972; Berthou, Rérat & Rérat, 1965), hydrogen bonding and ionic interactions involve the barbital oxygen atoms, but not the deprotonated nitrogen atom.

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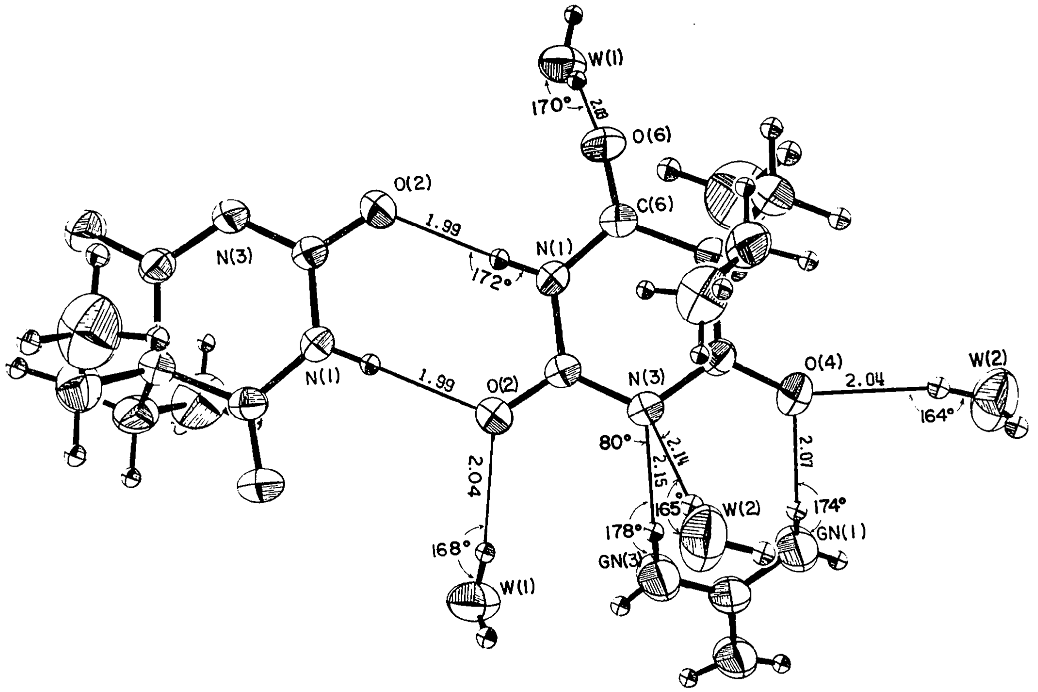

Fig. 4. The hydrogen bonding of the barbital anion [see also Table 2(*b*)].

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The Crystal Structure of Gallium Thiophosphate, $GaPS_4$

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$GaPS_4$ is monoclinic with $a=8\cdot603$ (4), $b=7\cdot778$ (3), $c=11\cdot858$ (5) Å, $\beta=135\cdot46°$, space group $P2_1/c$ and $Z=4$. The structure has been determined from 706 reflexions and refined to $R=0\cdot066$. It consists of puckered hexagonally close-packed sulphur layers. Of the interlayers only every other one is occupied by Ga and P cations. Filled and empty interlayers thus alternate, causing perfect cleavability parallel to (100). Ga and P are each surrounded by four sulphur atoms at the corners of distorted tetrahedra.

Introduction

Gallium thiophosphate belongs to a group of ternary metal–phosphorus–sulphur–compounds of the type MPS_4 (M = B, Al, Ga, In, Sb, Bi). The crystal structures of $AlPS_4$ and BPS_4 have been solved by Weiss & Schaefer (1960, 1963). The structure of $InPS_4$ has been determined by Carpentier, Diehl & Nitsche (1970).

Studying the crystal growth of metal-phosphorus–sulphur compounds by vapour transport, Nitsche & Wild (1970) obtained single crystals of $GaPS_4$. The crystals were grown by chemical transport with iodine in a temperature gradient from 650 to 600 °C. Cell constants and space group have been determined by Buck & Nitsche (1971). The platelike morphology of the crystals differs significantly from that of the other compounds mentioned above. It therefore seemed reasonable for a better understanding of the crystal chemistry of ternary phosphorus chalcogenides to determine also the crystal structure of $GaPS_4$.