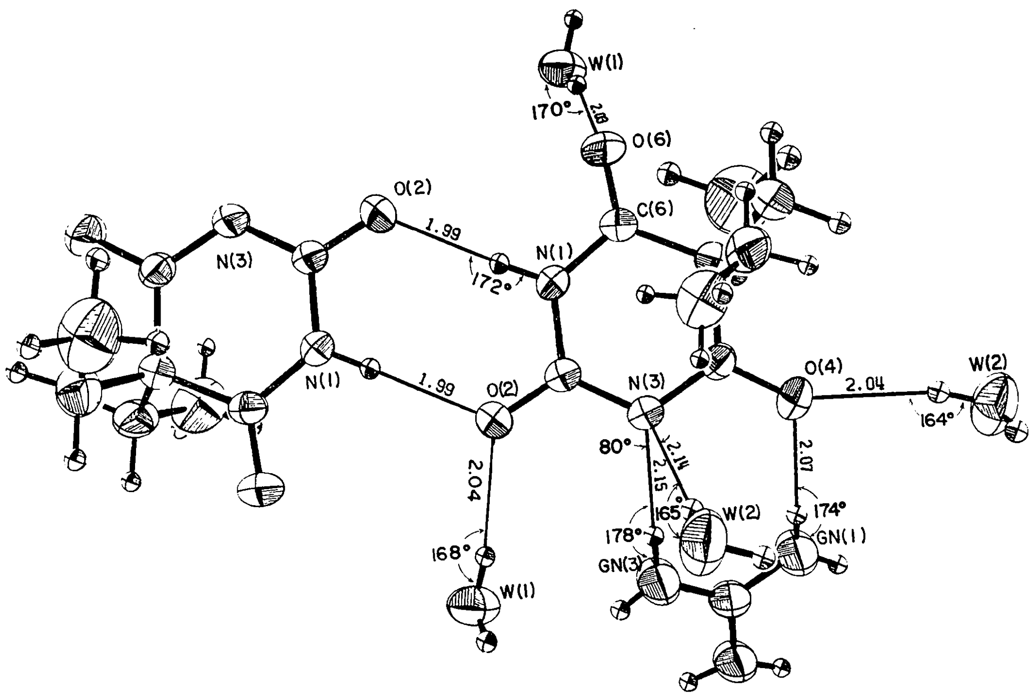

Fig. 4. The hydrogen bonding of the barbital anion [see also Table 2(*b*)].

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The Crystal Structure of Gallium Thiophosphate, $GaPS_4$

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$GaPS_4$ is monoclinic with $a=8{\cdot}603$ (4), $b=7{\cdot}778$ (3), $c=11{\cdot}858$ (5) Å, $\beta=135{\cdot}46°$, space group $P2_1/c$ and $Z=4$. The structure has been determined from 706 reflexions and refined to $R=0{\cdot}066$. 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 $GaPS_4$.

Crystal data

Least-squares refinement of powder data using the X-RAY 70 system (*PARAM*, Stewart, Kundell & Baldwin, 1970) gave the lattice constants listed in Table 1.

Table 1. *Crystal data for gallium thiophosphate* $GaPS_4$

$a = 8{\cdot}603\ (4)$ Å	Space group: $P2_1/c$ (No. 14)
$b = 7{\cdot}778\ (3)$	$Z = 4$
$c = 11{\cdot}858\ (5)$	$\varrho_{\exp} = 2{\cdot}65$ g cm^{-3}
$\beta = 135{\cdot}46°\ (4)$	$\varrho_{\text{calc}} = 2{\cdot}72$ g cm^{-3}
$U = 556{\cdot}54$ Å^3	

Systematic extinctions: $h0l$: $l = 2n+1$
$0k0$: $k = 2n+1$

Intensity data

Integrated b-axis equi-inclination Weissenberg photographs ($k = 0, 1, 2, 3, 4$) were collected by the three-film technique with Cu $K\alpha$ radiation. The intensities were measured with a Jenoptik photometer (estimated average accuracy 7–8%). Low intensities were estimated visually by means of a calibrated scale. 631 independent reflexions were recorded. Additionally, 75 reflexions with intensities not differing significantly from the background were set to zero and were included as 'less-than's' in the calculations. Intensity data were corrected for Lorentz and polarization factors. The crystal specimen used was of a polyhedral shape that could be approximated by a sphere with a diameter of 0·23 mm. Therefore an absorption correction for that sphere ($\mu R = 2{\cdot}4$) was applied to the intensity data.

Structure determination and refinement

The volume of the unit cell corresponds fairly well to the volume corresponding to a hexagonal close packing of 16 sulphur ions. The $d_{(100)}$ value of 6·05 Å is twice the distance of two sulphur layers. Therefore it was assumed that the structure contains close-packed sulphur layers. The perfect cleavability parallel to (100) suggested that the cations Ga and P were not distributed evenly among the interstices between all sulphur layers. It seemed likely, rather, that empty and filled interlayers were alternating in the structure.

Patterson projections were computed with $0kl$ (42 reflexions) and $h0l$ (82) intensities. The resolution of these Patterson maps was not very high but they confirmed the above model. The low resolution was not only due to the small number of reflexions used but also – as was seen later – to the fact that many Patterson vectors differed only slightly in direction and length.

With the atomic parameters derived from the Patter-

Table 2. *Observed and calculated structure factors*

0,0,L		
2	537	-527
4	1949	2072
6	144	131
8	493	491
10	318	350
1,0,L		
8	1962	-1900
6	497	500
4	1023	-1730
2	348	330
0	1251	-1134
-1,0,L		
2	402	337
4	723	590
6	115	-63
8	735	777
10	50	67
2,0,L		
8	327	327
6	632	-674
4	324	-280
2	471	-430
0	1643	-1502
-2,0,L		
2	63	67
4	1919	-1875
6	0*	-2
8	690	-630
10	190	-199
3,0,L		
6	64	-65
4	931	890
2	625	-567
0	1143	1039
-3,0,L		
2	605	-609
4	205	213
6	402	-400
8	105	-65
10	347	-353
4,0,L		
4	331	-300
2	650	606
0	60	-63
-4,0,L		
2	541	555
4	0*	-34
6	473	496
8	500	-523
10	444	413
12	601	-630
5,0,L		
2	[illegible]	65
0	361	354
-5,0,L		
2	106	65
4	[illegible]	920
6	0*	1
8	[illegible]	967
10	170	95
12	334	371
14	245	241
6,0,L		
2	155	-120
0	357	-352
-6,0,L		
2	0*	5
4	290	-210
6	0*	2
8	400	401
10	140	-151
12	170	914
7,0,L		
0	411	-412
-7,0,L		
2	233	-206
4	1078	-1067
6	46	-77
8	1443	-1510
10	177	81
12	1171	-1131
14	0*	7
-8,0,L		
4	774	776
6	377	-338
8	506	520
10	421	-440
12	64	-70
14	252	-209
-9,0,L		
4	135	169
6	510	554
8	519	517
10	370	407
12	379	642
-10,0,L		
8	343	-327
10	230	230
12	253	-227
0,1,L		
1	150	-119
2	92	-65
3	340	273
4	235	-193
5	212	-227
6	90	-96
7	413	453
8	249	-240
9	110	-87
1,1,L		
9	107	110
8	219	-191
7	240	209
6	0*	-64
5	0*	10
4	475	-464
3	510	505
2	256	-264
1	400	-444
0	762	-721
-1,1,L		
1	916	829
2	506	402
3	927	-935
4	656	570
5	680	669
6	311	273
7	696	-719
8	371	366
9	374	373
10	153	144
11	309	-307
2,1,L		
8	333	333
7	416	-407
6	91	103
5	312	338
4	406	391
3	691	-710
2	327	253
1	885	903
0	333	234
-2,1,L		
1	903	-906
2	425	-346
3	472	1006
4	327	-202
5	857	-802
6	71	-59
7	452	449
8	241	-206
9	499	-499
10	0*	66
11	0*	11
3,1,L		
7	136	123
6	180	-105
5	641	-613
4	0*	45
3	313	302
2	193	-104
1	649	-514
0	0*	-21
-3,1,L		
1	461	441
2	120	-159
3	556	-534
4	273	251
5	267	280
6	384	-347
7	74	-56
8	137	174
9	0*	-22
10	193	-175
11	0*	75
12	0*	-41
13	177	-104
4,1,L		
5	236	241
4	0*	-39
3	122	-104
2	214	-162
1	0*	27
0	209	190
-4,1,L		
1	0*	31
2	405	449
3	322	-318
4	212	-192
5	366	362
6	256	233
7	364	-389
8	174	270
9	560	534
10	67	-94
11	157	-201
12	341	361
13	312	398
5,1,L		
4	147	-103
3	0*	16
2	412	373
1	557	594
0	0*	-8
-5,1,L		
1	330	-317
2	271	-196
3	651	715
4	524	-500
5	623	-630
6	143	204
7	619	693
8	715	-772
9	501	-540
10	143	184
11	467	443
12	434	-446
13	219	-230
6,1,L		
2	172	-173
1	275	-290
0	521	-503
-6,1,L		
1	541	541
2	293	-239
3	370	-393
4	[illegible]	631
5	500	617
6	223	-231
7	423	-443
8	433	444
9	334	359
10	[illegible]	153
11	334	-355
12	0*	-47
13	111	72
14	201	272
7,1,L		
0	410	396
-7,1,L		
1	361	-356
2	257	250
3	170	110
4	67	-74
5	171	-246
6	90	-94
7	134	134
8	475	467
9	0*	-40
10	274	-250
11	0*	-33
12	402	401
13	64	63
14	0*	10
15	106	-105
-8,1,L		
1	150	-170
2	0*	41
3	123	-117
4	691	-646
5	266	-269
6	121	154
7	96	69
8	617	-650
9	320	-355
10	126	-157
11	326	330
12	227	-213
13	330	-306
14	370	-336
15	296	320
-9,1,L		
4	340	366
5	295	335
6	122	131
7	367	-349
8	0*	-7
9	306	307
10	360	347
11	411	-437
12	109	-140
13	301	337
14	195	213
-10,1,L		
6	264	-221
7	394	439
8	261	219
9	144	-147
10	0*	-47
11	244	260
12	0*	42
13	90	-81
0,2,L		
1	253	-141
2	340	315
3	305	277
4	591	640
5	266	-230
6	348	-420
7	235	267
8	519	526
9	190	-176
10	467	-405
1,2,L		
8	134	-130
7	167	-175
6	0*	-34
5	0*	61
4	0*	-20
3	269	-243
2	290	315
1	152	171
0	207	-140
-1,2,L		
1	317	416
2	1427	1366
3	300	-263
4	467	-511
5	378	320
6	1235	1190
7	101	-115
8	0*	-36
9	117	133
10	434	459
2,2,L		
8	266	-260
7	0*	-12
6	371	-354
5	154	-166
4	293	-173
3	0*	55
2	1120	-1371
1	334	-294
0	70	53
-2,2,L		
1	44	-71
2	1319	-1312
3	209	159
4	214	-170
5	164	194
6	53	77
7	140	-129
8	504	-483
9	290	275
10	642	694
11	165	-141
12	362	-351
3,2,L		
6	102	194
5	170	170
4	280	-281
3	93	92
2	97	-115
1	0*	-75
0	244	-192
-3,2,L		
1	290	-334
2	1242	-1311
3	334	344
4	245	280
5	555	-557
6	1977	-2009
7	387	394
8	305	303
9	415	-413
10	1276	-1356
11	179	171
12	64	-65
4,2,L		
5	164	160
4	333	305
3	103	-110
2	1260	1193
1	457	470
0	197	-190
-4,2,L		
1	350	343
2	1170	1163
3	573	-500
4	450	-401
5	330	370
6	1362	1395
7	347	-376
8	151	-175
9	70	69
10	194	210
11	90	-114
5,2,L		
4	371	390
3	167	193
2	644	-610
1	310	-243
0	732	670
-5,2,L		
1	219	-179
2	230	-217
3	202	196
4	610	596
5	0*	-1
6	587	659
7	0*	8
8	216	229
9	132	157
10	968	913
11	79	-55
12	155	140
6,2,L		
2	240	-257
1	53	-68
0	366	-326
-6,2,L		
2	352	-794
3	236	203
4	0*	2
5	136	-133
6	907	-958
7	260	255
8	138	178
9	99	-126
10	462	-477
11	150	182
7,2,L		
0	274	-282
-7,2,L		
1	206	162
2	422	377
3	160	-161
4	570	-534
5	206	213
6	176	175
7	138	-175
8	476	-506
9	144	167
10	0*	-27
11	170	-147
12	370	-333
13	105	104
-8,2,L		
2	170	-138
3	60	70
4	296	268
5	148	-177
6	149	-197
7	96	108
8	112	139
9	124	-158
10	315	-347
11	60	96
12	0*	27
13	115	-118
14	378	-377
-9,2,L		
5	0*	-6
6	276	303
7	132	-115
8	167	148
9	0*	-38
10	331	263
11	0*	-46
12	116	120
13	61	-70
0,3,L		
1	91	-85
2	103	82
3	256	221
4	204	-249
5	128	-156
6	128	147
7	366	377
8	248	-216
9	69	-49
1,3,L		
8	0*	-4
7	202	171
6	126	-106
5	0*	-52
4	174	-161
3	440	427
2	78	109
1	409	-421
0	486	-500
-1,3,L		
1	525	542
2	400	-430
3	695	-697
4	542	552
5	395	380
6	501	-512
7	510	-531
8	204	238
9	229	202
10	348	-322
11	202	-228
2,3,L		
7	350	-323
6	294	-291
5	325	298
4	105	104
3	404	-443
2	663	-661
1	627	603
0	321	340
-2,3,L		
1	442	-519
2	1234	1247
3	372	403
4	64	-113
5	533	-519
6	933	804
7	237	205
8	152	193
9	400	-399
10	416	401
11	0*	-8
3,3,L		
6	649	610
5	356	-353
4	94	-100
3	114	110
2	943	924
1	456	-416
0	0*	-17
-3,3,L		
1	333	320
2	662	-701
3	305	-279
4	308	-270
5	390	381
6	102	-117
7	0*	-35
8	254	-250
9	162	160
10	151	134
11	54	72
4,3,L		
3	120	-141
2	159	144
1	0*	-6
0	0*	-10
-4,3,L		
1	241	-219
2	761	-724
3	173	-145
4	0*	17
5	0*	39
6	674	-675
7	255	-254
8	233	-229
9	333	350
10	393	-351
11	290	-205
12	269	-311
13	374	363
5,3,L		
3	167	162
2	776	-737
1	245	201
0	0*	15
-5,3,L		
1	114	-110
2	302	307
3	437	453
4	172	171
5	444	-550
6	354	351
7	321	330
8	254	249
9	300	-290
10	270	262
11	430	370
12	0*	34
13	272	-257
6,3,L		
2	220	235
1	174	-137
0	0*	-33
-6,3,L		
1	624	505
2	0*	0
3	415	-380
4	0*	34
5	650	679
6	45	46
7	375	-382
8	215	207
9	324	333
10	60	-79
11	142	-170
12	452	-459
13	0*	-30
7,3,L		
0	0*	-4
-7,3,L		
1	415	-414
2	135	-164
3	126	129
4	275	-240
5	149	-102
6	161	136
7	[illegible]	-34
8	443	-453
9	112	147
10	273	251
11	154	-191
12	215	-231
13	132	141
-8,3,L		
2	219	-171
3	45	46
4	260	238
5	404	-374
6	260	-234
7	257	227
8	62	57
9	304	-332
10	133	134
11	242	241
12	271	-249
13	135	-117
14	410	413
-9,3,L		
5	253	269
6	439	-395
7	203	-214
8	220	246
9	126	138
10	753	-751
11	140	-141
12	273	233
-10,3,L		
6	240	-242
9	0*	-32
10	373	404
0,4,L		
1	325	-374
2	212	-197
3	795	787
4	1204	1191
5	476	-469
6	176	203
7	184	209
8	207	241
9	59	-54
1,4,L		
8	779	-711
7	607	-610
6	243	225
5	440	459
4	1906	-1122
3	797	-855
2	303	394
1	421	443
0	576	-623
-1,4,L		
1	597	504
2	0*	57
3	90	70
4	401	337
5	72	102
6	109	-101
7	378	361
8	510	542
9	0*	26
10	0*	20
2,4,L		
7	242	216
6	368	-380
5	119	-213
4	235	-105
3	0*	-13
2	143	-104
1	134	142
0	497	-953
-2,4,L		
1	374	359
2	103	81
3	442	-438
4	1020	1000
5	353	356
6	0*	-52
7	258	-267
8	362	-344
9	145	140
10	192	-217
11	0*	-28
3,4,L		
5	150	-156
4	714	648
3	450	429
2	314	-271
1	426	-405
0	621	673
-3,4,L		
1	525	-518
2	244	-251
3	344	342
4	119	151
5	382	-393
6	0*	-39
7	134	136
8	111	-153
9	317	-290
10	0*	-48
11	93	65
4,4,L		
4	239	-214
3	161	-147
2	299	235
1	438	395
0	0*	32
-4,4,L		
1	170	177
2	115	95
3	333	-369
4	54	57
5	275	266
6	90	95
7	342	-366
8	274	-286
9	293	292
10	212	185
11	374	-372
12	440	-439
5,4,L		
2	115	111
1	94	-120
0	75	123
-5,4,L		
1	235	-224
2	157	124
3	172	201
4	497	490
5	331	-327
6	0*	-22
7	268	224
8	634	617
9	157	-178
10	0*	-27
11	67	67
12	201	243
6,4,L		
1	101	-101
0	219	-209
-6,4,L		
1	288	255
2	63	67
3	42	118
4	192	-174
5	70	105
6	96	140
7	255	278
8	256	252
9	149	-161
10	0*	29
11	406	418
12	597	592
13	258	-226
7,4,L		
0	209	-221
-7,4,L		
1	146	161
2	297	-261
3	167	-193
4	665	-618
5	439	423
6	156	-157
7	374	-387
8	844	-926
9	509	503
10	0*	-27
11	376	-356
12	696	-708
13	306	306
-8,4,L		
3	167	146
4	513	494
5	461	-456
6	140	-177
7	239	154
8	341	329
9	303	-340
10	203	-238
11	0*	35
12	64	-65
13	126	-151
-9,4,L		
6	306	356
7	67	-77
8	365	340
9	67	-79
10	265	241
11	49	54
12	407	437

son syntheses a structure factor calculation was performed using the atomic scattering factors for Ga, P and S (neutral atoms) given in *International Tables for X-ray Crystallography* (1968). No dispersion correction was applied. The isotropic temperature factor was kept at $B=0$. The resultant reliability index was $R=0·27$.

A full-matrix refinement of atomic coordinates and isotropic temperature factors was performed using program *CRYLSQ* (X-RAY 70). No weighting scheme was applied to the observed reflexions. The reliability index converged to $R=0·069$ with zeros included and $R=0·066$ with them omitted. Observed and calculated structure factors are listed in Table 2. Final atomic coordinates and U values are given in Table 3.

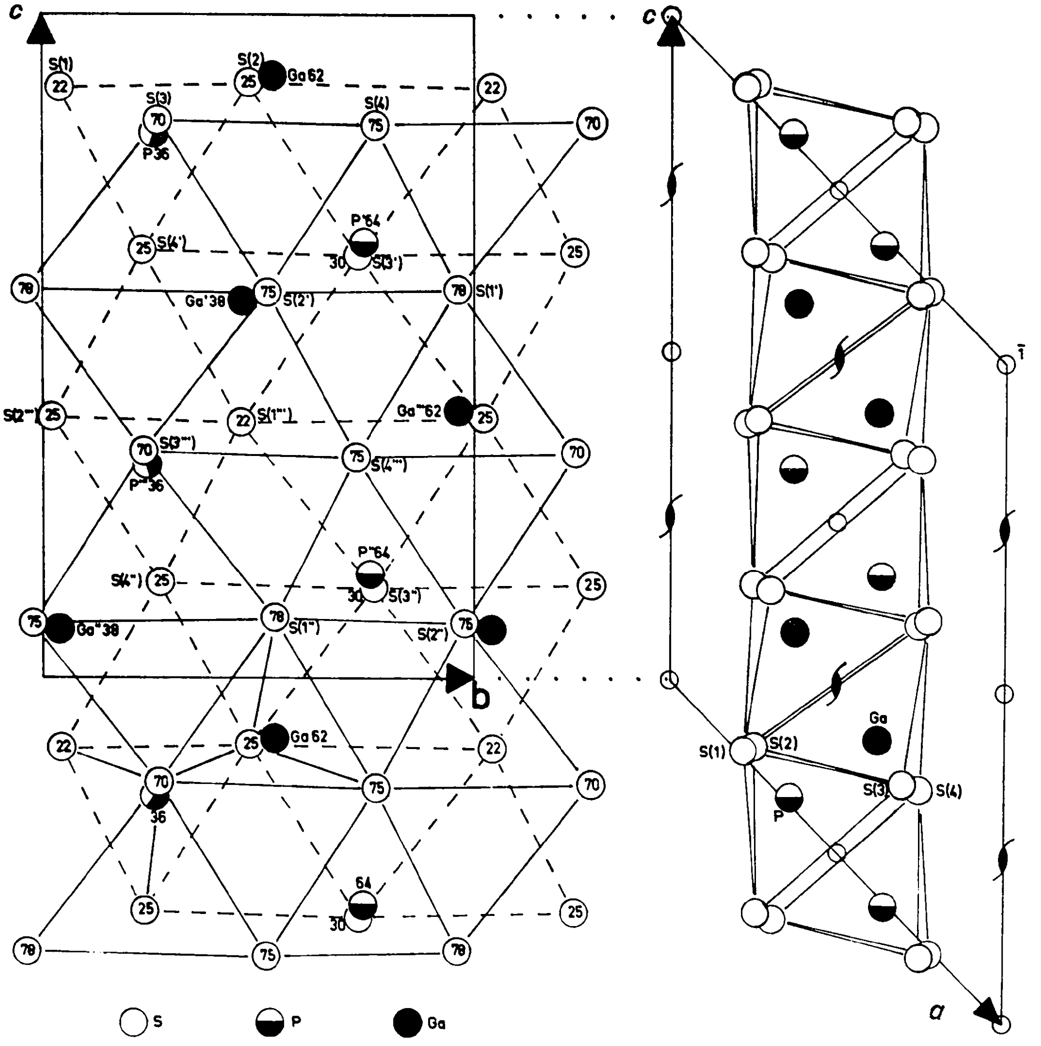
Table 3. *Final atomic parameters and their standard deviations*

	x	y	z	$U\times 10^2$
S(1)	0·2241 (5)	0·0401 (6)	0·0103 (4)	1·38 (6)
S(2)	0·2516 (5)	0·4795 (6)	0·0297 (4)	1·56 (7)
S(3)	0·6976 (5)	0·2683 (6)	0·2048 (4)	1·44 (6)
S(4)	0·7484 (5)	0·7732 (6)	0·2078 (4)	1·63 (7)
P	0·3586 (5)	0·2590 (6)	0·0103 (4)	1·04 (6)
Ga	0·6240 (2)	0·5369 (3)	0·2354 (2)	1·82 (3)

A difference Fourier-map was featureless with the highest positive values smaller than $\frac{1}{40}$ of the peaks in the Fourier-map.

Results and discussion

Fig. 1 shows the crystal structure of $GaPS_4$. All atoms occupy position 4(e) at (x,y,z; $\bar{x},\bar{y},\bar{z}$; $x,\frac{1}{2}+y,\frac{1}{2}-z$; $x,\frac{1}{2}-y,\frac{1}{2}+z$) with x,y,z given in Table 3. The structure can be derived from a hexagonal close-packed arrangement of sulphur atoms. The sulphur layers are stacked normally to (100). Of the interlayers only every other



(a) (b)

Fig. 1. The crystal structure of $GaPS_4$. (a) View normal to [100]; (b) view along the b axis.

one is occupied by cations [Fig. 1(*b*)]. Filled and empty interlayers thus alternate, causing the perfect cleavability. Ga and P are surrounded each by four sulphur atoms at the corners of distorted tetrahedra. The coordination tetrahedra of Ga and P are neighbouring and are linked together by edge-sharing. Because of this cation distribution the sulphur layers are slightly puckered and not planar as in ideal hexagonal close packing. The x coordinates of the sulphur atoms vary from 0·22 to 0·30 (0·25 in ideal case.)

In Fig. 1(*a*) (lower left) a gallium–sulphur and a phosphorus–sulphur tetrahedron are drawn. Table 4 gives the related interatomic distances and angles.

Table 4. *Interatomic distances and angles in distorted gallium–sulphur and phosphorus–sulphur tetrahedra*

Ga—S(1″)	2·275 (7) Å	S(1″)–Ga—S(2)	117·1 (3)°
Ga—S(2)	2·297 (5)	S(1″)–Ga—S(3)	105·0 (2)
Ga—S(3)	2·282 (7)	S(1″)–Ga—S(4)	107·4 (2)
Ga—S(4)	2·266 (7)	S(2)—Ga—S(3)	89·3 (2)
S(1″)–S(2)	3·901 (8)	S(2)—Ga—S(4)	116·7 (2)
S(1″)–S(3)	3·615 (10)	S(3)—Ga—S(4)	120·5 (3)
S(1″)–S(4)	3·661 (10)	S(1″)–S(4)—S(3)	56·6 (2)
S(2)—S(3)	3·218 (8)	S(3)—S(1″)–S(4)	65·7 (2)
S(2)—S(4)	3·884 (8)	S(4)—S(3)—S(1″)	57·7 (2)
S(3)—S(4)	3·948 (9)	S(1″)–S(4)—S(2)	62·2 (2)
		S(2)—S(1″)–S(4)	65·7 (2)
		S(4)—S(2)—S(1″)	56·1 (2)
		S(1″)–S(2)—S(3)	60·1 (2)
		S(3)—S(1″)–S(2)	50·5 (2)
		S(2)—S(3)—S(1″)	69·4 (2)
		S(2)—S(4)—S(3)	48·5 (2)
		S(3)—S(2)—S(4)	66·8 (2)
		S(4)—S(3)—S(2)	64·7 (2)
P—S(1)	2·048 (10)	S(1)—P—S(2)	113·4 (4)
P—S(2)	2·044 (10)	S(1)—P—S(3)	112·3 (4)
P—S(3)	2·059 (6)	S(1)—P—S(4′)	99·1 (4)
P—S(4′)	2·047 (8)	S(2)—P—S(3)	103·4 (3)
S(1)—S(2)	3·420 (9)	S(2)—P—S(4′)	114·1 (3)
S(1)—S(3)	3·411 (8)	S(3)—P—S(4′)	115·1 (4)
S(1)—S(4′)	3·117 (10)	S(1)—S(2)—S(4′)	54·1 (2)
S(2)—S(3)	3·218 (8)	S(4′)–S(1)—S(2)	63·1 (2)
S(2)—S(4′)	3·433 (9)	S(2)—S(4′)–S(1)	62·8 (2)
S(3)—S(4′)	3·464 (8)	S(1)—S(3)—S(4′)	53·9 (2)
		S(4′)–S(1)—S(3)	63·9 (2)
		S(3)—S(4′)–S(1)	62·2 (2)
		S(1)—S(2)—S(3)	61·7 (2)
		S(3)—S(1)—S(2)	62·1 (2)
		S(2)—S(3)—S(1)	62·1 (2)
		S(2)—S(4′)–S(3)	55·6 (2)
		S(3)—S(2)—S(4′)	62·7 (2)
Ga—P	2·892 (7)	S(4′)–S(3)—S(2)	61·7 (2)

Assuming pure ionic bonding (with ionic radii for S^{2-}, Ga^{3+}, P^{5+}: 1·85, 0·62, 0·35 Å, respectively) the following interatomic distances would result: Ga–S 2·47, P–S 2·20 and S–S 3·70 Å. The observed Ga–S and P–S distances however are both considerably shorter than these (Table 4). The sulphur ions thus seem to be strongly polarized by Ga and especially by P. All P–S distances in the P-tetrahedra are equal within the limits of the standard deviations. In the Ga-tetrahedra differences exist between the Ga–S distances, those pointing to the atoms shared with the P-tetrahedron being somewhat larger than those pointing to the remaining ones. The S–S distances on the other hand are considerably shortened in the P-tetrahedra. In the Ga-tetrahedra two S–S distances are about 3·70 Å (sum of ionic radii), three are remarkably longer, and only the S–S distance corresponding to the common edge with P-tetrahedra is significantly shorter. This distortion of the coordination tetrahedra can also be seen from the bond angles which vary from 48·5 to 69·4° for S–S–S angles (ideal 60°) and from 89·3 to 120·5° for S–cation–S angles (ideal 109·5°). Generally, the Ga-tetrahedra are more distorted than the P-tetrahedra.

The most densely occupied directions are [011], [010] and their symmetry equivalents (see Fig. 1). The most densely occupied planes containing these directions are the tetrahedral faces which lie approximately parallel to $\{100\}$, $\{011\}$, $\{11\bar{1}\}$, and $\{10\bar{2}\}$. This is reflected by the morphology: small polyhedral crystals show the aboved mentioned planes.

Comparison with other M^{III} thiophosphates

In Table 5 the crystal data of all known M^{III}PS$_4$ compounds are listed for comparison.

BPS$_4$, AlPS$_4$ and InPS$_4$ crystallize in acentric space groups with similar cell dimensions whereas GaPS$_4$ belongs to a centric space group. By transforming the monoclinic GaPS$_4$ cell by

$$\mathbf{a}'=\tfrac{1}{2}(\mathbf{a}+\mathbf{b}+\mathbf{c}),\quad \mathbf{b}'=\tfrac{1}{2}(\mathbf{a}-\mathbf{b}-\mathbf{c}),\quad \mathbf{c}'=\mathbf{a}$$

a triclinic cell commensurate with the other thiophosphates results (Table 5). In this setting the sulphur layers in all the compounds are parallel to (112). Their structures differ only in the cation distributions among the tetrahedral interstices between the sulphur layers. In GaPS$_4$ only alternating interlayers are occupied by

Table 5. *Crystal data of* M^{III}PS$_4$ *compounds*

Compound	BPS$_4$	AlPS$_4$	GaPS$_4$	GaPS$_4$ transformed	InPS$_4$
Unit cell	$a=5{\cdot}60$ Å	$a=5{\cdot}61$ Å	$a=$ 8·603 Å	$a'=$ 5·694 Å	$a=5{\cdot}60$ Å
	$b=5{\cdot}25$	$b=5{\cdot}67$	$b=$ 7·778	$b'=a'$	$c=9{\cdot}02$
	$c=9{\cdot}04$	$c=9{\cdot}05$	$c=$ 11·858	$c'=$ 8·603	
			$\beta=135{\cdot}46°$	$\alpha'=86{\cdot}15°$	
				$\beta'=89{\cdot}24$	
				$\gamma'=\beta'$	
	$Z=2$	$Z=2$	$Z=4$	$Z=2$	$Z=2$
Space group	$I\,222$	$P\,222$	$P\,2_1/c$		$I\,\bar{4}$

cations. In the other compounds all the interlayers are occupied by cations but individual differences in their distributions lead to various symmetries.

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Stereochemistry of an Unusual Trialkyl Sulfonium Ion. The Crystal Structure of 2,3-Dimethyl-2-butenyl-1,1,2-trimethylpropyl-methylsulfonium 2,4,6-Trinitrobenzenesulfonate

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The nature and crystal structure of the product obtained from the reaction of methylsulfonium 2,4,6-trinitrobenzenesulfonate with two molecules of 2,3-dimethyl-2-butene has been determined by X-ray methods and the product was found to be the title trialkyl sulfonium salt. The triclinic ($P\bar{1}$) lattice parameters are $a = 13{\cdot}128 \pm 0{\cdot}009$, $b = 12{\cdot}100 \pm 0{\cdot}006$, $c = 7{\cdot}992 \pm 0{\cdot}003$ Å, $\alpha = 93{\cdot}94 \pm 0{\cdot}04°$, $\beta = 102{\cdot}00 \pm 0{\cdot}04°$, and $\gamma = 74{\cdot}95 \pm 0{\cdot}04°$. The structure was solved by the heavy-atom technique and refined by full-matrix least-squares calculations to an R value of 0·057 using 3504 observed reflections measured on a diffractometer. Knowledge of the structure of the trialkyl sulfonium ion has led to a suggested mechanism for its formation. The sulfonium ion is pyramidal and it is distorted from $3m$ symmetry. The C–S$^+$ bond distances are 1·799, 1·830 and 1·882 Å and increase with increasing bulkiness of the alkyl group on S$^+$. The *ortho* nitro groups of the trinitrobenzenesulfonate anion are twisted by 54 and 61° to the benzene plane while the *para* nitro group is twisted by only 2·5°. There are a number of intermolecular contacts shorter than 3·4 Å. The shortest contacts are between the trinitrobenzenesulfonate anions.

Introduction

In an attempt to synthesize another example of a stable episulfonium salt such as that obtained from the reaction of the olefin cyclooctene with methyl sulfenium trinitrobenzene sulfonate (Pettit & Helmkamp, 1963), the latter was reacted with excess 2,3-dimethyl-2-butene (Carbin & Helmkamp, 1970). Two molecules of 2,3-dimethyl-2-butene reacted to give a crystalline product whose structure resisted spectroscopic analysis (Carbin & Helmkamp, 1970). The present X-ray study has unequivocally established the structure of the product (I) and has also led to the proposal of a probable reaction mechanism for its formation. A paper on the details of the chemical work and a brief report on the X-ray structure have been published elsewhere (Carbin, Helmkamp, Barnes & Sundaralingam, 1972).

Experimental

Colorless crystals of (I) grown in nitromethane and ether were supplied by Carbin & Helmkamp. The crystal data are as follows: $C_{19}H_{29}N_3O_9S_2$, triclinic, $P\bar{1}$, $Z = 2$; $a = 13{\cdot}128 \pm 0{\cdot}009$, $b = 12{\cdot}100 \pm 0{\cdot}006$, $c = 7{\cdot}992 \pm 0{\cdot}003$ Å, $\alpha = 93{\cdot}94 \pm 0{\cdot}04°$, $\beta = 102{\cdot}00 \pm 0{\cdot}04°$, $\gamma = 74{\cdot}95 \pm 0{\cdot}04°$ (obtained by least-squares fit of eleven reflections measured on a diffractometer), $D_{\text{obs}} = 1{\cdot}412$ g cm^{-3} (by flotation in CCl_4 and $C_2H_5P_2O$), $D_{\text{calc}} = 1{\cdot}406$ g cm^{-3}. The crystal data are consistent with the presence of one formula unit of the complex, $(C_{13}H_{27}S)^+(C_6H_2N_3O_9S)^-$ in the asymmetric unit of the structure. The calculated linear absorption coefficient for Cu $K\alpha$ radiation is 24·2 cm^{-1}.

The crystal used for the data collection was a plate of approximate dimensions $0{\cdot}25 \times 0{\cdot}05 \times 0{\cdot}7$ mm. The intensities of 3990 independent reflections were measured on a Picker four-circle diffractometer using nickel-

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