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The Crystal Structure of Tutton's Salts. I. Zinc Ammonium Sulfate Hexahydrate

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Zinc ammonium sulfate hexahydrate $Zn(NH_4)_2(SO_4)_2.6H_2O$ (a Tutton salt) is monoclinic:

$$a=9{\cdot}28,\ b=12{\cdot}57,\ c=6{\cdot}25\ \text{Å},\ \beta=106{\cdot}8^\circ,$$

space group $P2_1/a$, two molecules per unit cell. The atomic positions have been determined by three-dimensional Fourier and least-squares refinement of X-ray diffraction data. The zinc ion lies at a centre of symmetry surrounded by a slightly distorted octahedron of water molecules, ($Zn–H_2O$ 2·12 Å and 2·07 Å) and the sulfate ion (S–O 1·48 Å, O–S–O 109·4°) is bonded to the water molecules of the hexa-aquozinc ion by a series of hydrogen bonds varying in length from 2·72 Å to 2·85 Å.

Introduction

As part of a series of studies of octahedral arrangements of ligands about metals of the first transition group, a study has been begun on the double salts of ammonium sulfate with divalent transition metal sulfates (Tutton's salts). These salts were examined crystallographically by Hofmann (1931), but in the light of recent theoretical developments it has become of interest to investigate in detail the actual bond lengths and angles in the coordination polyhedra of the transition elements. The isomorphous Tutton salts, which have an octahedral arrangement of water molecules about the metal ion, should prove an excellent source of comparisons. This investigation reports the results for zinc ammonium sulfate hexahydrate, which was the first salt of this series to be examined in detail.

Experimental

Crystals of zinc ammonium sulfate hexahydrate in a rod-like habit elongated in the *c* axis direction were obtained by quick cooling of a water solution of the salt. Individual crystals were grown to a suitable size in a slowly evaporating solution. The cell dimensions were determined from rotation and zero-level Weissenberg photographs (Cu $K\alpha$ radiation) about the *c* axis, with superimposed reflections from sodium chloride ($a_0=5{\cdot}6387$ Å) for calibration. The angle β was measured from the a^*c^* net precession photograph (Mo $K\alpha$ radiation). The results are:

$$a=9{\cdot}27_9\pm0{\cdot}012,\ b=12{\cdot}56_8\pm0{\cdot}015,\ c=6{\cdot}25_3\pm0{\cdot}005\ \text{Å},$$
$$\beta=106^\circ\ 49'\pm6',\ Z=2\ .$$

Systematic absences (*h*0*l* absent when *h* is odd and 0*k*0 absent when *k* is odd) indicate the space group $P2_1/a$. This confirms Hofmann's data:

$$a=9{\cdot}205,\ b=12{\cdot}475,\ c=6{\cdot}227\ \text{kX},\ \beta=106^\circ\ 52'.$$

Intensities were obtained from five levels (*hk*0 through *hk*4) on a Nonius integrating Weissenberg camera, integrating in one direction only. The diffraction patterns were recorded by the multiple film technique (Kodak medical X-ray film) and the intensities were measured by a microphotometer of the Moll type, whose output was fed into a Leeds & Northrup recorder equipped with a logarithmic slide wire. The intensity of each reflection was taken to be proportional to the area under the photometer tracing. Intensities were corrected for Lorentz and polarization factors in the usual manner. In all, 1066 reflections were used, of which 206 had intensities less than the minimum observed value. The intensities of the remainder varied from 1 to 450.

The observed intensities were corrected for absorption essentially by the method of Bond (1959), programmed for the IBM 709. The crystal was of a regular hexagonal cross section, the diagonals of which did not differ by more than 0·02 mm. Accordingly it was treated as a cylinder ($\mu=61{\cdot}52$ cm^{-1} and $\mu R=0{\cdot}83$) and a correction was applied to each reflection from Bond's table.

All calculations except the final least-squares refinement were made with an IBM 650 computer (Brown, Lingafelter, Stewart & Jensen, 1959). The least-squares refinement was carried out with the Busing & Levy full-matrix program with a 704 simulator on an IBM 709.

Scattering factors for zinc were from Thomas & Umeda (1957) and for all other atoms from Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955).

Determination and refinement of the structure

The space group requires that the zinc atoms be at 0, 0, 0 and $\frac{1}{2}, \frac{1}{2}, 0$ and it was assumed that the other atoms were in the fourfold positions for the space group. The original parameters given by Hofmann for the magnesium salt were modified for the sulfate oxygen atoms to allow for a more reasonable value of the S–O bond distance (1·5 in place of 1·6 Å) and a series of electron-density projections on [001] were calculated. The refinement did not proceed readily below an R value of 0·25. The Hofmann parameters were therefore abandoned and a three-dimensional Patterson function calculated. From this, the position of sulfur (coincident with Hofmann's) was deduced. A three-dimensional Fourier synthesis was calculated with the use of phases determined only by the zinc and sulfur atoms. All atoms were located in this summation, but two (N and O(6)), which had low electron densities, were omitted from the next calculation. Two calculations were made — one using the measured intensities and one using intensities corrected for absorption. Agreement in the latter case was moderately better, and the uncorrected intensities were not used again. After the

Table 1. *Final atomic coordinates*

		$\sigma_x \times 10^4$	x/a	$\sigma_y \times 10^4$	y/b	$\sigma_z \times 10^4$	z/c
	Zn(1)		0·000		0·000		0·000
	S(2)	2·2	0·4073	1·5	0·1372	4·5	0·7400
	O(3)	8·1	0·4120	5·2	0·2278	13·1	0·5917
	O(4)	8·0	0·5476	6·1	0·0768	15·9	0·7853
	O(5)	6·7	0·2794	5·0	0·0671	13·1	0·6240
	O(6)	7·8	0·3857	5·3	0·1778	13·4	0·9489
	O(7)	6·8	0·1723	4·9	0·1080	12·2	0·1683
	O(8)	6·7	−0·1629	4·7	0·1113	13·1	0·0351
	O(9)	7·1	−0·0007	4·9	−0·0676	12·5	0·3024
	N(10)	9·4	0·1366	6·7	0·3454	17·8	0·3605
N	H(11)		0·050		0·302		0·227
	H(12)		0·203		0·298		0·354
	H(13)		0·101		0·380		0·397
	H(14)		0·144		0·418		0·307
O(7)	H(15)		0·173		0·096		0·290
	H(16)		0·239		0·137		0·095
O(8)	H(17)		−0·243		0·093		−0·020
	H(18)		−0·145		0·189		0·040
O(9)	H(19)		−0·099		−0·037		0·350
	H(20)		0·017		−0·171		0·339

Table 2

(*a*) Anisotropic temperature parameters (× 10²)

	β^{11}	β^{22}	β^{33}	β^{12}	β^{13}	β^{23}
Zn(1)	0·358	0·217	1·63	−0·019	0·057	0·019
S(2)	0·172	0·121	1·62	−0·034	−0·008	−0·013
O(3)	0·975	0·220	2·15	−0·186	0·502	0·105
O(4)	0·449	0·388	3·97	0·130	0·135	−0·154
O(5)	0·268	0·239	2·64	−0·145	0·110	−0·043
O(6)	0·828	0·263	1·99	−0·090	0·184	−0·264
O(7)	0·432	0·305	1·30	−0·157	0·069	−0·127
O(8)	0·318	0·208	2·50	−0·009	0·309	−0·062
O(9)	0·534	0·210	1·77	0·025	0·082	0·130
N(10)	0·498	0·285	2·59	0·129	−0·246	0·132
*H(11)	0·792	0·396	1·74	0·000	0·340	0·000
H(15)	0·634	0·317	1·40	0·000	0·272	0·000

(*b*) Standard deviations of temperature factors (× 10⁴)

	β^{11}	β^{22}	β^{33}	β^{12}	β^{13}	β^{23}
Zn(1)	1·67	0·8	6·9	0·9	2·5	1·7
S(2)	2·2	1·0	10·8	1·2	3·5	2·3
O(3)	10·0	3·9	30·4	4·9	13·4	7·9
O(4)	8·9	4·9	37·6	5·2	14·0	10·0
O(5)	7·6	3·8	31·3	4·0	11·6	7·7
O(6)	9·4	4·2	33·3	4·9	13·8	8·4
O(7)	7·8	4·1	27·6	4·3	11·0	7·2
O(8)	7·3	3·8	31·0	3·9	11·4	7·4
O(9)	8·5	3·7	30·0	4·3	11·8	7·1
N(10)	10·5	5·4	39·6	5·8	15·8	10·7

* Isotropic T.F. in anisotropic form. Not refined.

Table 3. *Observed and calculated structure factors*

(× 10)

Columns are k, $10F_o$ and $10F_c$. Unobserved reflections are marked * and extinctions with an E

0,K,0		
2	426E	537
4	539E	-635
6	88	77
8	406	371
10	133	88
12	200	186
14	348	381
16	237	241
1,K,0		
1	228	206
2	366	-416
3	651E	1204
4	44*	-21
5	194	192
6	84	-56
7	142	148
8	65*	-7
9	365	351
10	124	-44
11	441	465
12	159	138
13	70*	34
14	61*	59
15	52	65
2,K,0		
0	548E	770
1	473E	582
2	376	412
3	192	-165
4	470	542
5	234	-216
6	388	389
7	63*	-29
8	294	249
9	263	237
10	97	116
11	76*	29
12	223	214
13	184	-177
14	313	318
15	47*	-20
3,K,0		
1	453	497
2	207	-176
3	417	403
4	523	585
5	592E	712
6	220	188
7	319	303
8	174	-165
9	123	-100
10	321	-328
11	131	129
12	153	129
13	338	354
14	58	68
15	227	251
4,K,0		
0	95	-61
1	326	306
2	690E	904
3	251	-211
4	674E	775
5	368	-360
6	104	-72
7	78	-70
8	125	-106
9	309	293
10	322	292
11	74*	63
12	290	297
13	114	-101
14	180	198
5,K,0		
1	675E	820
2	118	-124
3	259	-206
4	110	89
5	239	196
6	109	102
7	494	495
8	76*	-67
9	322	326
10	122	-104
11	70*	26
12	94	104
13	210	216
6,K,0		
0	214	222
1	209	-156
2	507	529
3	70*	-27
4	321	267
5	98	78
6	94	94
7	76*	63
8	108	127
9	74*	14
10	383	384
11	63*	-30
12	215	216
13	42*	-21
7,K,0		
1	552	628
2	368	331
3	205	207
4	80	-57
5	77	21
6	84	-76
7	152	115
8	83	64
9	248	249
10	65	56
11	53*	44
12	147	-134
8,K,0		
0	255	268
1	332	-317
2	206	206
3	188	-182
4	764	258
5	111	96
6	313	417
7	69*	19
8	91	78
9	161	-129
10	62	66
11	116	133
9,K,0		
1	72*	65
2	328	274
3	426	401
4	68*	-38
5	285	263
6	172	-125
7	63	47
8	90	70
9	84	91
10,K,0		
0	352	313
1	61*	-49
2	122	145
3	57*	25
4	82	137
5	128	105
6	238	221
7	39	33
11,K,0		
1	190	243
2	59	-80
3	304	254
0,K,1		
0	161E	557
1	456	536
2	443	532
3	414	438
4	44*	43
5	300	255
6	451	523
7	62*	55
8	390	391
9	73*	88
10	457	496
11	294	-240
12	192	192
13	301	-304
14	62*	-29
15	80	99
1,K,1		
1	575E	869
2	380	-427
3	41*	39
4	396	417
5	383	402
6	323	345
7	473	510
8	170	-155
9	372	379
10	166	-149
11	82	-75
12	76*	31
13	297	302
15	196	226
14	61*	29
-1,K,1		
1	302	291
2	453E	-601
3	493E	657
4	265	-264
5	255	207
6	279	255
7	274	258
8	220	208
9	547	627
10	323	-299
11	319	304
12	151	156
13	106	109
14	80	71
15	50*	-2
2,K,1		
0	500	-567
1	526E	643
2	595E	836
3	495	537
4	676E	935
5	390	-370
6	211	204
7	67*	18
8	140	-110
9	76*	-12
10	384	381
11	76*	-17
12	361	376
13	68*	8
14	72	69
15	44*	-15
-2,K,1		
0	716E	1325
1	317	302
2	273	280
3	299	282
4	47*	39
5	394	357
6	547	628
7	349	-294
8	424	436
9	77	59
10	77*	-6
11	72*	-62
12	164	141
13	203	-172
14	326	342
15	87	96
3,K,1		
1	182	169
2	203	171
3	54*	-5
4	228	190
5	640	731
6	66*	-44
7	661	745
8	225	-214
9	281	276
10	192	191
11	77*	-18
12	72*	-43
13	195	201
14	52*	-41
15	198	225
-3,K,1		
1	205	-166
2	468	523
3	720E	1122
4	248	217
5	551	648
6	72	-56
7	94	-72
8	72*	37
9	112	73
10	190	-173
11	485	531
12	75*	41
13	165	163
14	96	-97
4,K,1		
0	219	223
1	180	-136
2	542	545
3	362	353
4	503	497
5	326	297
6	75	89
7	140	141
8	166	162
9	285	-286
10	294	275
11	139	-150
12	300	308
13	77	88
14	96	118
-4,K,1		
0	130	109
1	178	154
2	68	-24
3	274	258
4	437	501
5	316	291
6	558	631
7	106	-85
8	583	659
9	223	-210
10	78*	11
11	77*	-53
12	71*	38
13	67	52
14	273	299
5,K,1		
1	424	446
2	395	357
3	274	263
4	190	-168
5	218	197
6	76*	-35
7	316	299
8	173	151
9	282	273
10	78	66
11	222	220
12	245	-257
13	48*	34
-5,K,1		
1	459	525
2	183	146
3	349	310
4	151	-123
5	288	271
6	283	-236
7	273	249
8	118	96
9	104	84
10	241	212
11	370	378
12	147	-131
13	115	126
14	98	-103
6,K,1		
0	629	667
1	475	-491
2	234	219
3	316	-279
4	80	81
5	337	308
6	220	197
7	90	85
8	378	385
9	171	-142
10	164	185
11	60*	4
12	106	172
-6,K,1		
0	353	348
1	224	-172
2	367	352
3	70*	-50
4	378	366
5	282	252
6	76*	37
7	284	268
8	319	316
9	324	-292
10	362	350
11	133	-122
12	98	85
13	101	110
7,K,1		
1	77*	-34
2	376	364
3	421	408
4	78*	35
5	317	321
6	81	-41
7	197	240
8	77	94
9	222	220
10	57*	-63
11	246	273
-7,K,1		
1	506	566
2	273	246
3	76*	-13
4	162	146
5	77*	31
6	78*	-4
7	471	454
8	76*	-6
9	274	266
10	66*	24
11	58*	90
12	249	-264
8,K,1		
0	474	462
1	89	93
2	161	172
3	165	109
4	92	133
5	84	86
6	271	253
7	68	-77
8	205	204
9	51*	-22
10	67	33
-8,K,1		
0	184	-138
1	116	-94
2	189	170
3	78*	-14
4	473	463
5	78*	-4
6	276	292
7	73*	53
8	68*	91
9	93	-73
10	295	304
9,K,1		
3	348	354
4	168	163
5	245	252
6	55*	16
7	49*	40
8	136	-133
-9,K,1		
1	311	268
2	76*	43
3	163	206
4	77	54
5	191	185
6	71	57
7	237	215
8	107	-93
9	106	113
-10,K,1		
0	67*	48
1	158	129
2	184	173
3	181	158
4	267	259
5	132	-86
6	222	251
7	60	-52
8	36*	17
-11,K,1		
1	85	100
2	99	-61
3	162	162
4	122	115
5	169	167
0,K,2		
0	78	-60
1	265	-272
2	119	122
3	297	-300
4	567E	796
5	360	-364
6	405	444
7	303	280
8	197	192
9	74*	7
10	427	462
11	77*	-38
12	280	268
13	70	90
14	116	-110
1,K,2		
0	37*	-1
1	252	257
2	65	-50
3	276	277
4	51*	-11
5	282	264
6	281	-284
7	576E	684
8	75	-54
9	353	352
10	314	344
11	108	114
12	90	-86
13	97	91
14	72	-64
15	230	250
-1,K,2		
0	12*	0
1	594E	1084
2	497E	-750
3	136	118
4	277	-252
5	95	-56
6	410	438
7	461	522
8	69*	-52
9	339	343
10	76*	-44
11	77*	-45
12	74*	-43
13	256	288
14	101	100
15	279	293
2,K,2		
0	278	275
1	215	186
2	163	138
3	291	270
4	505	593
5	254	234
6	349	362
7	69*	-57
8	338	334
9	359	-375
10	189	172
11	75*	50
12	204	213
13	235	262
14	140	146
15	128	-120
-2,K,2		
0	382	-407
1	241	-210
2	294	341
3	256	258
4	495E	619
5	218	-214
6	484	553
7	65*	-49
8	255	251
9	259	240
10	411	449
11	77*	-46
12	218	200
13	210	-213
14	80	-60
15	69	60
3,K,2		
1	313	301
2	311	301
3	428	450
4	295	-271
5	347	359
6	470	-533
7	193	172
8	196	192
9	141	129
10	310	316
11	350	381
12	66*	-21
13	83	92
14	81	-90
-3,K,2		
1	241	239
2	112	81
3	307	330
4	237	-205
5	474	532
6	136	113
7	324	309
8	227	-198
9	354	353
10	155	-137
11	181	166
12	273	279
13	225	230
14	146	146
4,K,2		
0	346	340
1	267	-262
2	205	207
3	329	-324
4	170	150
5	310	288
6	348	345
7	76*	-30
8	494	561
9	134	-116
10	138	141
11	68*	50
12	59*	38
13	108	115
-4,K,2		
0	148	148
1	113	87
2	407	458
3	65	64
4	195	176
5	340	-312
6	484	545
7	387	-381
8	406	400
9	322	313
10	77*	58
11	261	243
12	98	89
13	107	-97
14	234	251
5,K,2		
1	70*	20
2	153	-143
3	376	352
4	183	-171
5	415	457
6	77*	65
7	170	204
8	237	238
9	216	212
10	101	-102
11	303	332
12	50*	-28
-5,K,2		
1	183	190
2	132	108
3	471	508
4	173	151
5	483	517
6	70*	16
7	120	-93
8	76*	-47
9	241	227
10	181	-137
11	384	386
12	96	82
13	118	113
6,K,2		
0	444	458
1	76*	44
2	300	301
3	76*	-8
4	77*	46
5	77*	21
6	278	260
7	74*	-26
8	279	297
9	98	101
10	103	113
11	89	-75
-6,K,2		
0	377	373
1	66*	-13
2	200	176
3	353	-351
4	70*	-41
5	72*	15
6	447	452
7	145	117
8	531	624
9	76*	38
10	76	100
11	66*	-46
12	60	22
7,K,2		
1	77*	82
2	279	-282
3	288	293
4	75*	-36
5	299	301
6	91	69
7	130	157
8	108	-101
9	188	210
10	44*	-34
-7,K,2		
1	153	137
2	181	-179
3	358	337
4	75*	-33
5	322	297
6	148	-129
7	140	156
8	139	122
9	240	235
10	69	62
11	301	295
12	86	-76
8,K,2		
2	127	166
3	207	189
4	155	149
5	265	-254
6	223	267
7	108	-99
8	127	164
9	189	164
-8,K,2		
0	370	387
1	177	-130
2	232	214
3	314	-296
4	228	219
5	133	81
6	148	123
7	132	126
8	173	189
9	152	-121
10	168	167
-9,K,2		
1	160	177
2	307	280
3	160	165
4	73*	82
5	215	206
6	219	-187
7	358	356
8	57*	10
9	121	116
10	88	75
-10,K,2		
0	71	-71
1	111	-77
2	133	133
3	65*	-31
4	354	370
5	59*	-8
6	136	161
7	63	-73
-11,K,2		
1	173	186
2	51*	29
3	49*	72
4	105	-103
5	76	115
0,K,3		
0	646E	832
1	166	-137
2	326	332
3	447	-477
4	236	226
5	344	351
6	356	365
7	181	152
8	182	151
9	260	-242
10	75	66
11	69*	3
12	213	203
13	194	178
14	191	206
1,K,3		
1	449	536
2	300	292
3	493	535
4	53*	1
5	259	245
6	456	-500
7	169	-145
8	123	111
9	188	179
10	228	198
11	328	332
12	62*	-17
13	167	170
14	67	-53
-1,K,3		
1	271	299
2	33*	-7
3	485	566
4	51	47
5	180	174
6	134	-130
7	340	327
8	257	253
9	258	221
10	71*	7
11	96	98
12	206	-209
13	153	158
14	89	-79
2,K,3		
0	348	377
1	158	116
2	394	412
3	129	-98
4	57*	-31
5	66	-62
6	375	357
7	136	-121
8	475	507
9	71*	-20
10	107	113
11	176	165
12	58*	4
13	104	102
14	213	224
-2,K,3		
0	398	412
1	341	-343
2	206	192
3	494	-586
4	553E	665
5	53*	-32
6	211	213
7	140	138
8	68*	1
9	75	45
10	302	279
11	70*	38
12	319	320
13	98	77
14	45*	37
3,K,3		
1	421	422
2	61*	-30
3	352	302
4	83	71
5	361	373
6	73	63
7	106	-82
8	92	-64
9	128	114
10	66*	-45
11	339	354
12	67	64
-3,K,3		
1	586E	755
2	160	142
3	214	193
4	71	-32
5	55*	-10
6	61*	4
7	434	445
8	103	-83
9	109	69
10	71*	-8
11	69*	17
12	98	82
13	223	221
14	43*	-3
4,K,3		
0	293	278
1	66*	40
2	410	423
3	68*	41
4	165	164
5	236	-226
6	222	204
7	71*	24
8	223	226
9	208	214
10	65	61
11	60	-67
12	46	53
-4,K,3		
0	244	277
1	84	73
2	436	446
3	374	365
4	517	555
5	260	-231
6	128	-96
7	246	-208
8	70*	45
9	175	146
10	364	365
11	122	109
12	239	241
13	115	-97
14	61	64
5,K,3		
1	297	282
2	461	-476
3	271	275
4	172	-158
5	260	251
6	319	300
7	97	98
8	84	-69
9	93	91
10	93	-88
11	130	146
-5,K,3		
1	406	349
2	56*	2
3	58*	22
4	61*	-26
5	319	291
6	175	145
7	443	449
8	224	-213
9	187	162
10	76	-58
11	106	115
12	151	137
13	112	111
6,K,3		
2	171	163
3	174	157
4	312	304
5	181	-153
6	219	245
7	61*	-19
8	99	102
9	157	141
10	153	168
-6,K,3		
0	384	383
1	62*	-59
2	431	453
3	84	-42
4	202	178
5	363	-338
6	115	98
7	72*	-6
8	172	150
9	242	213
10	140	174
11	73	63
12	126	124
13	104	-98
7,K,3		
7	210	211
8	49	-54
-7,K,3		
1	186	200
2	348	-318
3	382	372
4	71*	-9
5	336	326
6	261	252
7	74	-45
8	67*	-14
9	123	123
10	99	-95
11	235	224
12	61	-64
-8,K,3		
0	445	443
1	71*	25
2	250	263
3	71*	-28
4	121	-46
5	70*	-25
6	308	278
7	88	70
8	252	218
9	56*	2
10	45*	31
11	75	-24
-9,K,3		
1	70*	59
2	70*	-33
3	375	350
4	71	-44
5	274	260
6	134	-117
7	66	3
8	51*	-1
9	189	185
10	111	95
-10,K,3		
0	385	389
1	62*	26
2	233	228
3	60*	-10
4	57*	44
5	64	43
6	148	129
7	66	-82
-11,K,3		
1	177	177
2	205	169
3	137	141
4	41*	-13
5	119	108
0,K,4		
0	381	418
1	80	71
2	300	295
3	127	132
4	70*	-14
5	100	-91
6	347	339
7	107	74
8	347	356
9	88*	-22
10	115	120
11	78*	-27
12	65*	58
13	53*	-18
1,K,4		
1	334	334
2	67*	28
3	279	248
4	373	359
5	251	233
6	225	219
7	105	86
8	289	-280
9	189	204
10	109	-90
11	260	291
12	63*	-5
13	92	85
-1,K,4		
1	33*	-28
2	55	59
3	449	572
4	65*	-14
5	417	460
6	79*	-14
7	84*	-23
8	93	71
9	178	179
10	86*	10
11	213	201
12	157	-148
13	216	196
2,K,4		
0	452	465
1	281	247
2	377	357
3	271	245
4	134	127
5	359	-352
6	87*	27
7	89*	2
8	250	269
9	197	206
10	176	179
11	68*	-29
12	87	93
-2,K,4		
0	407	523
1	165	-218
2	307	361
3	142	-146
4	64*	83
5	347	373
6	341	381
7	96	91
8	96	59
9	201	-208
10	86*	19
11	84	-73
12	190	196
13	60	57
3,K,4		
1	314	294
2	214	-190
3	127	140
4	109	92
5	188	191
6	266	254
7	290	284
8	179	-161
9	114	119
10	135	-119
11	152	157
12	93	89
-3,K,4		
1	79	101
2	350	433
3	331	368
4	67*	32
5	291	295
6	160	-153
7	167	177
8	176	176
9	275	301
10	86*	-34
11	114	113
12	162	-161
13	124	130
4,K,4		
2	147	140
3	93	86
4	456	480
5	88*	7
6	166	193
7	83*	11
8	81	69
9	101	88
10	156	159
11	76	-80
-4,K,4		
0	299	325
1	58*	-12
2	306	322
3	67*	-47
4	207	196
5	253	254
6	127	124
7	135	-125
8	176	175
9	142	-136
10	238	265
11	76*	19
12	194	201
13	107	91
5,K,4		
3	143	153
4	85*	42
5	102	97
6	83	62
7	250	260
-5,K,4		
1	442	540
2	178	176
3	76*	-15
4	79*	26
5	83*	72
6	152	-147
7	334	357
8	88*	38
9	185	189
10	79*	11
11	72*	51
12	57*	47
13	92	89
-6,K,4		
0	77*	83
1	177	164
2	318	304
3	179	152
4	420	456
5	96	98
6	88*	-49
7	98*	-3
8	86*	61
9	81*	-49
10	238	238
11	117	-105
12	189	191
-7,K,4		
1	250	209
2	225	-201
3	87*	41
4	102	77
5	215	236
6	157	149
7	379	397
8	83*	-18
9	73*	65
10	105	-102
-8,K,4		
0	93	87
1	106	87
2	172	165
3	93	56
4	341	344
5	139	-120
6	106	122
7	77*	58
8	72*	69
9	81	56
10	118	106
-9,K,4		
1	182	183
2	153	-128
3	252	250
4	79*	52
5	102	107
6	147	130
7	65*	54
8	93	-70
9	75	83
-10,K,4		
0	329	319
1	134	117
2	86	104
3	221	222
4	66*	-9
5	62*	-30
6	217	203
7	56	-50
-11,K,4		
1	54*	67
2	52*	46
3	242	218

third Fourier summation ($R=0\cdot16$) a change was made to the least-squares program of refinement in order to allow for use of anisotropic temperature factors. A modified Hughes weighting scheme was used, with $w=0$ for unobserved reflections for which $F_c<F_{\min}$, $w=1$ for unobserved reflections where $F_c>F_{\min}$, $w=1$ for observed reflections for which $f_o<30$ and $w=30/F_o$ for $F_o>30$. The function minimized was $\Sigma w(F_o-F_c)^2$. After four cycles of least-squares refinement, parameters were selected, the bond lengths and angles calculated and estimates of the accuracy were made. At this stage R was 0·10 for 1066 reflections. A three-dimensional F_o-F_c synthesis based on these parameters was calculated and a self consistent set of hydrogen atomic positions were taken from this summation. Refinement was then continued but each hydrogen atom was given an averaged isotropic temperature factor (which was not refined) to correspond to the type of atom to which it was joined. After five further cycles, the changes in parameters were insignificant and a final selection of parameters was made (Tables 1 and 2). The R value (including hydrogen atoms) was 0·085 and the final values of calculated and observed structure factors are given in Table 3. No great accuracy can be claimed for the hydrogen parameters, and their bond lengths and angles are not listed.

The average shifts in the final cycle were $\overline{\delta x}=0\cdot000002$, $\overline{\delta y}=0\cdot0000013$, $\overline{\delta z}=0\cdot000056$, and the maximum shifts (for nitrogen) were $\delta x=0\cdot000085$, $\delta y=0\cdot000055$, $\delta z=0\cdot00030$.

Discussion

The main points of interest are the regularity and dimensions of the zinc coordination polyhedron. Bond lengths and angles are given in Table 4. The water molecules are arranged in a nearly regular octahedron about the zinc ion, the Zn–O bonds are of the expected length and the angles do not differ significantly from 90°. The S–O bond distances of 1·48 Å, and the O–S–O bond angles of 109·4°, are also normal.

Table 4. *Bond lengths and angles with estimated standard deviation in parenthesis for each bond type*

Bond length (Å)			Bond angle (°)		
Zn–O(7)	2·129	(0·012)	O(9)–Zn–O(7)	89·1	(0·04)
Zn–O(8)	2·117		O(8)–Zn–O(7)	90·6	
Zn–O(9)	2·075		O(8)–Zn–O(9)	89·2	
S–O(3)	1·477	(0·015)	O(3)–S–O(4)	109·6	(0·6)
S–O(4)	1·462		O(3)–S–O(5)	108·3	
S–O(5)	1·488		O(3)–S–O(6)	109·1	
S–O(6)	1·469		O(4)–S–O(5)	109·1	
			O(4)–S–O(6)	110·5	
			O(5)–S–O(6)	110·1	

The length of the equatorial Zn–O bonds, 2·123 Å is, within limits, the sum of the ionic radii of zinc and oxygen (Pauling, 1960). The axial bond Zn–O(9) (Fig. 1) is shorter by 0·048 Å, which is four times the standard deviation. It is possible that this shortening is a consequence of the rather close approach of atoms O(9) and O(9′). Other measurements of the Zn–H_2O bond in the hexa-aquo ion give 2·08 Å (Broomhead & Nicol, 1948) and 2·09 Å (Hargreaves, 1957). In dihydrate salts of zinc, two Zn–H_2O values are available: 2·06 Å (Klug, Alexander & Sumner, 1958) and 2·14 Å (van Niekerk, Schoening & Talbot, 1953). The hexa-aquo ion is joined to the sulfate groups by a series of hydrogen bonds, two for each water molecule (Table 5).

The structure given by Hofmann is almost the same as that given above, with the exception that the water octahedron and the sulfate tetrahedron are both tilted considerably (about 20°) relative to the

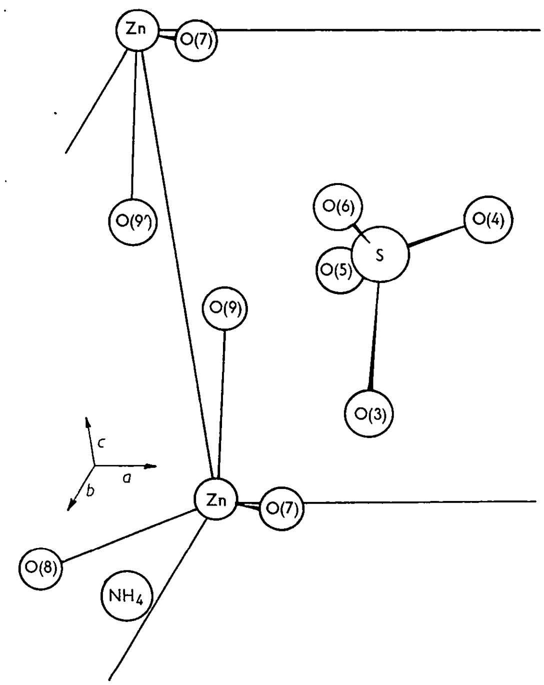

Fig. 1. Numbering of atoms.

Table 5. *Intermolecular distances*

Bond	Relative position of second atom*			Bond length (Å)
O(5)–O(7)	x,	y,	z	2·781 (0·027)
O(6)–O(7)	x,	y,	$z+1$	2·854
O(4)–O(8)	$x+1$	y,	$z+1$	2·723
O(6)–O(8)	$x+\frac{1}{2}$	$\frac{1}{2}-y$	$z+1$	2·768
O(3)–O(9′)	$x+\frac{1}{2}$	$\frac{1}{2}-y$	$z+1$	2·723
O(5)–O(9′)	x,	y	$z+1$	2·755
O(9)–O(9′)	x,	y	$z+1$	2·996
O(3)–N(10)	x,	y,	z	2·944

* This is the transformation relating each 'second atom' to the corresponding atom in the original asymmetric unit. O(9′) is −O(9).

present structure. Calculations based on data collected for the magnesium salt in this Laboratory (Montgomery & Lingafelter, to be published) and an independent structure determination by Margulis & Templeton (1962) show that the structure of this salt is essentially identical with the zinc compound.

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The Interpretation of Pseudo-Orthorhombic Diffraction Patterns

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Diffraction diagrams with pseudo-orthorhombic Laue symmetry may be produced by monoclinic crystals as a result of twinning. In such cases, the systematic absences often follow selection rules that are not characteristic of any orthorhombic space group. Various examples are discussed. In particular, it is shown that the absences may follow pseudo-selection rules. Monoclinic structures in which the projections down three mutually perpendicular axes have perfect rectangular symmetry constitute a special class of pseudo-orthorhombic structures and are said to be para-orthorhombic. The systematic absences and Laue symmetries of para-orthorhombic structures are discussed and examples are given.

Introduction

During the last few years, five crystals examined in the author's laboratory have been found to give X-ray photographs with *mmm* symmetry but with systematic absences that do not correspond to any orthorhombic space group. Crystallographic data are given in Table 1. More detailed examination has shown that each of these crystals is in fact monoclinic with all interaxial angles of a non-primitive unit cell exactly 90°. As we shall see, the unusual features of the X-ray diagrams are sometimes due simply to twinning, but it is sometimes necessary to invoke special 'para-orthorhombic' relationships between different sets of representative points in the monoclinic structures as well.

Table 1. *Crystallographic data for five pseudo-orthorhombic crystals*

I. 1-Anilino-4-chloropyromellitic acid diphenylimide,

$C_{24}H_{16}N_3O_4Cl$	
$a = 14·7$ Å	(1) $hkl = h+k=2n$
$b = 12·3$	(2) $hk0: h=2n\ (k=2n)$
$c = 26·6$	(3) hkl : if $h, k=2n$, $h+k+2l=4n$
$Z = 8$	

II. Cycloundecylamine hydrobromide, $C_{11}H_{21}NH_3{}^+Br^-$

$a = 65$ Å	(1) $hkl : h+k=2n$
$b = 9·75$	(2) $hk0 : h=2n\ (k=2n)$, $h+k=4n$
$c = 8·15$	(3) $h0l : h=4n$
	(4) $0kl : k=4n$, $l=2n$
$Z = 16$	(5) hkl : if $h, k=2n$, $h+k=4n$
	(6) All reflexions with h, k odd are weak