Cu–Cl distance of 3·05 Å in dichlorodipyridinecopper-(II) (Dunitz, 1957).

The crystal structure determination thus agrees well with the results of the spectroscopic investigations cited before. The Cu–Cl, Cu–Br and Cu–N bond lengths are all slightly shorter than the values reported for distorted octahedral coordination (see Table 7). This may be due to stronger Cu–Cl, Cu–Br and Cu–N bonds in the square planar coordination. The carbon-to-carbon and carbon-to-nitrogen bond distances found for the dimethylpyridine ring agree well with previous reported values (Dunitz, 1957; *International Tables for X-ray Crystallography*, 1962).

The authors are indebted to Dr W. Ludwig, Institut für anorganische Chemie, University of Zürich, for samples of dichlorobis-(2,3-dimethylpyridine)copper (II) and dibromobis-(2,3-dimethylpyridine)copper(II).

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The Crystal Chemistry of Zirconium Sulphates. IX. The Structure of $K_2[Zr(SO_4)_3].2H_2O$

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(*Received* 7 *September* 1970)

The structure of $K_2[Zr(SO_4)_3].2H_2O$ has been determined by single-crystal X-ray analysis and refined by least squares. The crystals are monoclinic, space group $P2_1/c$ and have unit-cell dimensions $a=7·40$, $b=13·96$, $c=12·79$ Å, $\beta=96·6°$. The structure consists of dimeric units of composition $[Zr_2(SO_4)_6(H_2O)_4]^{4-}$ which are held together by the potassium ions. Two of the sulphate groups form a double bridge between the pairs of zirconium atoms and two sulphate groups are doubly bonded to each of the zirconium atoms which are eight-coordinated to oxygen atoms. All the sulphate groups have two terminal oxygen atoms. Two water molecules are also coordinated to each of the zirconium atoms. It is seen that the structure of $K_2[Zr(SO_4)_3].2H_2O$ is closely related to those of $Zr(SO_4)_2.7H_2O$ and α- and β-$Zr(SO_4)_2.5H_2O$.

Introduction

The transformations among the neutral hydrates of $Zr(SO_4)_2$ and α-$Zr(SO_4)_2$ have previously been discussed (Bear & Mumme, 1970). The structures of these compounds showed striking similarities in their general three-dimensional arrangements of zirconium and sulphur atoms. The similarity of arrangement was found to prevail even though the hepta- and α- and β-pentahydrates contained isolated dimeric units, the tetra- and γ- and α-monohydrates were hydrogen bonded layer-type structures and α-$Zr(SO_4)_2$ a three-dimensional network of sulphate bridged zirconia polyhedra.

We are now examining the effect of introducing into these structures large ions such as the alkali metals and have previously determined the structure of the double salt $Na_2[Zr(SO_4)_3].3H_2O$ (Bear & Mumme, 1971). The present paper describes the crystal structure of the salt $K_2[Zr(SO_4)_3].2H_2O$ and relates its structure to that of $Na_2[Zr(SO_4)_3].3H_2O$ and the structures of the compounds already determined in our investigations of the $Zr(SO_4)_2$-H_2O system.

Experimental

Single crystals of $K_2[Zr(SO_4)_3].2H_2O$ were grown from solution following the method described by Sokol, Atana & Zaitser (1967). However, a single phase was not formed by this method and the crystals of $K_2[Zr(SO_4)_3].2H_2O$ used for the collection of single-crystal data and for powder data were handpicked on the basis of their crystal morphology. The powder data were obtained with a Guinier-type focusing camera using KCl as an internal standard, and Cu $K\alpha_{1,2}$ radiation.

Integrated Weissenberg data for the levels *h0l* to *h3l* and for *0kl* were collected using the multiple film pack technique and Cu $K\alpha_{1,2}$ radiation, from a single crystal which measured 0·02 × 0·02 × 0·04 mm. Intensities were measured by visual comparison with a calibrated scale.

All subsequent data handling including interlayer scaling procedures and the scattering curves for Zr, S and O were as described previously (Bear & Mumme, 1969). The scattering curve for un-ionized K was taken from *International Tables for X-ray Crystallography*, (1962).

Approximate unit cell parameters obtained from the single crystal data were used to index the powder data (Table 1) which were then refined by least-squares to give the precise lattice parameters listed in Table 2.

Table 1. *X-ray powder diffraction data for* $K_2[Zr(SO_4)_3].2H_2O$

$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	*hkl*
0·0070	0·0067	011
0·0111	0·0110	100
0·0135	0·0141	110
0·0154	0·0159	021
0·0163	0·0163	$11\bar{1}$
0·0172	0·0177	012
0·0196	0·0192	111
0·0252	0·0254	$12\bar{1}$
0·0270	0·0269	022
0·0387	0·0384	130
0·0408	0·0407	$13\bar{1}$
0·0430	0·0428	$11\bar{3}$
0·0439	0·0440	220
0·0454	0·0453	023
0·0487	0·0488	040

Table 2. *Crystallographic data for* $K_2[Zr(SO_4)_3].2H_2O$

Symmetry	Monoclinic
Unit-cell dimensions	$a = 7·40 \pm 0·01$ Å
	$b = 13·96 \pm 0·01$
	$c = 12·79 \pm 0·01$
	$\beta = 96·6° \pm (0·1)°$
Space group	$P2_1/c$
Z	4
D_x	2·41 g.cm^{-3}

Structure determination

The *b*- and *a*-axis Weissenberg photographs showed that the compound was monoclinic, and the systematic absences defined the space group as $P2_1/c$. The similarity of the unit-cell volume to that of $Na_2[Zr(SO_4)_3].3H_2O$ indicated *Z* to be 4.

Patterson functions $P(uw)$ and $P(vw)$ were used to determine a set of parameters for Zr. The positions of

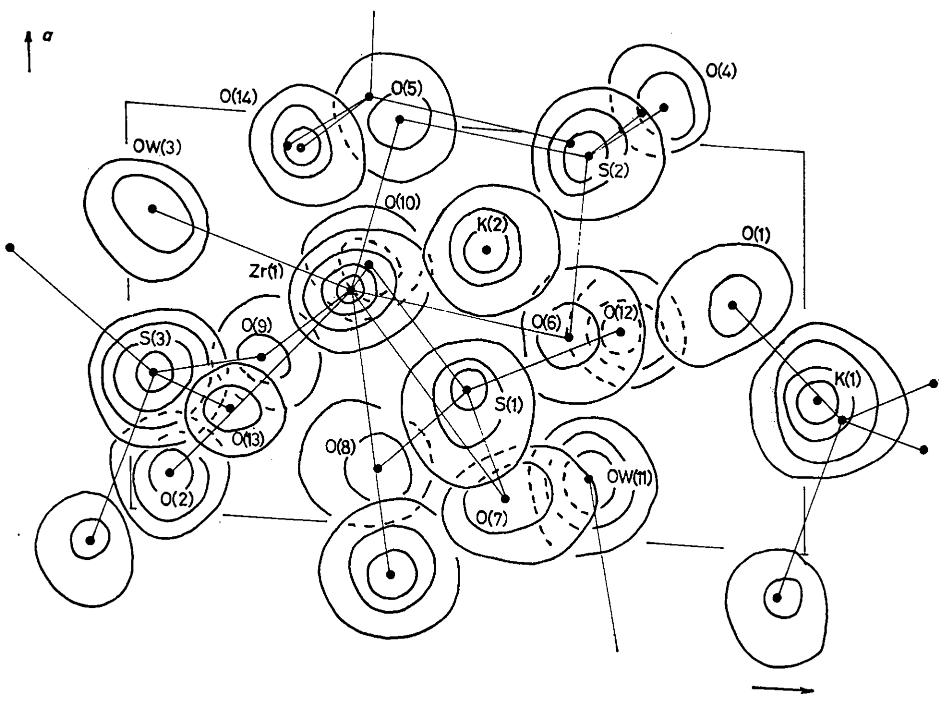

Fig. 1. Electron density distribution indicated by sections $\varrho_o(x,y,z)$ selected near the atom centres and projected on to (001).

Table 3. *Observed and calculated structure factors*

H	K	L	|Fo|	Fc
0	0	2	603	-1513
0	0	4	965	1077
0	0	6	1441	1664
0	0	8	361	378
0	0	10	664	-681
0	0	12	1723	1355
0	0	14	245	-280
0	0	16	93	-147
1	0	2	815	-870
1	0	4	897	963
1	0	6	415	417
1	0	8	734	-742
1	0	10	200	-147
1	0	12	177	89
1	0	14	606	-646
1	0	-2	1521	1234
1	0	-4	406	476
1	0	-6	173	-208
1	0	-8	1401	1458
1	0	-10	221	-308
1	0	-14	1009	915
1	0	-16	89	-69
2	0	0	1616	-1800
2	0	2	1557	-1339
2	0	4	414	327
2	0	6	730	-792
2	0	8	1374	-1210
2	0	10	1065	817
2	0	12	765	-607
2	0	14	813	-618
2	0	-2	593	576
2	0	-6	407	-520
2	0	-8	88	-119
2	0	-10	602	747
2	0	-12	1223	-1077
2	0	-14	147	225
2	0	-16	175	208
3	0	0	1630	-1767
3	0	2	251	263
3	0	4	321	-329
3	0	6	1505	-1359
3	0	8	220	227
3	0	10	146	-138
3	0	12	1107	-753
3	0	14	264	212
3	0	-2	333	-421
3	0	-4	1225	1236
3	0	-6	691	-742
3	0	-8	396	-405
3	0	-10	457	402
3	0	-12	573	-467
3	0	-14	435	-360
4	0	0	285	396
4	0	2	795	820
4	0	4	1433	-1122
4	0	6	468	461
4	0	12	361	-322
4	0	-2	2003	-1673
4	0	-4	472	-450
4	0	-6	301	250
4	0	-8	1031	-1052
4	0	-12	675	644
4	0	-14	811	-627
6	0	0	1045	940
6	0	2	1103	-902
6	0	4	1199	1117
6	0	8	222	-269
6	0	-2	770	773
6	0	-8	1160	1204
6	0	-10	337	-624
6	0	-12	169	226
7	0	0	695	-683
7	0	2	161	-18
7	0	4	291	249
7	0	6	369	-418
7	0	8	395	-472
7	0	-2	969	925
7	0	-4	175	150
7	0	-6	507	-560
7	0	-8	375	306
7	0	-10	272	219
8	0	0	847	-821
8	0	2	721	690
8	0	4	109	-154
8	0	6	557	-576
8	0	-2	179	114
8	0	-4	173	181
8	0	-6	113	187
8	0	-8	259	-315
9	0	0	133	-147
9	0	2	393	400
9	0	-2	517	-594
9	0	-4	193	244
0	1	2	788	531
0	1	3	231	-175
0	1	4	815	-1028
0	1	6	191	106
0	1	7	505	637
0	1	8	193	260
0	1	9	485	-389
0	1	10	341	-275
0	1	11	523	-367
0	1	12	377	-365
0	1	13	501	555
0	1	14	158	187
0	1	15	394	-274
1	1	0	978	1024
1	1	1	621	-484
1	1	2	737	-843
1	1	3	1137	-1234
1	1	4	353	-435
1	1	5	858	1130
1	1	6	921	931
1	1	7	419	-380
1	1	8	191	168
1	1	9	1101	-1039
1	1	10	454	-426
1	1	11	819	698
1	1	12	511	372
1	1	13	602	-509
1	1	14	77	-60
1	1	15	757	-644
1	1	-1	1385	2389
1	1	-2	609	-757
1	1	-3	656	-713
1	1	-5	629	-826
1	1	-6	1028	1419
1	1	-7	962	1160
1	1	-8	222	139
1	1	-10	158	-178
1	1	-11	94	-79
1	1	-12	551	405
1	1	-13	567	473
1	1	-14	113	84
1	1	-15	131	181
2	1	0	1005	841
2	1	1	1389	-1267
2	1	2	1664	-1525
2	1	3	993	983
2	1	4	813	887
2	1	5	637	617
2	1	6	411	-491
2	1	7	513	-608
2	1	8	453	413
2	1	9	408	322
2	1	10	267	-216
2	1	11	233	238
2	1	12	831	654
2	1	13	697	-574
2	1	14	389	-328
2	1	15	97	83
2	1	-1	503	-410
2	1	-2	1270	-1294
2	1	-3	1535	2018
2	1	-4	344	423
2	1	-6	695	-789
2	1	-7	462	-512
2	1	-8	447	509
2	1	-9	1234	1274
2	1	-10	785	-790
2	1	-11	503	-507
2	1	-13	273	-282
2	1	-15	923	738
3	1	0	259	-243
3	1	1	975	893
3	1	2	61	-51
3	1	3	1040	871
3	1	4	1031	218
3	1	5	759	-901
3	1	6	79	-52
3	1	7	121	-116
3	1	8	191	-160
3	1	9	231	226
3	1	10	503	406
3	1	12	121	119
3	1	13	375	-361
3	1	14	139	-56
3	1	-1	985	-823
3	1	-2	291	-272
3	1	-3	661	615
3	1	-4	348	-392
3	1	-5	345	318
3	1	-6	1100	-1149
3	1	-7	559	-607
3	1	-9	257	270
3	1	-10	74	-136
3	1	-11	571	574
3	1	-12	675	-598
3	1	-13	535	-533
3	1	-15	113	20
4	1	0	459	-504
4	1	1	712	834
4	1	2	769	792
4	1	3	109	-137
4	1	4	107	-173
4	1	5	1079	-1157
4	1	6	467	468
4	1	7	613	618
4	1	8	25	-124
4	1	9	61	-14
4	1	10	524	472
4	1	11	381	-710
4	1	12	513	-409
4	1	13	503	386
4	1	-1	1156	-1170
4	1	-2	450	446
4	1	-3	352	-390
4	1	-4	403	-411
4	1	-5	373	467
4	1	-7	305	-817
4	1	-8	551	-653
4	1	-9	231	-249
4	1	-10	690	658
4	1	-12	403	-470
4	1	-14	39	-3
5	1	0	703	636
5	1	1	443	380
5	1	2	220	232
5	1	3	681	-734
5	1	4	90	20
5	1	5	305	317
5	1	6	94	76
5	1	7	503	541
5	1	8	325	331
5	1	9	472	-452
5	1	10	115	-73
5	1	11	225	236
5	1	12	194	-137
5	1	-1	784	738
5	1	-2	167	-138
5	1	-3	1077	-1137
5	1	-4	600	546
5	1	-6	447	524
5	1	-7	689	685
5	1	-8	233	-255
5	1	-9	837	-786
5	1	-11	150	-107
5	1	-12	247	227
5	1	-13	395	382
6	1	0	753	687
6	1	3	267	-346
6	1	5	600	611
6	1	7	89	72
6	1	9	383	-412
6	1	10	181	-195
6	1	11	393	360
6	1	-1	717	727
6	1	-3	511	472
6	1	-4	516	576
6	1	-5	133	-135
6	1	-6	191	241
6	1	-7	327	339
6	1	-8	261	277
6	1	-9	453	551
6	1	-10	144	-144
6	1	-11	575	-594
6	1	-12	485	449
7	1	0	133	149
7	1	1	594	-580
7	1	2	417	-450
7	1	3	673	644
7	1	5	241	219
7	1	7	534	-621
7	1	8	322	-316
7	1	9	85	138
7	1	-1	189	184
7	1	-3	728	729
7	1	-4	295	-248
7	1	-5	344	-319
7	1	-7	95	152
7	1	-8	231	238
7	1	-9	516	538
7	1	-10	161	-146
7	1	-11	158	-134
8	1	1	197	231
8	1	2	633	-624
8	1	3	423	479
8	1	4	260	272
8	1	5	525	-491
8	1	6	355	-325
8	1	-1	665	-620
8	1	-2	167	-185
8	1	-3	391	470
8	1	-4	139	-130
8	1	-5	307	365
8	1	-6	503	-501
8	1	-7	501	-489
8	1	-8	233	233
8	1	-9	[illegible]	449
9	1	0	272	-260
9	1	1	103	121
9	1	-1	207	-261
9	1	-3	325	-402
9	1	-4	113	130
0	2	3	137	281
0	2	4	1455	-1715
0	2	5	187	-194
0	2	6	1875	1706
0	2	7	336	359
0	2	8	969	-1028
0	2	9	361	313
0	2	10	495	397
0	2	11	752	-731
0	2	15	221	169
1	2	0	922	-918
1	2	1	574	-603
1	2	2	556	-540
1	2	3	1577	-1719
1	2	5	414	-489
1	2	6	503	620
1	2	7	556	425
1	2	8	391	-296
1	2	9	720	-559
1	2	10	251	-261
1	2	11	[illegible]	-692
1	2	12	[illegible]	407
1	2	13	277	267
1	2	14	[illegible]	-277
1	2	15	[illegible]	-351
1	2	-1	[illegible]	-723
1	2	-2	[illegible]	[illegible]
1	2	-3	1306	-1365
1	2	-4	377	-510
1	2	-5	72	53
1	2	-6	491	-578
1	2	-7	221	298
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1	2	-9	1177	-1210
1	2	-10	247	-235
1	2	-11	193	187
1	2	-12	551	-407
1	2	-13	221	236
1	2	-14	741	591
1	2	-15	473	-332
2	2	0	1218	1214
2	2	1	1105	-1112
2	2	2	609	-663
2	2	3	935	-1058
2	2	4	1275	1391
2	2	5	410	469
2	2	6	40	12
2	2	7	527	-613
2	2	8	353	-342
2	2	9	778	-745
2	2	10	687	548
2	2	11	408	436
2	2	12	92	95
2	2	13	202	204
2	2	14	462	-382
2	2	15	375	-290
2	2	-1	133	-5
2	2	-2	245	-306
2	2	-3	836	-1145
2	2	-4	223	287
2	2	-5	1160	-1427
2	2	-6	723	-885
2	2	-7	501	578
2	2	-8	459	540
2	2	-9	800	-800
2	2	-10	231	-221
2	2	-11	1005	-945
2	2	-13	109	58
2	2	-14	157	-159
3	2	0	1109	-1095
3	2	2	1911	1754
3	2	3	1487	1315
3	2	4	259	325
3	2	5	695	728
3	2	6	641	-618
3	2	7	187	-248
3	2	8	623	646
3	2	9	763	642
3	2	10	68	55
3	2	11	790	755
3	2	12	540	-428
3	2	14	195	157
3	2	-1	801	791
3	2	-2	519	462
3	2	-3	939	970
3	2	-4	1166	1239
3	2	-5	1061	-1101
3	2	-6	519	-510
3	2	-7	203	-206
3	2	-9	373	339
3	2	-10	429	541
3	2	-11	361	-396
3	2	-12	161	-152
3	2	-13	489	-463
3	2	-14	179	-112
3	2	-15	371	244
4	2	0	982	990
4	2	1	594	568
4	2	3	1362	1228
4	2	4	516	-474
4	2	5	369	310
4	2	6	273	-278
4	2	7	355	405
4	2	8	133	255
4	2	9	867	733
4	2	10	454	-425
4	2	11	191	181
4	2	13	119	-203
4	2	-2	1319	-1207
4	2	-3	957	1102
4	2	-4	777	615
4	2	-5	[illegible]	351
4	2	-6	333	380
4	2	-7	142	-143
4	2	-8	537	-562
4	2	-9	[illegible]	525
4	2	-10	152	128
4	2	-11	421	357
4	2	-12	373	365
4	2	-13	[illegible]	-312
4	2	-14	472	-323
5	2	0	[illegible]	567
5	2	1	552	504
5	2	3	336	286
5	2	4	1330	-932
5	2	5	[illegible]	[illegible]
5	2	6	[illegible]	560
5	2	7	695	567
5	2	9	402	352
5	2	10	741	-632
5	2	11	393	-377
5	2	12	431	410
5	2	-1	255	-257
5	2	-2	202	-155
5	2	-3	260	253
5	2	-4	109	-70
5	2	-5	772	741
5	2	-6	198	275
5	2	-7	235	-255
5	2	-9	272	-233
5	2	-10	322	-340
5	2	-11	309	-336
5	2	-13	130	-110
5	2	-14	257	234
6	2	0	463	[illegible]
6	2	1	571	560
6	2	2	371	-394
6	2	3	361	-369
6	2	4	60	-42
6	2	5	67	-100
6	2	6	161	[illegible]
6	2	7	337	357
6	2	8	73	[illegible]
6	2	9	613	-630
6	2	10	476	[illegible]
6	2	11	[illegible]	-235
6	2	-1	139	134
6	2	-2	899	[illegible]
6	2	-3	437	-475
6	2	-4	1077	-1048
6	2	-5	331	435
6	2	-6	410	477
6	2	-7	332	336
6	2	-8	265	250
6	2	-9	103	-106
6	2	-10	177	-176
6	2	-12	225	-137
6	2	-13	309	402
7	2	0	703	-735
7	2	1	329	-365
7	2	2	66	23
7	2	3	320	-345
7	2	4	255	221
7	2	5	149	140
7	2	6	253	-285
7	2	7	231	-269
7	2	9	465	-608
7	2	-1	359	347
7	2	-2	235	242
7	2	-3	427	-411
7	2	-4	210	258
7	2	-5	417	-472
7	2	-6	565	-604
7	2	-7	336	335
7	2	-8	200	176
7	2	-9	119	129
7	2	-10	237	295
7	2	-11	393	-233
8	2	1	505	-431
8	2	4	435	442
8	2	5	125	175
8	2	6	407	-399
8	2	-2	353	-339
8	2	-3	117	162
8	2	-4	513	545
8	2	-5	533	-446
8	2	-6	355	-329
8	2	-7	117	-143
8	2	-9	210	271
9	2	0	206	262
9	2	-1	233	-135
9	2	-2	333	-377
9	2	-3	355	443
9	2	-4	221	224
0	3	1	241	-297
0	3	2	817	[illegible]
0	3	3	156	-241
0	3	4	497	-576
0	3	5	216	268
0	3	8	1296	1358
0	3	9	467	286
0	3	10	497	-358
0	3	11	295	-246
0	3	12	664	-526
0	3	13	406	296
0	3	14	516	325
0	3	15	94	40
1	3	0	1441	1225
1	3	1	429	-421
1	3	2	294	227
1	3	3	999	-1119
1	3	4	139	131
1	3	5	929	223
1	3	6	739	271
1	3	7	297	-339
1	3	8	128	152
1	3	9	139	-123
1	3	10	715	-718
1	3	11	792	733
1	3	12	297	[illegible]
1	3	13	76	75
1	3	14	423	346
1	3	-1	873	993
1	3	-2	532	-528
1	3	-3	829	[illegible]
1	3	-4	65	-119
1	3	-5	92	-151
1	3	-6	1025	1143
1	3	-8	229	-274
1	3	-9	495	-422
1	3	-10	387	[illegible]
1	3	-11	281	-259
1	3	-12	604	522
1	3	-13	153	-108
1	3	-14	153	128
1	3	-15	146	-121
2	3	0	94	106
2	3	1	75	118
2	3	2	229	-273
2	3	3	249	-290
2	3	4	723	-790
2	3	5	425	374
2	3	6	1105	1351
2	3	7	317	-358
2	3	8	1303	-1307
2	3	9	273	271
2	3	10	417	327
2	3	11	437	83
2	3	13	51	[illegible]
2	3	15	170	169
2	3	-1	441	-363
2	3	-2	1035	1112
2	3	-3	343	-273
2	3	-4	1365	-1635
2	3	-5	376	-433
2	3	-6	269	372
2	3	-7	747	-786
2	3	-10	658	-577
2	3	-11	465	-473
2	3	-12	539	-459
2	3	-13	449	-330
2	3	-14	681	592
2	3	-15	128	121
3	3	0	110	64
3	3	1	328	220
3	3	2	640	-563
3	3	3	275	197
3	3	4	1234	1256
3	3	5	219	196
3	3	6	233	-224
3	3	7	135	-102
3	3	8	405	-491
3	3	9	379	[illegible]
3	3	10	803	695
3	3	12	295	324
3	3	13	245	-232
3	3	14	466	-374
3	3	-1	371	-529
3	3	-2	943	881
3	3	-4	811	-749
3	3	-5	47	73
3	3	-6	579	-536
3	3	-7	131	-113
3	3	-8	351	425
3	3	-10	255	-216
3	3	-11	337	403
3	3	-12	875	-850
3	3	-13	303	-260
3	3	-14	89	127
3	3	-15	65	-77
4	3	0	421	-300
4	3	1	790	622
4	3	2	151	100
4	3	3	187	130
4	3	4	796	702
4	3	5	386	-362
4	3	6	1321	-1360
4	3	7	344	382
4	3	8	920	872
4	3	9	279	243
4	3	10	361	354
4	3	11	473	-446
4	3	12	441	-461
4	3	13	343	239
4	3	-1	525	-492
4	3	-2	377	-347
4	3	-3	807	750
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4	3	-7	139	98
4	3	-8	322	335
4	3	-9	317	405
4	3	-10	322	357
4	3	-11	307	295
4	3	-13	117	100
4	3	-14	630	-633
5	3	0	75	22
5	3	1	100	132
5	3	2	601	555
5	3	3	481	-310
5	3	4	530	-469
5	3	5	237	292
5	3	6	86	66
5	3	7	135	-146
5	3	8	321	737
5	3	9	271	-291
5	3	10	319	-336
5	3	12	211	-200
5	3	-1	571	675
5	3	-2	211	-292
5	3	-3	256	-215
5	3	-4	747	335
5	3	-5	70	-35
5	3	-6	379	410
5	3	-7	801	[illegible]
5	3	-8	807	[illegible]
5	3	-9	412	-415
5	3	-10	243	270
5	3	-11	323	291
5	3	-12	395	326
5	3	-13	452	423
5	3	-14	417	-576
6	3	0	871	[illegible]
6	3	1	160	-112
6	3	2	290	192
6	3	3	275	-272
6	3	4	391	-307
6	3	6	635	800
6	3	8	72	193
6	3	9	241	-201
6	3	10	465	-463
6	3	-1	365	-343
6	3	-2	172	-153
6	3	-3	158	-133
6	3	-4	[illegible]	[illegible]
6	3	-5	500	-476
6	3	-6	953	924
6	3	-7	132	-171
6	3	-9	163	-141
6	3	-10	297	-252
6	3	-11	239	-227
6	3	-12	454	323
6	3	-13	89	23
7	3	0	323	356
7	3	1	557	-657
7	3	2	551	-545
7	3	3	161	126
7	3	4	156	109
7	3	6	331	401
7	3	7	177	-232
7	3	8	509	-606
7	3	-1	251	-272
7	3	-2	251	263
7	3	-3	59	-62
7	3	-4	821	-737
7	3	-5	573	-655
7	3	-6	299	276
7	3	-7	107	-125
7	3	-8	367	434
7	3	-9	111	-140
7	3	-10	350	-394
7	3	-11	291	-297
8	3	0	624	-671
8	3	1	156	110
8	3	3	231	229
8	3	4	156	221
8	3	5	167	-215
8	3	-1	259	-330
8	3	-2	667	673
8	3	-3	245	257
8	3	-4	291	-324
8	3	-6	550	-597
8	3	-7	295	-395
8	3	-8	106	105
9	3	0	191	-255
9	3	1	128	250
9	3	-1	273	331
9	3	-2	64	91
9	3	-4	462	535

Table 4. *Fractional atomic parameters and temperature factors*

	x	*y*	*z*	*B*
Zr(1)	0·1983 (3)	0·9335 (6)	0·1548 (2)	0·92 (4) Å²
S(1)	0·1706 (9)	0·7464 (17)	0·2426 (5)	1·27 (13)
S(2)	0·4631 (9)	−0·0078 (18)	0·3148 (5)	1·41 (13)
S(3)	0·1602 (8)	0·1474 (17)	0·0160 (5)	0·86 (10)
O(1)	0·2818 (25)	0·3559 (42)	0·4260 (14)	1·36 (36)
O(2)	0·0282 (24)	0·8937 (36)	0·0285 (14)	1·18 (35)
O*W*(3)	0·3588 (22)	0·9199 (36)	0·0161 (13)	0·63 (30)
O(4)	0·4539 (34)	0·4289 (43)	0·0976 (19)	3·08 (57)
O(5)	0·4843 (28)	0·0411 (44)	0·2072 (16)	1·95 (43)
O(6)	0·2590 (30)	0·0134 (45)	0·3114 (17)	2·23 (45)
O(7)	0·0590 (29)	0·8467 (44)	0·2543 (16)	1·86 (39)
O(8)	0·0583 (32)	0·6568 (46)	0·1941 (18)	2·95 (52)
O(9)	0·2159 (26)	0·0826 (39)	0·1004 (15)	1·36 (39)
O(10)	0·2934 (25)	0·7775 (39)	0·1664 (14)	1·50 (39)
O*W* (11)	0·0668 (27)	0·5162 (40)	0·3007 (16)	1·86 (42)
O(12)	0·2695 (31)	0·7236 (43)	0·3424 (17)	2·65 (51)
O(13)	0·1473 (31)	0·2512 (42)	0·0585 (18)	2·69 (51)
O(14)	0·5330 (36)	0·1009 (44)	0·3311 (20)	3·36 (58)
K(1)	0·2047 (12)	0·6430 (19)	−0·0019 (7)	3·66 (19)
K(2)	0·3233 (10)	0·2518 (16)	0·2511 (6)	2·47 (15)

all other atoms except the hydrogen atoms were located by Fourier syntheses using the three-dimensional X-ray data collected along the *b* axis (Fig. 1).

All atomic positions, together with individual isotropic temperature factors, were refined by a number of least-squares cycles, with all the collected data included. Refinement was halted when the shift of each variable was less than one quarter of the standard deviation. The final *R* was 12·6 for 704 reflexions. A comparison between F_o and F_c is given in Table 3. the atomic parameters, the temperature factors and their estimated standard deviations in Table 4 and the interatomic distances in Table 5.

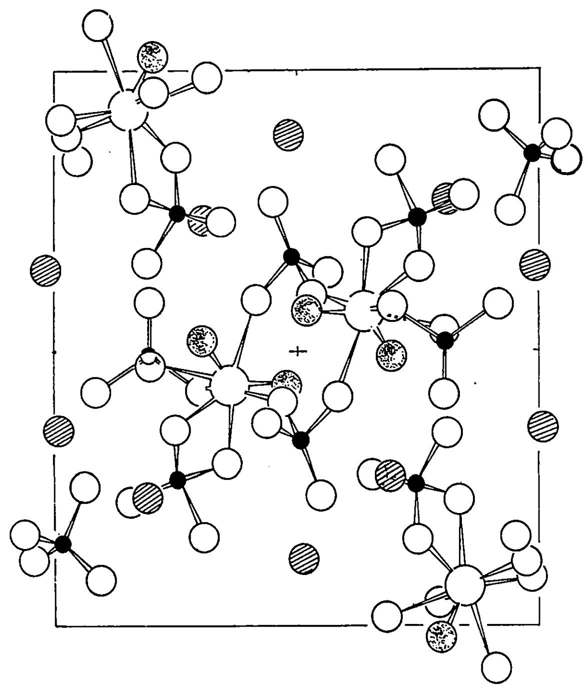


Fig. 2. The structure of $K_2[Zr(SO_4)_3].2H_2O$ projected on to (100). Large open circles: zirconium atoms; filled circles: sulphur atoms; medium open circles: oxygen atoms; stippled circles: water molecules; and shaded circles: potassium atoms.

Table 5. *Interatomic distances (Å) and angles (°) with e.s.d.'s in brackets*

(1) Zirconium polyhedron

Zr(1)–O(2)		2·03 (2)
	O(3)	2·23 (2)
	O(7)	2·10 (2)
	O(10)	2·30 (2)
	O(5)	2·18 (2)
	O(11′)	2·35 (2)
	O(6′)	2·14 (2)
	O(9′)	2·18 (2)

(2) Sulphate groups

S1 tetrahedron

S(1) O(7)	1·64 (3)	O(7)—S(1)–O(8)	117° (1)
O(8)	1·60 (3)	O(7)—S(1)–O(10)	100 (1)
O(10)	1·46 (2)	O(7)—S(1)–O(12)	109 (1)
O(12)	1·45 (2)	O(10)–S(1)–O(12)	111 (1)
		O(8)—S(1)–O(12)	112 (1)
		O(10)–S(1)–O(8)	108 (1)

S2 tetrahedron

S(2)–O(5)	1·48 (2)	O(5)—S(2)–O(6)	99° (1)
O(6)	1·50 (2)	O(5)—S(2)–O(14)	111 (1)
O(14)	1·62 (3)	O(5)—S(2)–O(4′)	114 (1)
O(4′)	1·39 (2)	O(6)—S(2)–O(14)	111 (1)
		O(6)—S(2)–O(4′)	107 (1)
		O(14)–S(2)–O(4′)	115 (1)

S3 tetrahedron

S(3)–O(9)	1·45 (2)	O(9)—S(3)–O(13)	111° (1)
O(13)	1·54 (2)	O(9)—S(3)–O(2′)	103 (1)
O(2′)	1·57 (2)	O(9)—S(3)–O(11)	110 (1)
O(1′)	1·43 (2)	O(13)–S(3)–O(2′)	113 (1)
		O(13)–S(3)–O(11)	111 (1)
		O(2′) –S(3)–O(11)	109 (1)

(3) Potassium polyhedra

K(1)–O(14)	2·69 (3)
O(8)	2·83 (3)
O(10)	2·88 (3)
O(13)	3·04 (3)
O(6′)	2·96 (3)
O(7′)	3·09 (3)
O(12)	2·71 (3)

Table 5 (*cont.*)

K(2)–O(13)	2·69 (3)
O(9)	3·12 (3)
O(12′)	3·32 (3)
O(8′)	3·23 (3)
O(7′)	3·13 (3)
O(10′)	2·82 (3)
O(4)	3·34 (3)

(4) Possible hydrogen bonds

O*W*(3)

O*W*(3)–O(2)	2·47 (3)
O(1)	2·80 (3)
O(5)	3·00 (3)
O(10′)	3·14 (3)
O(9′)	2·94 (3)

O(2)——O*W*(3)—O(1)	147° (1)
O(2)——O*W*(3)—O(5)	108 (1)
O(2)——O*W*(3)—O(10′)	75 (1)
O(2)——O*W*(3)—O(9)	75 (1)
O(1)——O*W*(3)—O(5)	61 (1)
O(1)——O*W*(3)—O(10′)	74 (1)
O(1)——O*W*(3)—O(9′)	114 (1)
O(5)——O*W*(3)—O(10′)	57 (1)
O(5)——O*W*(3)—O(9′)	58 (1)
O(9′) —O*W*(3)—O(10′)	91 (1)

O*W*(11)

O*W*(11)–O(8)	2·40 (3)
O*W*(11)–O(9)	2·60 (3)
O*W*(11)–O(6)	2·78 (3)

O(8)——O*W*(11)–O(9)	89° (1)
O(8)——O*W*(11)–O(6)	80 (1)
O(6)——O*W*(11)–O(9)	67 (1)

Description

The structure of $K_2[Zr(SO_4)_3].2H_2O$ viewed in (100) projection is given in Fig. 2. The main structural units are dimers of composition $[Zr_2(SO_4)_6(H_2O)_4]^{4-}$, each of which contains two zirconium polyhedra, four doubly attached sulphate groups and two bridging sulphate groups. Each of the sulphate groups has two terminal oxygen atoms, and the S–O distances and O–S–O angles (Table 5) show that they are all distorted from ideal tetrahedral symmetry. There are three non-equivalent sulphate groups in this unit cell as there were in $Na_2[Zr(SO_4)_3].3H_2O$.

Each zirconium atom is coordinated to eight oxygen atoms, six from the sulphate groups and two from water molecules. The ZrO_8 polyhedron is dodecahedral similar to those in $Zr(SO_4)_27H_2O$, α- and β-$Zr(SO_4)_2.5H_2O$ and $Na_2[Zr(SO_4)_3].3H_2O$.

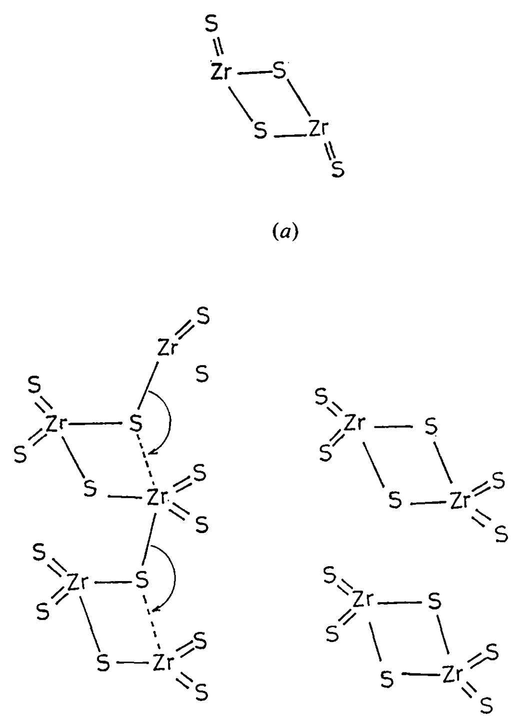
The potassium atoms occupy positions between the dimeric units and bond them together. Each one exhibits sevenfold coordination with K–O bond distances varying from 2·69 to 3·09 Å for K(1) and from 2·69 to 3·32 Å for K(2).

There are probable hydrogen bonds (Table 5) involving the two coordinated water molecules, namely O(2)–O*W*(3)–O(1) or O(5) in one case, and O(8)–O*W*(11)–O(9) or O(6) in the other. Two possible bonds connecting O*W*(3)–O(5) and O*W*(11)–O(8) would serve the additional function of holding the structure together, as they bond between adjacent dimeric units.

Discussion

The structure of $K_2[Zr(SO_4)_3].2H_2O$ is quite similar to those of $Zr(SO_4)_2.7H_2O$, α- and β-$Zr(SO_4)_2.5H_2O$. Each one has as a structural basis a dimeric unit containing doubly bridging sulphate groups. In $K_2[Zr(SO_4)_2].2H_2O$ however there are two additional terminal sulphate groups doubly bonded to the zirconium atoms of the dimers which thus have a formal charge of −4, and it is the potassium atoms which provide the bonds to hold the dimeric units together rather than hydrogen bonding as is the case for the neutral dimers in $Zr(SO_4)_2.7H_2O$ and α- and β-$Zr(SO_4)_2.5H_2O$. On the other hand, $Na_2[Zr(SO_4)_3].3H_2O$ has single bridging of zirconium atoms by sulphate groups, characteristic of that found in $Zr(SO_4)_2.4H_2O$, and the basis of its structure is infinite spiral arrangements of coordination polyhedra.

However, a simple relationship does exist between these two compounds and is illustrated in Fig. 3. Fig. 3(*a*) is a schematic representation such as we have previously used for the isolated dimers found in $Zr(SO_4)_2.7H_2O$ and α- and β-$Zr(SO_4)_2.5H_2O$. Fig. 3(*b*) is a similar



(*a*) (*b*) (*c*)

Fig. 3. A schematic representation illustrating the relationship between (*a*) the dimeric units of $Zr(SO_4)_2.7H_2O$, α- and β-$Zr(SO_4)_2.5H_2O$; (*b*) $Na_2[Zr(SO_4)_3]3H_2O$ and (*c*)$K_2[Zr(SO_4)_3].2H_2O$. Only oxygen bridges are shown.

representation of the dimeric units of $K_2[Zr(SO_4)_3]$. $2H_2O$. Examination of this structure shows that breaking and remaking one oxygen bridge in each dimeric ring of $K_2[Zr(SO_4)_3].2H_2O$ would result in the formation of infinite –Zr–O–S–O–Zr– chains similar to those found in $Na_2[Zr(SO_4)_3].3H_2O$ [Fig. 3(*c*)] and we see that in these two compounds we have an extension of the structural arrangements already found in the neutral hydrates of $Zr(SO_4)_2$ and anhydrous α-$Zr(SO_4)_2$.

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The Determination of the Crystal Structure of *trans*-2,4-Dihydroxy-2,4-Dimethylcyclohexane-*trans*-1-Acetic Acid γ-Lactone, $C_{10}H_{16}O_3$, using Rotation and Translation Functions in Reciprocal Space.

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(*Received* 23 *April* 1970)

Crystals of *trans*-2,4-dihydroxy-2,4-dimethylcyclohexane-*trans*-1-acetic acid γ-lactone, $C_{10}H_{16}O_3$, have an orthorhombic unit cell with $a=10{\cdot}09_6$, $b=14{\cdot}02_8$, $c=7{\cdot}03_9$ Å. The space group is $P2_12_12_1$ and there are four molecules per unit cell. The structure was solved using a known grouping of atoms to calculate a search Patterson function. The rotation function of Rossmann & Blow was used to obtain the relative orientation of the known and unknown Patterson functions. The *Q*-functions of Tollin were used to obtain the translational parameters of the known group relative to the 2_1 axes present in the crystal structure. The 988 observed reflections, collected on a Picker four-circle automatic diffractometer were used to refine the structure to give a conventional *R* value of 0·068. The molecular structure consists of a lactone ring fused to a cyclohexane ring distorted by the closeness of the $-CH_3$ and –OH groups attached to C(2) and C(4). The lactone ring is non-planar with one atom, C(1), lying 0·55 Å from the least-squares plane through the other four atoms. The C–O bond lengths in the lactone ring differ by 0·130 Å, the shorter bond being adjacent to the carbonyl group.

Introduction

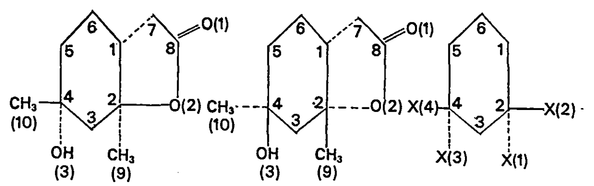
The rotation function (Rossmann & Blow, 1962) has been used to evaluate the degree of superposition of two sets of Patterson vectors when one set is rotated with respect to the other. A fuller account of this method has been given by Tollin (1970) and by Rossmann (1971). Tollin & Rossmann (1966) suggest the use of this method in the solution of the following problems:

(*A*) Determining the relative orientation of identical groups of atoms within the same crystallographic asymmetric unit.

(*B*) Determining the absolute orientation of a rigid group with known chemical structure in a molecular crystal.

(*C*) Determining the relative orientations of identical groups in different crystal forms, when the chemical structure is unknown.

The method has been successful in the investigation of several protein structures; that of hemoglobin (Rossmann & Blow, 1962), insulin (Dodson, Harding, Hodgkin & Rossmann, 1966), and α-chymotrypsin (Blow, Rossmann & Jeffery, 1964) illustrate problems of type (*A*) while the comparison of horse oxyhemoglobin with seal myoglobin (Lattman & Love, 1970) illustrates type (*C*) problems. We report here the solution of a small molecular crystal structure, for part of which the configuration was known, representing an application of the rotation function to a problem of type (*B*).



(I) (II) (III)

In a chemical study Wolinsky & Chan (1966) indicated the configuration of *trans*-2,4-dihydroxy-2,4-

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