intramolecular nucleophilic displacement of some group (likely pyrophosphate) in the α orientation at C(10). This would invert the configuration at C(10) and would normally place the methyl group in the α configuration. However, if one examines this system carefully, it is seen that although inversion occurs, the formation of the highly strained cyclopropane ring causes a pseudo-inversion such that the methyl group is still in the β orientation. The α orientation of the C(5) hydroxyl group of axivalin is in accord with other evidence (Battersby, 1972) that biological hydroxylations occur with retention of configuration.

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The Crystal Structure of Tsumcorite, a New Mineral from the Tsumeb Mine, S.W. Africa

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Tsumcorite, $Pb(Zn,Fe^{3+},Fe^{2+})_2(OH,OH_2)_2(AsO_4)_2$, crystallizes in the monoclinic space group $C2/m$ with $a=9{\cdot}124$ (3), $b=6{\cdot}329$ (2), $c=7{\cdot}577$ (2) Å, $\beta=115°17$ (2)′, $Z=2$. The crystal structure has been determined from X-ray diffractometer data by Patterson and Fourier methods and refined to $R=0{\cdot}03$ for 594 observed F_{hkl}. It consists of layers of composition $[(Zn,Fe)(OH,OH_2)AsO_4]^-$ parallel to the a, b plane which are formed by the coordination octahedra around (Zn,Fe) and the AsO_4 tetrahedra *via* shared edges and corners. The Pb atoms occupy special positions with site symmetry $\bar{1}$ between these layers. There are six short Pb–O bonds of 2·591 Å (2 ×) and 2·597 Å (4 ×) and two weaker bonds of 2·955 Å. Iron and zinc atoms replace each other in one crystallographic site with a mean (Zn,Fe)–O distance in the $(Zn,Fe)(OH,OH_2)_2O_4$ coordination octahedron of 2·065 Å. Crystal chemical and analytical evidence strongly suggests that the iron in tsumcorite is mostly Fe^{3+}.

Introduction

The mineral tsumcorite from the Tsumeb mine, S.W. Africa, was first described by Geier, Kautz & Müller (1971) who proposed the chemical formula $PbZnFe(AsO_4)_2.H_2O$ based on several chemical analyses. Crystal data for tsumcorite are reported by Geier, Kautz & Müller (1971) as $a=9{\cdot}131$, $b=6{\cdot}326$, $c=7{\cdot}583$ Å, $\beta=115{\cdot}3°$, $Z=2$, space group $C2/m$. Tsumcorite occurs in crusts several mm thick in the second (deep) oxidation zone of the Tsumeb mine, with other Pb–Fe-arsenate and sulphate minerals such as beudantite, $PbFe_3[(OH)_6/SO_4/AsO_4]$, anglesite, $PbSO_4$, mimetite, $Pb_5(AsO_4)_3Cl$ and carminite, $PbFe_2[(OH)AsO_4]_2$. After registration of the mineral with the Commission on New Minerals and Mineral Names, IMA, other so-far unidentified or wrongly classified specimens in the British Museum, London, were identified as tsumcorite. One of these (specimen Nr. MB 1929,93) which comes from the first oxidation zone of the Tsumeb mine has been used for this investigation.

It is surprising that all the iron in tsumcorite is reported to be in the divalent state, while nearly all other minerals found together with tsumcorite in the oxidation zones of the Tsumeb mine contain only trivalent iron. In addition, the cell content of two formula units per cell requires that the two water molecules occupy one of the twofold positions in space group $C2/m$ which all have the site symmetry $\bar{1}$. This site symmetry however does not correspond to the geometry of the water molecule unless the hydrogen atoms are disordered. The crystal structure was determined in order to obtain definite information about the chemical formula and crystal chemistry of tsumcorite.

As has been pointed out by Geier, Kautz & Müller (1971) the lattice constants of tsumcorite are very similar to those of brackebuschite, $Pb_2(Mn,Fe)(VO_4)_2.H_2O$, which crystallizes in space group $P2_1/m$

with $a=7{\cdot}68$, $b=6{\cdot}15$, $c=8{\cdot}88$ Å and $\beta=111°50'$. (Donaldson & Barnes, 1955). A refinement of the crystal structure of brackebuschite is in progress and a comparison of the two structures will be reported later.

Experimental

A sample of tsumcorite (Nr. MB 1929,93) given to the Institute of Mineralogy, Karlsruhe, by Dr P. G. Embrey, British Museum, London, was put at our disposal by Dr K. Kautz, Essen. Most crystals of the specimen were twinned but a few single crystals could be selected from the sample. The crystal used for data collection was wedge-shaped and did not show well developed faces. Crystal data and the details of data collection are listed in Table 1. The lattice constants are based on the refinement of the setting of 12 high-angle reflexions which had been centred on an automatic 4-circle diffractometer. They are in good agreement with the values found by Geier, Kautz & Müller (1971). The systematic extinctions (*hkl* only present with $h+k=2n$) are consistent with space group $C2/m$. Intensities were collected on the diffractometer with Mo $K\alpha$ radiation ($\lambda=0{\cdot}7107$ Å, graphite monochromator), θ–2θ step-scan mode with 70 steps of 0·01° and 2 s counting time per step. The background intensity was measured for 20 s at each end of the scanning interval. The intensities were corrected for Lorentz–polarization and absorption effects and the individual values of the squared structure amplitudes and their standard deviations were averaged for equivalent reflexions. For the absorption correction, the irregular shape of the crystal was approximated by five boundary planes. Their indices and distances from an arbitrary origin on the surface of the crystal are given in Table 1. The transmission factors were in the range 0·21–0·69. Standard deviations $\sigma(I)$ were calculated according to the formula

$$\sigma(I)=\{\mathrm{CT}+(t_c/2t_b)^2(B_1+B_2)+(c_1I)^2+[c_2(I_A-I]^2\}^{1/2}$$

Table 1. *Crystal data, details of data collection and R values*

a	9·124 (3) Å
b	6·329 (2)
c	7·577 (2)
β	115°17 (2)′
V	395·5 (4) Å^3
Z	2
Space group	$C2/m$
D_x	5·39 g cm^{-3}
F.W.	641·3
μ(Mo $K\alpha$)	337·0 cm^{-1}
Number of non-unique I_{hkl}	2804
Number of unique I_{hkl}	747
Number of $I_{hkl}=0$	153
$2\theta_{\max}$	64°
$R_1=\sum \lvert\lvert F_o\rvert-\lvert F_c\rvert\rvert/\sum \lvert F_o\rvert$	0·030
$R_2=[\sum w(\lvert F_o\rvert-\lvert F_c\rvert)^2/\sum wF_o^2]^{1/2}$	0·036
R_1 (including $F_{hkl}=0$)	0·070

Boundary planes and their distances from an arbitrary origin on the surface of the crystal (mm)

h	k	l	d
0	$\bar{1}$	0	0·0
0	1	0	0·155
4	0	$\bar{1}$	0·0
$\bar{2}$	0	1	0·021
0	0	$\bar{1}$	0·0

Crystal volume $9\cdot10^{-4}$ mm^3

Table 2. *Tsumcorite, observed and calculated structure factors* (×2·9)

L	FO	FC
H,K= 0, 0		
1	154	167
2	342	331
3	108	111
4	781	753
5	337	335
6	319	307
7	69	-60
8	283	295
9	151	148
10	228	239
H,K= 0, 2		
0	519	521
1	679	697
2	0	39
3	487	466
4	168	161
5	705	691
6	82	81
7	137	132
8	0	32
9	338	348
H,K= 0, 4		
0	879	904
1	98	110
2	233	235
3	0	22
4	528	526
5	244	244
6	245	241
7	65	-63
8	216	228
9	110	116
H,K= 0, 6		
0	255	263
1	329	353
2	71	-65
3	224	230
4	110	109
5	388	396
6	0	16
7	81	85
H,K= 0, 8		
0	352	367
1	0	35
2	102	116
3	0	-25
4	226	239
5	104	110
H,K= 1, 1		
-10	99	104
-9	0	23
-8	67	68
-7	362	361
-6	365	364
-5	118	115
-4	87	84
-3	339	334
-2	767	733
-1	509	504
0	101	112
1	161	165
2	622	603
3	609	591
4	205	204
5	112	107
6	165	165
7	325	325
8	261	263
9	0	49
H,K= 1, 3		
-10	76	79
-9	0	9
-8	84	81
-7	330	329
-6	287	286
-5	94	90
-4	115	113
-3	290	288
-2	526	523
-1	424	415
0	167	166
1	105	109
2	425	427
3	532	523
4	219	213
5	72	61
6	123	120
7	306	304
8	244	246
9	0	26
H,K= 1, 5		
-8	0	31
-7	244	244
-6	264	269
-5	80	80
-4	0	8
-3	205	212
-2	454	470
-1	284	284
0	0	12
1	99	98
2	368	383
3	350	355
4	112	107
5	72	69
6	122	123
7	211	211
8	180	175
H,K= 1, 7		
-7	189	192
-6	144	146
-5	0	40
-4	60	56
-3	141	146
-2	242	250
-1	195	196
0	65	68
1	0	39
2	190	195
3	264	270
4	118	116
5	0	10
6	0	51
H,K= 1, 9		
-3	83	88
-2	195	207
-1	115	115
0	0	-13
1	0	33
2	162	166
H,K= 2, 0		
-10	0	-30
-9	323	334
-8	196	198
-7	281	285
-6	228	-222
-5	470	462
-4	505	500
-3	536	538
-2	251	-225
-1	443	428
0	259	286
1	942	945
2	181	-150
3	318	312
4	66	58
5	489	466
6	159	160
7	213	213
8	79	-67
9	172	177
H,K= 2, 2		
-10	155	166
-9	160	155
-8	337	339
-7	0	-8
-6	203	197
-5	84	80
-4	717	694
-3	85	84
-2	557	523
-1	283	-207
0	520	535
1	491	486
2	492	476
3	228	-208
4	320	307
5	233	225
6	445	439
7	71	-66
8	90	94
9	0	61
H,K= 2, 4		
-9	266	272
-8	146	144
-7	216	219
-6	162	-158
-5	351	345
-4	331	331
-3	430	422
-2	140	-129
-1	329	291
0	175	183
1	666	670
2	64	-49
3	210	207
4	0	26
5	386	377
6	132	129
7	162	166
8	0	-64
H,K= 2, 6		
-8	228	234
-7	0	-18
-6	99	102
-5	0	41
-4	419	425
-3	65	62
-2	217	214
-1	117	-95
0	346	355
1	231	235
2	250	255
3	114	-114
4	196	199
5	128	124
6	271	276
7	0	-47
H,K= 2, 8		
-5	173	174
-4	129	129
-3	209	215
-2	0	-60
-1	132	121
0	67	60
1	315	328
2	0	-14
3	90	99
4	0	-15
H,K= 3, 1		
-10	204	213
-9	113	118
-8	0	42
-7	185	189
-6	525	519
-5	375	374
-4	117	120
-3	193	196
-2	572	560
-1	702	689
0	349	373
1	154	156
2	198	194
3	511	504
4	403	401
5	117	111
6	74	74
7	135	136
8	236	238
H,K= 3, 3		
-10	161	172
-9	99	100
-8	0	56
-7	161	161
-6	415	409
-5	345	343
-4	142	137
-3	118	117
-2	420	390
-1	648	599
0	342	350
1	69	65
2	126	124
3	465	462
4	368	367
5	77	68
6	55	52
7	139	141
8	212	218
H,K= 3, 5		
-9	84	79
-8	0	0
-7	123	124
-6	360	360
-5	240	242
-4	0	27
-3	104	96
-2	375	349
-1	422	389
0	183	192
1	81	81
2	131	134
3	300	300
4	257	254
5	91	89
6	0	51
7	74	78
H,K= 3, 7		
-7	87	82
-6	204	204
-5	172	175
-4	0	64
-3	0	32
-2	186	173
-1	318	296
0	162	168
1	0	2
2	0	48
3	244	250
4	201	204
5	0	19
H,K= 3, 9		
-3	0	27
-2	155	149
-1	168	163
0	0	65
1	0	23
H,K= 4, 0		
-11	0	1
-10	0	50
-9	0	45
-8	477	487
-7	135	138
-6	245	246
-5	142	-127
-4	726	721
-3	398	404
-2	430	431
-1	53	65
0	496	523
1	215	226
2	727	725
3	54	49
4	244	244
5	64	52
6	422	421
7	146	148
8	130	133
H,K= 4, 2		
-10	69	-66
-9	221	227
-8	170	169
-7	402	404
-6	0	22
-5	178	174
-4	145	142
-3	895	875
-2	116	113
-1	333	335
0	103	-75
1	714	737
2	366	370
3	268	258
4	95	-84
5	356	363
6	207	199
7	259	260
8	0	-25
H,K= 4, 4		
-10	0	45
-9	0	26
-8	372	377
-7	108	106
-6	191	189
-5	175	-111
-4	511	495
-3	303	293
-2	368	342
-1	0	-34
0	330	333
1	181	183
2	531	535
3	0	11
4	176	174
5	0	39
6	335	338
7	99	104
H,K= 4, 6		
-8	111	109
-7	242	249
-6	0	-24
-5	111	108
-4	94	88
-3	482	464
-2	0	35
-1	175	170
0	0	-44
1	385	396
2	186	184
3	167	166
4	74	-69
5	205	214
H,K= 4, 8		
-5	82	-84
-4	220	224
-3	141	134
-2	189	180
-1	0	-63
0	140	140
1	94	88
2	263	273
3	0	-32
H,K= 5, 1		
-11	0	59
-10	235	246
-9	174	181
-8	0	48
-7	0	20
-6	237	240
-5	456	461
-4	254	253
-3	63	27
-2	121	122
-1	436	460
0	419	433
1	177	182
2	57	49
3	144	139
4	373	371
5	236	234
6	0	33
7	0	50
H,K= 5, 3		
-10	200	204
-9	161	168
-8	64	64
-7	0	2
-6	186	184
-5	428	425
-4	259	253
-3	0	-16
-2	85	72
-1	429	437
0	397	401
1	118	115
2	0	27
3	158	156
4	332	331
5	188	183
6	0	28
7	0	62
H,K= 5, 5		
-9	118	126
-8	0	14
-7	0	19
-6	185	184
-5	301	296
-4	158	150
-3	0	32
-2	108	93
-1	272	274
0	279	280
1	140	140
2	0	31
3	80	75
4	257	256
5	187	183
6	0	17
H,K= 5, 7		
-7	0	-11
-6	95	92
-5	239	238
-4	151	143
-3	0	-24
-2	0	26
-1	241	238
0	223	222
1	0	44
2	0	2
3	90	96
H,K= 6, 0		
-11	218	236
-10	0	-53
-9	88	98
-8	141	140
-7	452	463
-6	62	45
-5	300	297
-4	115	-103
-3	553	566
-2	279	278
-1	366	386
0	89	-92
1	268	270
2	211	218
3	461	471
4	75	-79
5	95	95
6	66	70
7	285	294
H,K= 6, 2		
-11	91	99
-10	136	149
-9	111	-115
-8	278	286
-7	236	238
-6	383	382
-5	113	-111
-4	180	165
-3	288	285
-2	675	669
-1	116	-113
0	210	212
1	63	48
2	483	493
3	121	111
4	158	154
5	0	-45
6	212	218
H,K= 6, 4		
-10	0	-47
-9	74	73
-8	106	97
-7	366	370
-6	0	39
-5	203	201
-4	102	-87
-3	448	438
-2	222	213
-1	271	274
0	93	-89
1	222	223
2	169	169
3	356	361
4	63	-69
5	84	85
H,K= 6, 6		
-8	184	193
-7	138	131
-6	228	227
-5	73	-73
-4	125	111
-3	142	139
-2	397	385
-1	0	-49
0	121	123
1	0	3
2	304	311
3	85	74
4	102	102
H,K= 6, 8		
-5	95	88
-4	0	-70
-3	233	237
-2	113	99
-1	119	125
0	0	-71
H,K= 7, 1		
-11	0	-14
-10	117	129
-9	278	289
-8	172	178
-7	62	49
-6	83	79
-5	339	327
-4	430	434
-3	232	232
-2	0	38
-1	169	168
0	437	451
1	311	318
2	105	105
3	0	55
4	165	163
5	274	280
6	127	127
H,K= 7, 3		
-10	91	101
-9	257	271
-8	166	170
-7	0	18
-6	0	49
-5	329	311
-4	386	386
-3	165	159
-2	0	17
-1	173	177
0	383	388
1	242	246
2	91	92
3	68	69
4	142	136
5	228	231
H,K= 7, 5		
-9	189	196
-8	109	110
-7	0	37
-6	0	54
-5	209	197
-4	286	277
-3	173	163
-2	0	15
-1	91	79
0	294	295
1	234	235
2	65	60
3	0	10
4	114	117
H,K= 7, 7		
-6	0	8
-5	181	177
-4	219	211
-3	83	63
-2	0	-10
-1	102	98
0	204	208
1	129	120
H,K= 8, 0		
-11	87	89
-10	187	203
-9	0	-61
-8	106	99
-7	122	120
-6	435	420
-5	0	47
-4	190	190
-3	124	-126
-2	538	541
-1	235	241
0	187	187
1	123	-118
2	298	302
3	211	208
4	233	243
5	0	-75
H,K= 8, 2		
-10	0	76
-9	73	71
-8	125	-127
-7	386	383
-6	195	188
-5	219	219
-4	117	-112
-3	248	250
-2	235	229
-1	397	403
0	68	-65
1	194	197
2	63	43
3	327	336
4	89	84
5	118	122
H,K= 8, 4		
-9	0	-61
-8	0	78
-7	103	96
-6	342	335
-5	0	22
-4	142	139
-3	88	-87
-2	424	416
-1	171	169
0	151	147
1	95	-94
2	232	237
3	157	154
4	195	201
H,K= 8, 6		
-7	239	238
-6	113	109
-5	159	153
-4	84	-85
-3	140	142
-2	146	132
-1	272	268
0	0	-57
1	103	110
2	0	17
H,K= 9, 1		
-10	0	-21
-9	147	147
-8	262	255
-7	110	111
-6	0	-28
-5	71	60
-4	288	292
-3	266	271
-2	92	79
-1	0	-34
0	132	134
1	302	299
2	139	129
3	0	13
4	0	28
H,K= 9, 3		
-10	0	-27
-9	150	147
-8	237	234
-7	78	77
-6	0	-28
-5	92	77
-4	255	258
-3	209	213
-2	89	76
-1	0	-6
0	110	110
1	249	247
2	137	128
3	0	26
H,K= 9, 5		
-8	186	180
-7	101	93
-6	0	-22
-5	0	22
-4	208	207
-3	206	210
-2	0	48
-1	0	-45
0	104	101
1	235	231
2	97	84
H,K= 9, 7		
-4	150	149
-3	115	112
H,K=10, 0		
-10	109	101
-9	217	221
-8	91	-93
-7	91	87
-6	191	189
-5	377	385
-4	0	-44
-3	95	96
-2	0	14
-1	437	438
0	77	69
1	87	82
2	0	-37
3	232	236
H,K=10, 2		
-10	239	241
-9	0	19
-8	0	67
-7	0	-45
-6	358	366
-5	95	98
-4	173	182
-3	0	-61
-2	203	194
-1	165	156
0	284	291
1	0	-60
2	92	91
3	0	41
H,K=10, 4		
-8	91	-83
-7	0	75
-6	147	142
-5	300	300
-4	0	-41
-3	77	80
-2	0	0
-1	349	346
0	0	52
1	83	71
H,K=10, 6		
-5	0	62
-4	110	113
-3	0	-67
-2	139	133
H,K=11, 1		
-9	0	2
-8	172	180
-7	219	219
-6	74	64
-5	0	-36
-4	120	115
-3	263	268
-2	172	166
-1	0	45
0	0	9
1	144	145
2	198	211
H,K=11, 3		
-8	153	159
-7	179	178
-6	0	61
-5	0	-17
-4	94	90
-3	215	222
-2	161	159
-1	0	53
0	0	-10
1	117	118
H,K=11, 5		
-6	0	37
-5	0	-48
-4	83	85
-3	201	204
-2	112	107
H,K=12, 0		
-9	0	82
-8	113	122
-7	135	-145
-6	119	124
-5	166	171
-4	196	203
-3	94	-101
-2	86	98
-1	0	34
0	249	247
H,K=12, 2		
-8	0	-10
-7	0	47
-6	0	-58
-5	263	281
-4	72	61
-3	104	102
-2	88	-104
-1	169	159
0	140	127
H,K=12, 4		
-6	95	100
-5	133	131
-4	171	172
-3	0	-85
H,K=13, 1		
-7	151	164
-6	128	133
-5	0	10
-4	0	-42
-3	110	107
-2	191	171

(Corfield, Doedens & Ibers, 1967; Coppens, Leiserowitz & Rabinovich, 1965), where CT is the total integrated count in time t_c, B_1 and B_2 are the background counts each in time t_b, c_1 and c_2 are empirical constants which were set to 0·03 and 0·008 respectively. I_A is the intensity corrected for absorption and I the intensity for which

$$I = \mathrm{CT} - (t_c/2t_b)\,(B_1 + B_2)\,.$$

Any intensity measured to be less than twice its standard deviation was considered to be zero. The following computer programs were used in the course of the work:

1. The Fourier program *SFS* by Neukäter & Biedl (unpublished).
2. The least-squares program *ORFLS* by Busing, Martin & Levy (1962), modified by W. C. Hamilton & J. A. Ibers.
3. The data reduction program *DATAPH* by Coppens, Leiserowitz & Rabinovich (1965).
4. The program *SADIAN* 69 for the calculation of interatomic distances and angles by Baur & Wenninger (unpublished).
5. The crystallographic function and error program *ORFFE* by Busing, Martin & Levy (1964).

All programs were modified for use at the Telefunken TR 440 computer of the Ruhr-Universität Bochum.

Patterson and Fourier methods were used to solve the structure. After interpretation of the Patterson synthesis the lead atom was placed in special position 2(*a*) of space group $C2/m$ (site symmetry $\bar{1}$). The iron and zinc atoms were assumed to occupy statistically the special position 4(*f*) (ZF-site). Two cycles of structure-factor calculations and Fourier syntheses gave a complete model of the structure. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). For the ZF-site the scattering factor curve $(0{\cdot}5f_{\mathrm{Zn}} + 0{\cdot}5f_{\mathrm{Fe}})$ was used. The function minimized in refinement was $\sum w(|F_o| - |F_c|)^2$. The weight w was defined as $1/\sigma^2(F_o)$. Unobserved reflexions were given zero weight. Four cycles of full-matrix least-squares refinement with anisotropic temperature factors gave an R of 0·03. In the final difference synthesis the strongest maxima and minima were $\pm 1{\cdot}3$ e Å^{-3} in the vicinity of the lead atom. Hydrogen atoms could not be located.

The observed and calculated structure amplitudes are listed in Table 2. Table 3 contains the final positional and thermal parameters and Table 4 shows the magnitude of the anisotropic thermal motion of all atoms.

Table 4. *Root-mean-square thermal displacements along principal axes*

	Axis 1	Axis 2	Axis 3
Pb	0·124 (1) Å	0·149 (1) Å	0·168 (1) Å
As	0·071 (4)	0·089 (2)	0·102 (3)
(Zn, Fe)	0·082 (3)	0·083 (3)	0·104 (3)
O(*W*1)	0·071 (24)	0·121 (13)	0·128 (15)
O(2)	0·078 (22)	0·118 (13)	0·137 (14)
O(3)	0·092 (12)	0·100 (12)	0·128 (10)
O(4)	0·080 (18)	0·146 (16)	0·201 (13)

Description and discussion of the crystal structure

The prominent feature of the crystal structure is infinite chains of edge-sharing $(\mathrm{Zn,Fe})\mathrm{O_4(OH,OH_2)_2}$ octahedra parallel to **b** (Fig. 1). Fig. 2 shows a projection of the structure parallel to the direction of the chains and illustrates the connexion between parallel chains. In the direction of **a**, parallel chains are connected by two $\mathrm{AsO_4}$ tetrahedra *via* common corners to form layers of composition $[(\mathrm{Zn,Fe})\,(\mathrm{OH,OH_2})\mathrm{AsO_4}]^-$ parallel to the a,b plane. The lead atoms are located between these layers. The only other connexion between two individual layers is the hydrogen bond donated by O(*W*1) to O(4) of the $\mathrm{AsO_4}$ tetrahedral group. Interatomic distances and angles are given in Table 5.

The lead atom is coordinated by eight oxygen atoms with six Pb–O distances of almost equal length (2 × 2·591 Å and 4 × 2·597 Å) and two longer Pb–O bonds of 2·955 Å. The $\mathrm{PbO_8}$ coordination polyhedron can be described as a distorted tetragonal prism or as an octahedron formed by six oxygen atoms [2 × O(4) and 4 × O(3) at distances of 2·591 Å and 2·597 Å] with two additional coordinating oxygen atoms [2 × O(2)] centred above two opposite octahedral faces (*cf.* Fig. 2). The lead atom is located on a centre of symmetry; therefore, in this crystal structure, there is no tendency to the one-sided coordination which is often found for divalent lead because of its lone pair of electrons in

Table 3. *Fractional atomic coordinates and vibrational parameters* (Å^2) *with the significant figures of the estimated standard deviations in parentheses*

The definition of the Debye–Waller temperature factor is $\exp\left(-\frac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3} B_{ij}h_ih_ja_i^*a_j^*\right)$.

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pb	0	0	0	1·83 (2)	1·73 (4)	1·24 (2)	0	0·34 (2)	0
As	0·9179 (1)	0·5	0·2155 (1)	0·52 (4)	0·80 (5)	0·57 (4)	0	0·32 (2)	0
(Zn, Fe)	0·25	0·25	0·5	0·60 (4)	0·53 (5)	0·62 (4)	0·00 (2)	0·14 (3)	0·00 (2)
O(*W*1)	0·3405 (9)	0·5	0·4066 (9)	0·6 (2)	1·3 (3)	1·1 (2)	0	0·6 (2)	0
O(2)	0·3104 (8)	0·0	0·3545 (9)	0·7 (2)	1·5 (3)	1·1 (2)	0	0·6 (2)	0
O(3)	0·0348 (6)	0·2808 (8)	0·2650 (6)	0·8 (1)	0·8 (2)	0·9 (2)	0·0 (2)	0·2 (2)	−0·2 (2)
O(4)	0·2215 (9)	0·5	0·0147 (9)	1·0 (2)	3·2 (4)	0·7 (3)	0	−0·1 (2)	0

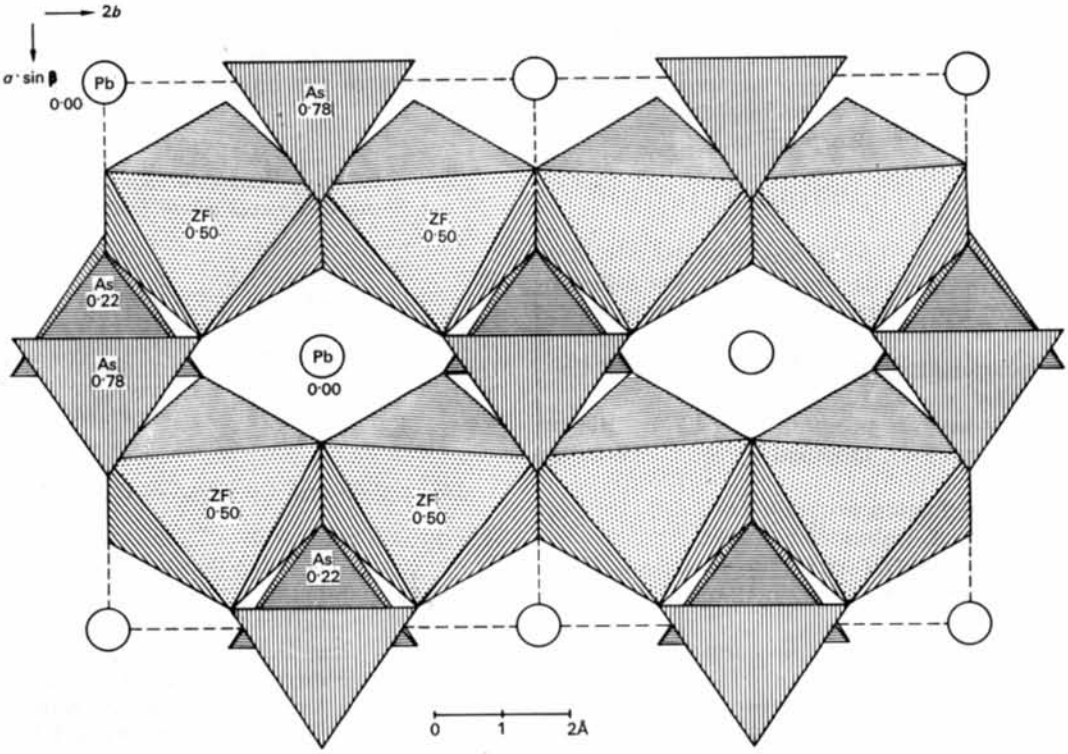

Fig. 1. Tsumcorite, projection parallel to [001]. The central cations of the coordination polyhedra are identified, and their height is given in fractional coordinates. The ZF–position is statistically occupied by Fe and Zn.

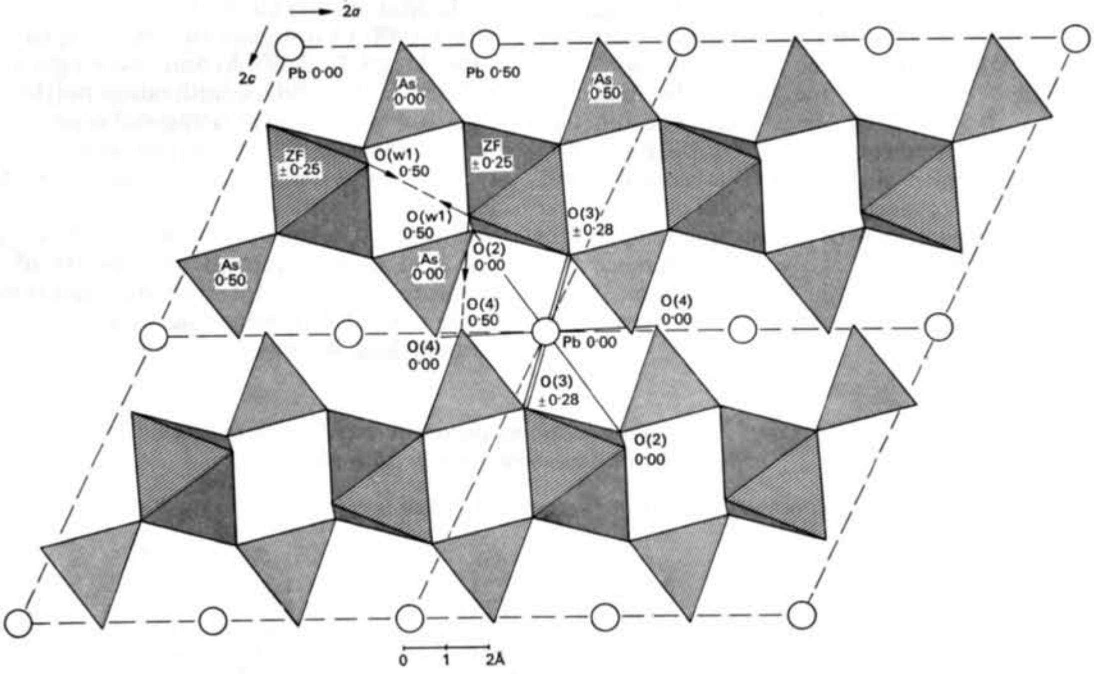

Fig. 2. Tsumcorite, projection parallel to [010]. Hydrogen bonds are marked by arrows pointing to the acceptor atom. The height of atoms is given in fractional coordinates.

Table 5. *Interatomic distances and angles*

Standard deviations are 0·006 Å for Pb–O, As–O and (Zn, Fe)–O bonds and 0·009 Å for O–O bonds. Bond angles have a standard deviation of 0·3°. For each coordination polyhedron AX_n the A–X distances are given first, followed by the X–A–X angles and the X–X distances.

(*a*) Coordination around Pb			
Pb–O(4)		2·591 Å	(2×)
Pb–O(3)		2·597	(4×)
Pb–O(2)		2·955	(2×)
Mean		2·685	
O(4)–O(3)	76·4°	3·208	(4×)
O(3)–O(2)	62·9	2·913	(4×)
O(4)–O(3)	103·6	4·077	(4×)
O(3)–O(2)	117·1	4·741	(4×)
O(4)–O(2)	122·5	4·866	(2×)
O(4)–O(2)	57·5	2·687	(2×)
O(3)–O(3)	86·4	3·555	(2×)
O(3)–O(3)	93·6	3·787	(2×)
O(3)–O(3)	180·0	5·194	(2×)
O(4)–O(4)	180·0	5·182	
O(2)–O(2)	180·0	5·911	
(*b*) Coordination around As			
As–O(4)		1·663 Å	
As–O(3)		1·691	(2×)
As–O(2)		1·719	
Mean		1·691	
O(4)–O(3)	111·1°	2·765 Å	(2×)
O(4)–O(2)	105·2	2·686	
O(3)–O(3)	110·2	2·774	
O(3)–O(2)	109·6	2·786	(2×)
(*c*) Coordination around the ZF-site (Zn, Fe)			
ZF–O(3)		2·019 Å	(2×)
ZF–O(*W*1)		2·046	(2×)
ZF–O(2)		2·131	(2×)
Mean		2·065	
O(3)——O(3)	180·0°	4·038	
O(3)——O(*W*1)	89·8	2·868	(2×)
O(3)——O(*W*1)	90·2	2·881	(2×)
O(3)——O(2)	89·1	2·913	(2×)
O(3)——O(2)	90·9	2·958	(2×)
O(*W*1)–O(*W*1)	180·0	4·092	
O(2)——O(2)	180·0	4·262	
O(*W*1)–O(2)	80·6	2·702	(2×)
O(*W*1)–O(2)	99·4	3·186	(2×)
(*d*) Coordination around O(*W*1)			
O(*W*1)–ZF		2·046 Å	(2×)
O(*W*1)–O(*W*1)		2·636	
O(*W*1)–O(4)		2·690	
ZF——ZF	101·3°	3·165	
ZF——O(*W*1)	109·3	3·834	(2×)
ZF——O(4)	110·4	3·908	(2×)
O(*W*1)–O(4)	115·1	4·496	

the 6*s* orbital. The AsO_4 tetrahedra share three of their four corners with the coordination octahedra around (Zn, Fe) and the PbO_8 polyhedra. The fourth oxygen atom is coordinated only to As and Pb and in addition receives a hydrogen bond from O(*W*1).

In the first stages of the refinement the ZF position was assumed to be statistically occupied by zinc and divalent iron. This assumption however was not supported by the results of the refinement. As can be seen from Table 5, the mean (Zn, Fe)–O distance is 2·065 Å. According to Shannon & Prewitt (1969) the effective ionic radii for Fe^{2+} and Zn are almost equal at 0·77 and 0·75 Å respectively, while the ionic radius of Fe^{3+} is 0·645 Å. The mean value of 70 individual Fe^{2+}–O bonds is 2·138 Å, the mean Fe^{3+}–O distance of 69 individual bonds is 2·011 Å (Baur, 1970). The mean Zn–O distance in seven well-determined crystal structures which contain zinc in octahedral coordination is 2·112 Å (Baur, 1973, private communication). Thus the mean (Zn, Fe)–O distance of 2·065 Å found in tsumcorite indicates that iron must be predominantly in the trivalent state.

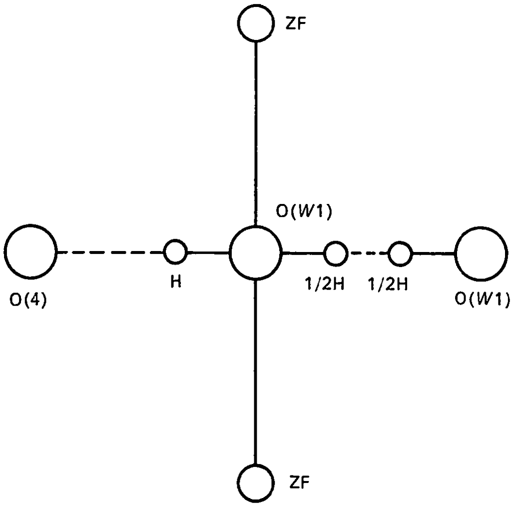

Fig. 3. Bonding around O(*W*1).

A wet chemical determination of the FeO content of tsumcorite gave 2·6 wt.% FeO which means that about one quarter of the total iron content is Fe^{2+} and three quarters are Fe^{2+}. The determination was made by means of a photometric micromethod developed by Wilson (1960) and modified by Langer & Nickel (1973). Mimetite, $Pb_5(AsO_4)_3Cl$ was used for a blank determination.

Based on an occupancy of the ZF-site of 50% Zn, 12% Fe^{2+} and 38% Fe^{3+} the theoretical mean (Zn, Fe)–O distance is 2·076 Å which is close to the observed distance of 2·065 Å.

While a number of compounds are known in which Zn and Fe^{2+} replace each other (*cf.* Brehler 1969), the statistical occupation of one crystallographic site by Zn and Fe^{3+} is rather unusual. A similar case has been found in $Ba_2Zn_2Fe_{12}O_{22}$ (Townes & Fang, 1970), where one octahedral site has the population $Fe^{3+}_{0\cdot6}Zn_{1\cdot4}$ with a mean (Zn, Fe)–O distance of 2·088 Å.

With trivalent instead of divalent iron ions in tsumcorite it has to be assumed that the O(*W*1) position is statistically occupied by OH and H_2O in order to retain the electrostatic charge balance of the chemical formula. This is also borne out by the fact that there is a short oxygen–oxygen contact [O(*W*1)–O(*W*1)] of 2·636 Å across a centre of symmetry, which is most probably due to a hydrogen bond. O(*W*1) is tetrahe-

Table 6. *Electrostatic bond strengths p(O) in tsumcorite*

	Pb	(Zn, Fe)	As	H(*D*)	H(*A*)	$\sum = p$(O)
O(*W*1)	–	2 × 0·396	–	1·5 × 0·83	0·5 × 0·17	2·12
O(2)	0·25	2 × 0·396	1·25	–	–	2·29
O(3)	0·25	0·396	1·25	–	–	1·90
O(4)	0·25	–	1·25	–	0·17	1·67

drally surrounded by two (Zn,Fe) atoms, by oxygen atom O(4) of the AsO_4 group and by the symmetrically equivalent O(*W*1) molecule (see Fig. 3). The O(*W*1)–O(4) distance is 2·690 Å, a distance which is consistent with a hydrogen bond. The next shortest distance between the O(*W*1) molecule and another oxygen atom, which does not belong to the same coordination octahedron around (Zn,Fe), is 3·013 Å [O(*W*1)–O(3)]. Although the hydrogen atoms could not be located in the difference synthesis because of the presence of the heavy lead atoms the most likely interpretation of the bonding situation around O(*W*1) is that the O(*W*1) position is statistically occupied by OH and H_2O. One of the two symmetrically equivalent O(*W*1) positions is occupied by a water molecule which donates one hydrogen bond to O(4) and another to the equivalent O(*W*1) position which is then occupied by OH and also donates one hydrogen bond to a different O(4) atom.

The electrostatic bond-strength sums p(O) (Pauling 1960; Baur 1970) received by each oxygen atom from the surrounding cations are given in Table 6. They correspond well to the observed interatomic distances with respect to the correlations between interatomic distances and bond-strength sums p (Baur, 1970). In view of the crystal chemical and analytical evidence tsumcorite should properly be formulated as $Pb(Zn,Fe^{3+},Fe^{2+})_2(OH,OH_2)_2(AsO_4)_2$.

We wish to thank Dr K. Kautz, Essen, who suggested the crystal structure determination, for a specimen of tsumcorite. Thanks are also due to Professor K. Langer and Mr S. Nickel, Bochum, for their determination of the FeO content and Professors W. H. Baur, Chicago, and V. Kupčik, Göttingen, for useful discussions. Computing time was provided by the Computing Centre of the Ruhr-Universität Bochum.

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