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The Crystal Structure Analysis of Zirconium Sulphate Tetrahydrate*

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Zirconium sulphate tetrahydrate is orthorhombic, space group *Fddd*, with

$$a = 25{\cdot}92,\quad b = 11{\cdot}62,\quad c = 5{\cdot}532\ \text{Å}\ ,$$

and has eight formula units per unit cell. The structure has been determined by X-ray Fourier methods, and refined by least-squares, using data obtained from spherical crystals with a Geiger counter. The structure consists of layers of composition $Zr(SO_4)_2 . 4\,H_2O$ normal to the *a* axis. These layers are probably held together by hydrogen bonds. The hydrate oxygen and one of the sulphate oxygens form an antiprism about the zirconium atom at an average Zr–O distance of 2·180 Å. The sulphate group has a small but significant departure from tetrahedral symmetry, the two non-equivalent S–O bonds being 1·443 and 1·486 Å, both ±0·014 Å. The relationship between this structure and that of uranium (IV) sulphate tetrahydrate is discussed.

Introduction

Work on the crystal structure of zirconium sulphate tetrahydrate was initiated during the course of a Los Alamos program of measuring the magnetic susceptibilities of 'oxygen dilute' compounds of the 5*f* elements, particularly compounds of plutonium. We have often found it expedient in this laboratory to study in detail substances isomorphous with plutonium compounds rather than the plutonium compounds themselves. In this manner the health hazard is eliminated and, usually, the scattering power of the substituted atom is significantly smaller than plutonium, thus permitting more accurate location of light atoms.

Cerium and plutonium sulphate tetrahydrates each have two polymorphic forms, one in space group *Fddd* and one in space group *Pnma*. The analogous zirconium and uranium compounds have only one form, and are isomorphous with the *Fddd* and *Pnma* forms respectively. Crystallographic data for those compounds having the *Pnma* form have been summarized by Staritzky & Truitt (1954) and the structure of the uranium salt has recently been determined by Kierkegaard (1956). Crystallographic data for the zirconium salt have been reported by Staritzky & Singer (1956). The lattice constant and space group data for these compounds are collected in Table 1.

Experimental

Data for the initial Fourier analysis were obtained from multiple film Weissenberg photographs with Mo $K\alpha$ radiation. Small, plate-like, single crystal fragments were rotated about the *b* and *c* axes. Intensities were estimated visually with the aid of an intensity scale made by timed oscillations through a strong reflection on multiple films. About 1200 independent reflections were observed. No absorption corrections were applied to these data.

Intensity data for final refinement of the structure were obtained from spherical crystals by means of a Geiger counter attachment on a Weissenberg camera (Evans, 1953). Cu $K\alpha$ radiation was used. Data from a *c* axis mounting for $l=0$ through 3 were obtained from a crystal 0·35 mm. in diameter. A spherical crystal 0·32 mm. in diameter was used for *b* axis data for $k=0$ through 7 and also for the zero level on the (011) axis. The last mounting was necessary for the correlation of the even and odd numbered layers to a common scale factor because of the nature of the systematic extinctions for a face-centered lattice. The calculated linear absorption coefficient is 169 cm.$^{-1}$ and absorption corrections for spherical crystals from the tables of Evans & Ekstein (1952) were applied. Of the 393 possible reflections, 376 were observed.

Table 1. *Lattice constants and space groups for* $M(SO_4)_2 . 4\,H_2O$ *compounds*

M	*a* (Å)	*b* (Å)	*c* (Å)	Space group	Reference
Zr	25·92 ±0·02	11·62 ±0·02	5·532 ± 0·005	*Fddd*	Swanson *et al.* (1957)
Ce	26·59 ±0·04	11·93 ±0·04	5·73 ±0·02	*Fddd*	
Pu	26·49 ±0·04	11·99 ±0·04	5·70 ±0·02	*Fddd*	
Pu	14·57 ±0·04	11·01 ±0·04	5·66 ±0·02	*Pnma*	Singer (1951)
U	14·674 ± 0·005	11·093 ± 0·005	5·688 ± 0·005	*Pnma*	Kierkegaard (1956)

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Reflections which had been measured either two or three times were compared according to the method suggested by Ibers (1956) and the average error in F^2 was found to be 11·2%.

The lattice constants for zirconium sulphate tetrahydrate determined by Swanson *et al.* (1957), and shown in Table 1, are probably more reliable than those reported by Staritzky & Singer (1956) and will be used in this paper. The calculated density of the compound having eight formula units per unit cell is 2·83 g.cm.$^{-3}$, and the measured density is 2·80 g.cm.$^{-3}$ (Staritzky & Singer, 1956).

Determination of the approximate structure

The Patterson projection on 001 and the Harker sections on the d glide planes were computed on X-RAC with the visual intensity data. These vector diagrams were found to be compatible with zirconium in the position $8(a)$ and with sulphur atoms in $16(e)$ with $x \approx 0·31$, the origin being taken at 222. The contributions of these atoms were sufficient to establish the signs of most of the structure factors, and a three-dimensional Fourier and a Fourier projection on 001 were computed, again on X-RAC. Fig. 1 is an X-RAC view of this projection. The oxygen atoms were located from these Fourier series and their parameters and the improved sulphur parameter are given in Table 2.

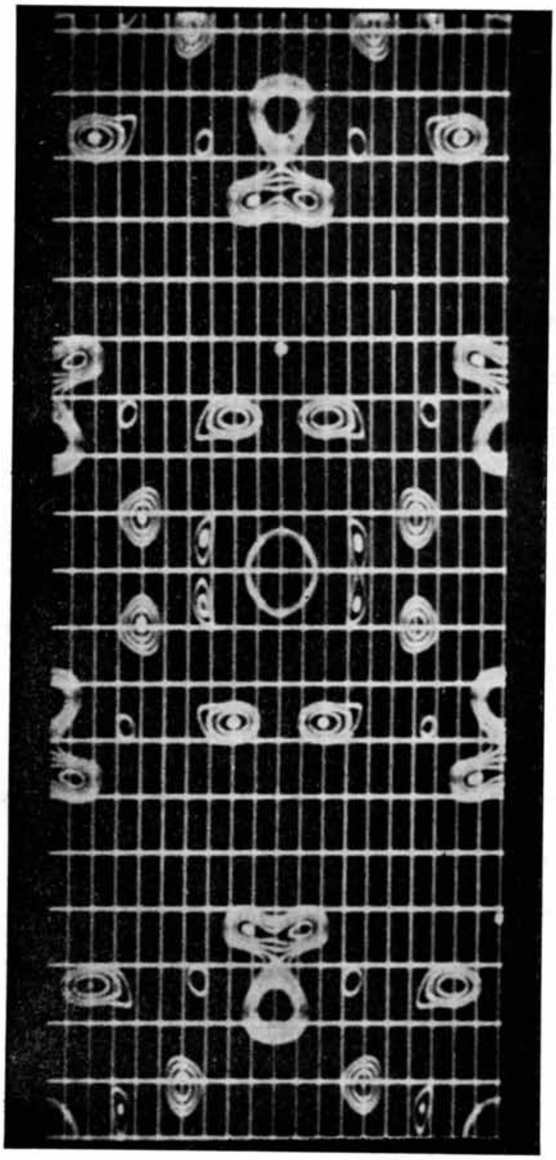

Fig. 1. Fourier projection $hk0$ made on X-RAC with the original visual Mo $K\alpha$ data.

Table 2. *Parameters from the several stages of refinement*

	Fourier with Mo $K\alpha$ data	Fourier with Cu $K\alpha$ data	Final least-squares with Cu $K\alpha$ data
$B(Zr)$	1·00	—	0·453 ± 0·034
$B(S)$	1·50	—	0·881 ± 0·078
$B(O_1)$	2·00	—	1·46 ± 0·19
$B(O_2)$	2·00	—	1·63 ± 0·19
$B(O_3)$	2·00	—	1·74 ± 0·19
$x(S)$	0·3065	0·3061	0·3065 ± 0·0001
$x(O_1)$	0·0887	0·0859	0·0874 ± 0·0003
$x(O_2)$	0·0220	0·0215	0·0223 ± 0·0003
$x(O_3)$	0·0645	0·0634	0·0659 ± 0·0003
$y(O_1)$	0·2350	0·2332	0·2292 ± 0·0007
$y(O_2)$	0·1460	0·1498	0·1486 ± 0·0007
$y(O_3)$	0·0620	0·0536	0·0551 ± 0·0007
$z(O_1)$	0·5430	0·5409	0·5375 ± 0·0015
$z(O_2)$	0·7620	0·7875	0·7847 ± 0·0015
$z(O_3)$	0·2390	0·2211	0·2170 ± 0·0015

Although the parameters obtained with the visual intensity data seemed quite reasonable, the structure factor agreement was not particularly satisfactory. In addition, the oxygen atom contours were rather asymmetric. It is probable that these difficulties arose from errors in placing reflections having all odd indices on the same scale as those having all even indices. For further refinement it was decided to collect new intensity data using spherical crystals and a Geiger counter.

Refinement of the structure

A least-squares refinement was made with the Geiger counter data, using as initial values the parameters derived above. The scale factor, an isotropic temperature factor for each atom, and the atomic coordinates were simultaneously refined. Off diagonal terms were omitted. All reflections were weighted equally and the unobserved reflections were omitted. Reflections 800 and 220 were also omitted from the refinement because their intensities had been erroneously recorded during the Geiger counter measurements, as was evidenced by inspection of Weissenberg films. The form factors for zirconium and sulphur were taken from the *Internationale Tabellen* (1935), and for oxygen, McWeeney's (1951) form factor was used. Most of the calculations were done on Maniac I, but the last few cycles were calculated on the IBM 704. The final least-squares parameters are given in Table 2. The standard devia-

Table 3. *R values for the parameters of the least-squares refinement*

hkl	*R*	Number of reflections
All	0·071	376
0*kl*	0·063	10
*h*0*l*	0·068	23
*hk*0	0·084	47
$h+k+l=4n+2$	0·177	53

tions listed in Table 2 were calculated from the usual diagonal approximation. The final set of observed and calculated structure factors is given in Table 4. The reliability indices for various classes of reflections are shown in Table 3. The class in which $h+k+l=4n+2$ has no zirconium or sulphur contribution. *R* for this class is high because most of these reflections were very weak and hence the error is likely to be larger than for the other reflections.

Fourier sections through the oxygen atoms and the sulphur atom were computed on Maniac I with the counter data. The contours in these sections were all quite round. The peak positions from these Fourier sections are also recorded in Table 2. No series termination corrections were applied to these last parameters.

Discussion of the structure

The important interatomic distances and bond angles are listed in Table 5. Fig. 2 is a view of the essential features of the structure as projected on 001. The slightly distorted Archimedean antiprism surrounding the zirconium atom consists of half of the sulphate oxygens, namely O_2, and the hydrate oxygen, O_3. The average distance of 2·180 Å compares favorably with the value of 2·21 Å found recently in $Zr(IO_3)_4$

Table 4. *Observed and calculated structure factors for* $Zr(SO_4)_2.4\,H_2O$

The origin for these structure factor calculations is at the center of symmetry

h	k	ℓ	Fo	Fc
4	0	0	337	-373
8	0	0	0	-90
12	0	0	335	-330
16	0	0	274	252
20	0	0	165	-137
24	0	0	30	26
28	0	0	0	-14
2	2	0	0	-77
6	2	0	358	403
10	2	0	223	-190
14	2	0	260	253
18	2	0	208	-184
22	2	0	79	68
26	2	0	247	-237
30	2	0	215	207
0	4	0	465	-476
4	4	0	86	49
8	4	0	60	47
12	4	0	280	262
16	4	0	286	-280
20	4	0	300	281
24	4	0	162	-152
28	4	0	38	55
2	6	0	146	119
6	6	0	460	-481
10	6	0	320	300
14	6	0	82	-71
18	6	0	47	38
22	6	0	100	-91
26	6	0	197	187
0	8	0	330	300
4	8	0	229	-208
8	8	0	151	139
12	8	0	143	-125
16	8	0	153	144
20	8	0	214	-199
24	8	0	121	108
2	10	0	62	37
6	10	0	253	229
10	10	0	268	-246
14	10	0	100	92
18	10	0	81	-74
22	10	0	191	174
0	12	0	227	-210
4	12	0	171	160
8	12	0	89	-78
12	12	0	104	86
16	12	0	176	-157
2	14	0	103	99
6	14	0	177	-163
1	1	1	181	-166
3	1	1	337	-395
5	1	1	43	29
7	1	1	289	316
9	1	1	75	-69
11	1	1	203	-185
13	1	1	147	136
15	1	1	151	151
17	1	1	154	-140
19	1	1	143	-144
21	1	1	41	39
23	1	1	160	156
25	1	1	49	-48
27	1	1	89	-86
29	1	1	152	151
31	1	1	10	11
1	3	1	110	-111
3	3	1	367	391
5	3	1	119	-95
7	3	1	165	-153
9	3	1	273	-266
11	3	1	25	-4
13	3	1	315	337
15	3	1	53	-52
17	3	1	118	-113
19	3	1	190	179
21	3	1	30	42
23	3	1	194	-186
25	3	1	83	-86
27	3	1	63	68
29	3	1	132	132
31	3	1	30	-41
1	5	1	123	111
3	5	1	155	133
5	5	1	245	-252
7	5	1	155	-144
9	5	1	203	189
11	5	1	25	25
13	5	1	203	-192
15	5	1	25	-28
17	5	1	235	235
19	5	1	88	85
21	5	1	70	-71
23	5	1	150	-149
25	5	1	17	17
27	5	1	136	136
29	5	1	99	-104
1	7	1	137	137
3	7	1	274	-272
5	7	1	35	23
7	7	1	167	153
9	7	1	213	201
11	7	1	63	-54
13	7	1	250	-246
15	7	1	0	18
17	7	1	84	70
19	7	1	133	-126
21	7	1	42	-39
23	7	1	181	169
25	7	1	70	72
27	7	1	38	-49
1	9	1	25	-24
3	9	1	209	-200
5	9	1	57	52
7	9	1	235	230
9	9	1	81	-77
11	9	1	61	-59
13	9	1	117	112
15	9	1	87	82
17	9	1	124	-119
19	9	1	153	-144
21	9	1	29	31
23	9	1	124	122
1	11	1	109	-102
3	11	1	153	142
5	11	1	21	6
7	11	1	142	-132
9	11	1	80	-76
11	11	1	135	125
13	11	1	134	131
15	11	1	52	-51
17	11	1	77	-74
19	11	1	100	91
1	13	1	44	44
3	13	1	174	165
5	13	1	44	-44
7	13	1	138	-139
9	13	1	119	109
11	13	1	21	-5
2	0	2	125	84
6	0	2	219	194
10	0	2	446	-478
14	0	2	143	123
18	0	2	25	-22
22	0	2	292	294
26	0	2	261	-256
30	0	2	95	107
0	2	2	197	-179
2	2	2	45	32
4	2	2	372	391
6	2	2	48	25
8	2	2	233	-233
10	2	2	103	-90
12	2	2	33	22
14	2	2	35	39
16	2	2	267	-257
18	2	2	17	-3
20	2	2	221	232
22	2	2	0	0
24	2	2	70	-69
26	2	2	0	2
28	2	2	61	63
30	2	2	10	-7
2	4	2	259	245
4	4	2	56	-46
6	4	2	257	-268
8	4	2	65	44
10	4	2	374	397
12	4	2	25	22
14	4	2	130	-116
16	4	2	27	14
18	4	2	57	-37
20	4	2	39	-38
22	4	2	145	-140
24	4	2	23	-16
26	4	2	182	178
28	4	2	19	20
0	6	2	242	227
2	6	2	81	-66
4	6	2	203	-179
6	6	2	37	37
8	6	2	21	11
10	6	2	36	22
12	6	2	96	-86
14	6	2	33	27
16	6	2	321	326
18	6	2	23	-19
20	6	2	233	-228
22	6	2	0	0
24	6	2	65	72
26	6	2	0	7
2	8	2	134	-116
4	8	2	35	-27
6	8	2	139	123
8	8	2	21	1
10	8	2	252	-237
12	8	2	45	-38
14	8	2	184	177
16	8	2	35	24
18	8	2	66	-60
20	8	2	0	16
22	8	2	125	117
24	8	2	14	7
0	10	2	365	-336
2	10	2	19	15
4	10	2	230	208
6	10	2	0	9
8	10	2	37	-32
10	10	2	0	-10
12	10	2	95	94
14	10	2	30	-18
16	10	2	225	-212
18	10	2	19	-11
20	10	2	131	127
2	12	2	82	75
4	12	2	25	19
6	12	2	154	-150
8	12	2	41	32
10	12	2	192	184
12	12	2	30	-21
14	12	2	119	-116
1	1	3	61	-57
3	1	3	133	129
5	1	3	63	62
7	1	3	281	-300
9	1	3	62	-59
11	1	3	132	140
13	1	3	166	164
15	1	3	39	-32
17	1	3	118	-118
19	1	3	174	176
21	1	3	52	50
23	1	3	162	-179
25	1	3	89	-95
27	1	3	63	70
1	3	3	149	158
3	3	3	246	252
5	3	3	54	-53
7	3	3	238	-241
9	3	3	168	172
11	3	3	32	36
13	3	3	256	-259
15	3	3	35	25
17	3	3	76	76
19	3	3	149	151
21	3	3	0	-0
23	3	3	145	-148
25	3	3	72	80
27	3	3	29	36
1	5	3	126	128
3	5	3	103	-102
5	5	3	152	-158
7	5	3	154	158
9	5	3	108	104
11	5	3	39	-44
13	5	3	194	-198
15	5	3	17	13
17	5	3	176	184
19	5	3	106	-107
21	5	3	35	-37
23	5	3	106	132
25	5	3	36	39
1	7	3	112	-104
3	7	3	183	-162
5	7	3	43	-30
7	7	3	118	111
9	7	3	103	-99
11	7	3	55	-50
13	7	3	241	237
15	7	3	42	46
17	7	3	110	-111
19	7	3	147	-147
21	7	3	27	35
23	7	3	147	150
1	9	3	100	-92
3	9	3	189	185
5	9	3	45	46
7	9	3	173	-171
9	9	3	48	-51
11	9	3	57	55
13	9	3	137	135
15	9	3	79	-74
17	9	3	112	-112
19	9	3	120	122
1	11	3	116	120
3	11	3	149	148
5	11	3	10	-21
7	11	3	114	-115
9	11	3	68	64
11	11	3	93	94
13	11	3	129	-129
0	0	4	460	-467
4	0	4	217	206
8	0	4	0	-13
12	0	4	150	154
16	0	4	207	-214
20	0	4	153	154
24	0	4	41	-45
2	2	4	89	78
4	2	4	0	-6
6	2	4	227	-227
8	2	4	46	41
10	2	4	209	210
12	2	4	80	-80
14	2	4	146	-151
16	2	4	19	29
18	2	4	97	90
20	2	4	17	17
22	2	4	82	-92
24	2	4	10	7
0	4	4	281	282
2	4	4	70	76
4	4	4	126	-123
6	4	4	46	-49
8	4	4	30	23
10	4	4	29	-28
12	4	4	143	-138
14	4	4	30	-22
16	4	4	209	218
18	4	4	33	34
20	4	4	193	-203
22	4	4	0	-2
24	4	4	92	100
2	6	4	88	-80
4	6	4	25	-27
6	6	4	265	262
8	6	4	51	47
10	6	4	226	-230
12	6	4	27	16
14	6	4	90	89
16	6	4	0	12
18	6	4	41	-39
20	6	4	47	-46
22	6	4	79	96
1	1	5	103	117
3	1	5	210	236
5	1	5	0	-22
7	1	5	109	-115
9	1	5	95	100
11	1	5	61	61
13	1	5	116	-132
15	1	5	86	-96
17	1	5	93	107
19	1	5	62	80
21	1	5	19	-26
1	3	5	35	46
3	3	5	171	-184
5	3	5	36	24
7	3	5	80	85
9	3	5	114	124
11	3	5	25	-28
13	3	5	153	-169
15	3	5	72	85
17	3	5	107	117
19	3	5	99	-117
1	5	5	57	-61
3	5	5	139	-153
5	5	5	60	61
7	5	5	99	113
9	5	5	123	-125
11	5	5	38	-42
13	5	5	112	128
15	5	5	39	49
17	5	5	102	-116
1	7	5	70	-75
3	7	5	187	185
5	7	5	37	43
7	7	5	145	-141
9	7	5	134	-137
11	7	5	42	45
13	7	5	120	126
15	7	5	43	-20
2	0	6	39	51
6	0	6	161	-170
10	0	6	199	206
14	0	6	99	-93
0	2	6	178	200
2	2	6	0	-16
4	2	6	136	-148
6	2	6	17	-13
8	2	6	63	63
10	2	6	60	59
12	2	6	68	-80
14	2	6	25	-30
2	4	6	71	-74
4	4	6	30	33
6	4	6	151	168
8	4	6	29	-26
10	4	6	176	-192
12	4	6	17	-16
0	6	6	157	-188
2	6	6	46	47
4	6	6	116	125
6	6	6	27	-28

(Larson & Cromer, 1959) where an antiprism coordination also occurs. Another zirconium compound with an antiprism coordination is $ZrOCl_2 . 8\,H_2O$ (Clearfield & Vaughan, 1956), in which the Zr–O distance is reported to be 2·24 Å.

Table 5. *Interatomic distances and bond angles*

The standard deviation of Zr–O and S–O distances is 0·014 and of O–O distances 0·020 Å

Within the antiprism			Within the sulphate group	
Zr–O_2	2·176 Å		S–O_1	1·443 Å
Zr–O_3	2·183		S–O_2	1·486
			O_1–O_2	2·365
O_2–O_3	2·623	square faces	O_1–O_1	2·400
O_2–O_3	2·531		O_2–O_2	2·365
O_3–O_3	2·719	triangular faces	∠ O_1–S–O_1	112° 32′ ± 48′
O_2–O_3	2·859		∠ O_2–S–O_2	106° 56′ ± 48′
O_2–O_2	2·648		∠ O_1–S–O_2	107° 41′ ± 48′

Possible hydrogen bonds

O_2–O_3	2·623 Å
O_1–O_3	2·685

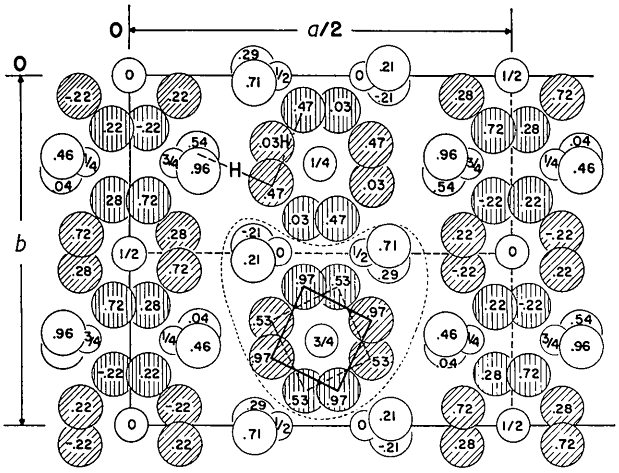

Fig. 2. A portion of the structure projected on 001. The large circles are oxygen atoms, the medium circles are the zirconium atoms and the small circles are the sulphur atoms. The O_1 atoms are unshaded, the O_2 atoms are shaded with vertical lines and the O_3 atoms are shaded with diagonal lines. The letter *H* indicates possible hydrogen bonds. The *z* coordinate is given in the center of each atom.

The sulphate group shows a small but significant departure from the ideal tetrahedral symmetry. The two S–O bonds differ by 0·043 Å, which is three times the standard deviation of the bond lengths. Also, the O_1–S–O_1 angle is significantly different from the tetrahedral angle. The shorter of the S–O bonds involves the oxygen atom that is not shared with a zirconium atom.

The structure is made up of layers of $Zr(SO_4)_2 . 4\,H_2O$ normal to the *a* axis. The hydrate oxygen atom has three close oxygen neighbors, which is suggestive of hydrogen bonds. Two of these neighbors are O_2 atoms on the square face of the antiprism and the third is an O_1 atom of a neighboring sulphate group. The O_3–O_1 contact, at 2·685 Å, is very likely a hydrogen bond because this would serve to hold the layers together. If there is a second hydrogen bond in the structure it is most likely from O_3 to O_2, at 2·623 Å, as shown in Fig. 2. The apparent H–O–H angle is then about 95°. The other O_3–O_2 distance of 2·531 Å is rather short for a hydrogen bond, although hydrogen bonds this short have been observed. A more important reason for ruling out the last case is that a nearly linear water molecule would result if one accepts the O_3–O_1 contact as a hydrogen bond.

Within the layers, each zirconium atom is in contact with four sulphate groups, and each sulphate group is in contact with two zirconium atoms. Also, each zirconium atom is in contact with four water molecules, and each water molecule is in contact with one zirconium atom. The sulphate oxygen atoms that are not in contact with zirconium atoms are linked to water molecules via hydrogen bonds. A view of one of these layers, as seen along the *a* axis, is shown in Fig. 3.

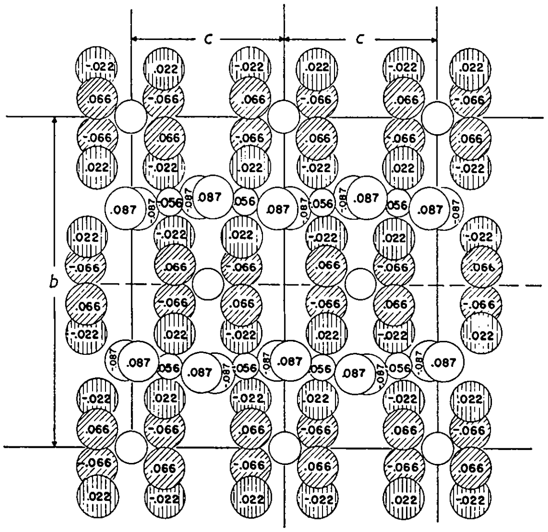

Fig. 3. The layer centered at $x=0$ as viewed along the *a* axis. The designation of the atoms is the same as in Fig. 2.

This structure is closely related to the structure of $U(SO_4)_2 . 4\,H_2O$ in space group *Pnma* (Kierkegaard, 1956) as one might expect from the similarity of the lattice constants. The *Pnma* structure can be derived from the *Fddd* structure by the following operations. The asymmetric units of the structure, as outlined by the dotted line in Fig. 2, are alternately rotated about the twofold screw axes by $+22\frac{1}{2}°$ and $-22\frac{1}{2}°$ within each layer. Then, alternate layers are shifted by $\frac{1}{4}b$. These operations halve the unit cell and result in the somewhat puckered layers of the *Pnma* form. The O_1 atoms become Kierkegaard's O_3 and O_4 atoms, the O_2 and O_3 atoms of the lower square faces of the antiprisms become his O_2, O_5 and O_6 atoms, and the

O_2 and O_3 atoms of the upper square faces of the antiprisms become his O_1 and O_7 atoms.

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The Crystal Structure of $MoCl_5$*

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$MoCl_5$ has the $NbCl_5$ type structure. The crystal system is monoclinic with

$$a=17{\cdot}31,\quad b=17{\cdot}81,\quad c=6{\cdot}079\ \text{Å},\quad \beta=95{\cdot}7^\circ.$$

The space group is $C2/m$, and there are 12 $MoCl_5$ units in the unit cell. The structure consists of dimers (Mo_2Cl_{10}) with the chlorine atoms forming two octahedra which share a common edge. The molybdenum atoms occupy the centers of the octahedra and are joined by two chlorine bridge bonds. The Mo–Cl bridge bond length is 2·53 Å; the Mo–Cl non-bridge bond length is 2·24 Å.

Introduction

The structural unit of $MoCl_5$ in the vapor phase, determined by electron diffraction (Ewens & Lister, 1938), is the trigonal bipyramid. The trigonal bipyramid unit is also present in gaseous $NbCl_5$ (Skinner & Sutton, 1940); however, solid $NbCl_5$ consists of Nb_2Cl_{10} dimers (Zalkin & Sands, 1958). Measurements of the Trouton constants of the niobium and tantalum pentahalides (Fairbrother & Frith, 1951), and of the electrical conductivities of NbF_5 and TaF_5 (Fairbrother, Frith & Woolf, 1954) suggest dimerization in these compounds in the liquid state.

Vapor density measurements by Debray (Remy, 1956) at 350 °C. support the molecular formula $MoCl_5$ in the gaseous state. Mesnage (1939) found two spectra for $MoCl_5$, *A* occurring between 100 and 200 °C., and *B* above 300 °C.; the transition from *A* to *B* is attributed to depolymerization.

Experimental

The molybdenum pentachloride was obtained from the Climax Molybdenum Company. Samples of the extremely hygroscopic, bluish-black powder were transferred in an argon-filled dry box to 0·3 mm. quartz capillaries. Crystals suitable for diffraction studies were grown by heating the capillaries to about 230 °C. and cooling over a period of several hours to room temperature.

X-ray measurements revealed that single crystals of at least three phases were obtained by this technique. The $MoCl_5$ was identified by color, density, melting point, and the similarity of the X-ray patterns to $NbCl_5$; a specimen of this material was selected for the structural investigation. The other materials present were believed to be oxychlorides.

Oscillation, Weissenberg, and precession photographs, using Cu $K\alpha$ radiation ($\lambda=1{\cdot}5418$ Å) show a monoclinic unit cell with:

$$a=17{\cdot}31\pm0{\cdot}01,\quad b=17{\cdot}81\pm0{\cdot}01,\quad c=6{\cdot}079\pm0{\cdot}005\ \text{Å};\quad \beta=95{\cdot}7\pm0{\cdot}1^\circ.$$

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