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The Crystal Structure of $Zr_2(OH)_2(SO_4)_3(H_2O)_4$

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The crystal structure of $Zr_2(OH)_2(SO_4)_3(H_2O)_4$ has been determined from Patterson and Fourier projections and completed by a three-dimensional least-squares refinement. The crystals are monoclinic with $a = 13.056 \pm 0.002$ Å., $b = 6.5075 \pm 0.0006$ Å., $c = 15.092 \pm 0.002$ Å., $\beta = 96.21 \pm 0.01°$, and $Z = 4$. The data are compatible with space group C2/c. The structure is built up of sheets of zirconium and sulfate ions, and the zirconium ions of adjacent sheets are connected by double hydroxide bridges. The structure may be viewed as being composed of dimers $Zr_2(OH)_2^{6+}$. The coordination of zirconium is eightfold with the oxygen atoms forming a dodecahedron with triangular faces ($Mo(CN)_8^{4-}$ coordination). The mean Zr–O distance is 2.19 Å. The structures and interrelationships of several zirconium basic salts are discussed.

Although the hydrolysis of tetravalent metal ions has received considerable attention in recent years, little data on the configuration of the hydrolysis products in solutions or in basic salts has been presented. In the Royal Institute of Technology in Stockholm, the crystal structures of several hydroxide and oxide complexes of tetravalent metal ions have been investigated in an attempt to elucidate the configuration of the hydrolysis products.[2a] This study was extended to the system ZrO_2–SO_3–H_2O and has been presented.[2b] A more complete report is given below.

Experimental Section

The compounds investigated were all made by the technique of hydrothermal hydrolysis. $Zr(SO_4)_2(H_2O)_4$ was made by dissolving $ZrOCl_2(H_2O)_8$ (Johnson, Matthey and Co., Ltd.) in dilute sulfuric acid and evaporating to dryness. Solutions of 3–5 g. of the neutral salt in 5 ml. of water were sealed in thick-walled Pyrex tubes or autoclaves and heated to temperatures ranging from 100 to 300°. After heating for periods of from 1 day to several weeks, the tubes were cooled rapidly and opened. The crystals were filtered off, washed with water, and air dried. Using this technique it was possible to make a series of basic zirconium sulfates. The temperature range and formulas were: (1) 100–150°, $Zr_2(OH)_2(SO_4)_3(H_2O)_4$; (2) 175–225°, $Zr(OH)_2SO_4$(I); and (3) 250–300°, $Zr(OH)_2SO_4$(II). Salts 2 and 3 have the same composition but different structures. The crystal structure of the first salt is presented below and those of the other salts will be published separately. A salt with the composition $Zr_2(OH)_2(SO_4)_3(H_2O)_4$ was first prepared by Hauser and Herzfeld.[3]

The chemical analysis was done was follows: the amount of ZrO_2 was determined by ignition to a constant weight and the amount of SO_3 by a sodium carbonate fusion followed by the precipitation of $BaSO_4$. The water content was determined by the Hartwig–Bendig modification of Brush and Penfield's method.[4] The density was determined from the loss of weight in benzene. *Anal.* Calcd.: H_2O, 15.7; SO_3, 41.6; ZrO_2, 42.7; density, 3.00. Found: H_2O, 15.6; SO_3, 41.5; ZrO_2, 43.1; density, 2.98.

$Zr_2(OH)_2(SO_4)_3(H_2O)_4$ is monoclinic. The accurate lattice parameters, obtained from a Guinier powder pattern internally calibrated with KCl ($a_{KCl} = 6.29284$ Å. at 22°) were $a = 13.056 \pm 0.002$ Å., $b = 6.5075 \pm 0.0006$ Å., $c = 15.092 \pm 0.002$ Å., and $\beta = 96.21 \pm 0.01°$; the number of formula units per unit cell is four. The systematically absent reflections were: hkl with $h + k \neq 2n$ and $h0l$ with $l \neq 2n$ $(h \neq 2n)$. The space groups compatible with these absences are Cc and C2/c. Since a plausible structure, giving good agreement between observed and calculated F values, could be obtained assuming the centrosymmetric C2/c, only this space group was considered.

The crystals were prisms approximately 0.1 mm. on a side; $\mu = 200$ cm.$^{-1}$. The $h0l$ to $h3l$ and $hk0$ Weissenberg photographs were recorded using Cu K radiation and the multiple film technique. The intensities were estimated visually by means of a standard scale and were corrected for polarization and Lorentz effects. No correction was applied for the absorption. The scattering curves used in the structure factor calculations were: for Zr that given by Thomas and Umeda,[5] for S that given by Tomiie and Stam,[6] and for O that given by Berghuis, *et al.*[7]

Structure Determination

From the data it follows that there are 8 Zr, 12 S, and 72 O atoms in the unit cell. It is unlikely that any of these atoms would occupy a center of symmetry; therefore, only the point positions 4(e) and 8(f) need be considered. At least four sulfur atoms should be situated in the special position 4(e).

From the Patterson projections $P(u0w)$ and $P(uv0)$ a unique set of parameters for Zr 8(f), S_1 4(e), and S_2 8(f) was found. The signs of the structure factors calculated for these zirconium and sulfur positions were used with the observed structure factors to calculate the Fourier projections $\rho(x0z)$ and $\rho(xy0)$. From these electron density projections it was possible to find the positions of the nine sets of oxygen atoms in 8(f). The parameters were partially refined using difference $(F_o - F_c)$ electron density projections.

The refinement of the structure was continued using a block diagonal least-squares program written by Åsbrink and Brändén for the Swedish computer FACIT EDB.[8] The weighting factor suggested by Hughes was used.[9] The final R value was 0.103 for the 658 observed reflections used in the refinement. The

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TABLE I

ATOMIC PARAMETERS FOR $Zr_2(OH)_2(SO_4)_3(H_2O)_4$

Atom position	x σ_x	y σ_y	z σ_z	B, Å.^{2} σ_B
Zr in 8(f)	0.1053	0.0188	0.0842	0.26
	0.0001	0.0004	0.0001	0.02
S_I in 4(e)	0	0.7201	$^1/_4$	0.31
		0.0016		0.10
S_2 in 8(f)	0.2098	0.4796	0.0662	0.56
	0.0004	0.0012	0.0003	0.07
O_1 (OH) in 8(f)	0.0414	0.1209	0.9590	0.3
	0.0009	0.0031	0.0008	0.2
O_2 in 8(f)	0.0713	0.8507	0.2070	0.3
	0.0009	0.0030	0.0008	0.2
O_3 in 8(f)	0.0610	0.6044	0.3189	1.0
	0.0011	0.0035	0.0009	0.3
O_4 in 8(f)	0.1435	0.3478	0.0904	1.0
	0.0011	0.0034	0.0009	0.3
O_5 in 8(f)	0.1426	0.7062	0.0485	1.0
	0.0011	0.0033	0.0009	0.2
O_6 in 8(f)	0.2509	0.4619	0.9816	0.7
	0.0010	0.0030	0.0009	0.2
O_7 in 8(f)	0.2919	0.5581	0.1357	0.8
	0.0010	0.0033	0.0009	0.2
O_8 (H_2O)	0.9872	0.2031	0.1439	0.5
in 8(f)	0.0010	0.0030	0.0008	0.2
O_9 (H_2O)	0.2354	0.0359	0.1885	0.5
in 8(f)	0.0010	0.0029	0.0008	0.2

atomic parameters and individual isotropic temperature factors are listed in Table I and the calculated and observed structure factors in Table II.

As no corrections for absorption and extinction were made, no physical significance can be given to the individual temperature factors. The standard deviations given in Table I are those calculated from the residuals and the inverse matrix in the least-squares refinement.

The positions of the H atoms could not be determined directly. However, of the oxygen atoms in the structure (*cf.* Table III) (a) O_2–O_7 belong to sulfate groups, (b) O_1 is in contact with two Zr atoms, and (c) O_8 and O_9 are bonded to only one Zr atom. The most plausible arrangement of the 40 H atoms in the unit cell should then be that eight of them form OH^- ions with O_1 and the remaining hydrogen atoms form water molecules with O_8 and O_9.

Description and Discussion of the Structure

The structure is composed of sheets perpendicular to $\vec{b} \times (\vec{a} - \vec{c})$ as shown in Figure 1b. In the sheet, each zirconium atom is connected by four sulfate groups to adjacent zirconium atoms (Figure 1a). Eight of the sulfate groups are bonded to three zirconium atoms, and the remaining four sulfate groups are bonded to two. The sheets are connected by hydroxide double bridges between the zirconium atoms as shown in Figure 1b.

The structure may be viewed as being composed of dimers of zirconium atoms bonded by double hydroxide bridges. The Zr–Zr distance in the dimer is 3.545 Å.

TABLE II

COMPARISON OF CALCULATED AND OBSERVED STRUCTURE FACTORS

h	k	l	F_o	F_c
0	0	2	161	202
0	0	4	124	-124
0	0	6	236	-265
0	0	8	209	-202
0	0	10	52	39
0	0	12	181	172
0	0	14	110	82
0	0	16	<36	- 16
0	0	18	158	-179
2	0	$\bar{18}$	74	- 76
2	0	$\bar{16}$	93	74
2	0	$\bar{14}$	118	65
2	0	$\bar{12}$	38	28
2	0	$\bar{10}$	198	-213
2	0	$\bar{8}$	222	-228
2	0	$\bar{6}$	42	22
2	0	$\bar{4}$	246	349
2	0	$\bar{2}$	152	182
2	0	0	34	24
2	0	2	293	-454
2	0	4	260	-319
2	0	6	136	-122
2	0	8	256	298
2	0	10	190	177
2	0	12	66	50
2	0	14	197	-175
2	0	16	198	-184
2	0	18	43	- 37
4	0	$\bar{18}$	33	27
4	0	$\bar{16}$	232	220
4	0	$\bar{14}$	<40	25
4	0	$\bar{12}$	118	-108
4	0	$\bar{10}$	149	-143
4	0	$\bar{8}$	<30	3
4	0	$\bar{6}$	158	159
4	0	$\bar{4}$	125	134
4	0	$\bar{2}$	152	-154
4	0	0	32	- 39
4	0	2	136	-150
4	0	4	172	168
4	0	6	291	338
4	0	8	214	240
4	0	10	158	-160
4	0	12	161	-144
4	0	14	156	-132
4	0	16	56	50
6	0	$\bar{18}$	124	131
6	0	$\bar{16}$	<36	6
6	0	$\bar{14}$	207	-175
6	0	$\bar{12}$	118	-117
6	0	$\bar{10}$	120	-118
6	0	$\bar{8}$	176	195
6	0	$\bar{6}$	101	98
6	0	$\bar{4}$	103	-100
6	0	$\bar{2}$	222	-277
6	0	0	173	-174
6	0	2	143	138
6	0	4	147	169
6	0	6	<36	5
6	0	8	74	67
6	0	10	168	-198
6	0	12	39	- 34
6	0	14	61	54
6	0	16	104	104
8	0	$\bar{16}$	152	-147
8	0	$\bar{14}$	103	- 87
8	0	$\bar{12}$	161	154
8	0	$\bar{10}$	158	186
8	0	$\bar{8}$	149	160
8	0	$\bar{6}$	170	-190
8	0	$\bar{4}$	163	-179
8	0	$\bar{2}$	133	-128
8	0	0	142	145
8	0	2	232	247
8	0	4	141	129
8	0	6	46	- 43
8	0	8	99	- 90
8	0	10	128	-123
8	0	12	131	100
8	0	14	81	66
10	0	$\bar{14}$	155	146
10	0	$\bar{12}$	181	187
10	0	$\bar{10}$	122	-108
10	0	$\bar{8}$	94	- 89
10	0	$\bar{6}$	177	-200
10	0	$\bar{4}$	<38	- 29
10	0	$\bar{2}$	120	112
10	0	0	172	170
10	0	2	<38	- 27
10	0	4	170	-197
10	0	6	260	-247
10	0	8	<39	30
10	0	10	128	106
10	0	12	161	-153
12	0	$\bar{14}$	70	78
12	0	$\bar{12}$	38	36
12	0	$\bar{10}$	110	- 97
12	0	$\bar{8}$	<39	- 41
12	0	$\bar{6}$	39	21
12	0	$\bar{4}$	199	183
12	0	$\bar{2}$	<40	1
12	0	0	47	- 36
12	0	2	203	-178
12	0	4	82	- 64
12	0	6	72	68
12	0	8	204	190
12	0	10	141	135
14	0	$\bar{10}$	131	-124
14	0	$\bar{8}$	<32	21
14	0	$\bar{6}$	93	82
14	0	$\bar{4}$	61	49
14	0	$\bar{2}$	76	- 72
14	0	0	47	- 38
14	0	2	129	-115
14	0	4	80	69
14	0	6	61	51
14	0	8	52	47
16	0	$\bar{6}$	120	129
16	0	$\bar{4}$	113	31
16	0	$\bar{2}$	156	-160
16	0	0	50	- 36
1	1	$\bar{18}$	120	-150
1	1	$\bar{17}$	28	14
1	1	$\bar{16}$	45	- 28
1	1	$\bar{15}$	107	98
1	1	$\bar{14}$	193	180
1	1	$\bar{13}$	<28	- 20
1	1	$\bar{12}$	192	204
1	1	$\bar{11}$	70	- 68
1	1	$\bar{10}$	<25	13
1	1	$\bar{9}$	57	- 47
1	1	$\bar{8}$	153	-149
1	1	$\bar{7}$	58	- 51
1	1	$\bar{6}$	119	-115
1	1	$\bar{5}$	136	-110
1	1	$\bar{4}$	147	-125
1	1	$\bar{3}$	117	113
1	1	$\bar{2}$	158	172
1	1	$\bar{1}$	87	- 78
1	1	0	169	230
1	1	1	80	65
1	1	2	81	54
1	1	3	115	-103
1	1	4	59	- 65
1	1	5	158	142
1	1	6	200	-200
1	1	7	71	64
1	1	8	58	44
1	1	9	23	9
1	1	10	132	136
1	1	11	62	- 55
1	1	12	34	- 30
1	1	13	<28	5
1	1	14	60	- 30
1	1	15	58	- 51
1	1	16	152	-153
1	1	17	<23	16
1	1	18	77	- 83
3	1	$\bar{18}$	82	83
3	1	$\bar{17}$	<23	- 25
3	1	$\bar{16}$	160	156
3	1	$\bar{15}$	34	35
3	1	$\bar{14}$	109	100
3	1	$\bar{13}$	72	- 82
3	1	$\bar{12}$	131	-133
3	1	$\bar{11}$	26	- 24
3	1	$\bar{10}$	235	-261
3	1	$\bar{9}$	43	43
3	1	$\bar{8}$	225	-243
3	1	$\bar{7}$	82	71
3	1	$\bar{6}$	26	- 15
3	1	$\bar{5}$	17	11
3	1	$\bar{4}$	225	251
3	1	$\bar{3}$	43	42
3	1	$\bar{2}$	255	331
3	1	$\bar{1}$	94	-100
3	1	0	37	- 26
3	1	1	18	23
3	1	2	185	-203
3	1	3	64	- 52
3	1	4	129	-127
3	1	5	126	122
3	1	6	51	44
3	1	7	59	- 50
3	1	8	161	180
3	1	9	<25	5
3	1	10	121	123
3	1	11	39	- 35
3	1	12	<28	3
3	1	13	54	45
3	1	14	101	- 89
3	1	15	<26	2
3	1	16	86	- 85
3	1	17	25	23
3	1	18	56	56
5	1	$\bar{18}$	99	110
5	1	$\bar{17}$	56	- 54
5	1	$\bar{16}$	53	41
5	1	$\bar{15}$	47	38
5	1	$\bar{14}$	125	-111
5	1	$\bar{13}$	<28	- 19
5	1	$\bar{12}$	125	-121
5	1	$\bar{11}$	76	69
5	1	$\bar{10}$	70	- 69
5	1	$\bar{9}$	68	69
5	1	$\bar{8}$	159	169
5	1	$\bar{7}$	67	54
5	1	$\bar{6}$	282	358
5	1	$\bar{5}$	151	-155
5	1	$\bar{4}$	48	- 40
5	1	$\bar{3}$	66	- 58
5	1	$\bar{2}$	136	-150
5	1	$\bar{1}$	29	- 25
5	1	0	233	-248
5	1	1	58	- 44
5	1	2	188	-175
5	1	3	77	- 60
5	1	4	185	174
5	1	5	61	49
5	1	6	220	248
5	1	7	66	- 64
5	1	8	131	133
5	1	9	50	40
5	1	10	91	- 94
5	1	11	20	- 24
5	1	12	235	-245
5	1	13	95	94
5	1	14	101	- 92
5	1	15	<24	1
5	1	16	51	48
7	1	$\bar{17}$	33	- 34
7	1	$\bar{16}$	81	- 80
7	1	$\bar{15}$	72	67
7	1	$\bar{14}$	107	- 98
7	1	$\bar{13}$	<28	8
7	1	$\bar{12}$	<28	1
7	1	$\bar{11}$	49	52
7	1	$\bar{10}$	89	86
7	1	$\bar{9}$	60	- 50
7	1	$\bar{8}$	71	76
7	1	$\bar{7}$	25	28
7	1	$\bar{6}$	64	- 52
7	1	$\bar{5}$	92	- 87
7	1	$\bar{4}$	184	-199
7	1	$\bar{3}$	22	5
7	1	$\bar{2}$	167	-199
7	1	$\bar{1}$	47	44
7	1	0	43	- 29
7	1	1	<22	4
7	1	2	240	274
7	1	3	51	- 51
7	1	4	189	206
7	1	5	35	30
7	1	6	26	23
7	1	7	37	- 24
7	1	8	161	-178
7	1	9	68	68
7	1	10	177	-160
7	1	11	<28	- 12
7	1	12	47	37
7	1	13	59	54
7	1	14	136	145
7	1	15	35	- 34
7	1	16	125	155
9	1	$\bar{16}$	91	- 87
9	1	$\bar{15}$	38	33
9	1	$\bar{14}$	<25	- 21
9	1	$\bar{13}$	40	- 23
9	1	$\bar{12}$	116	120
9	1	$\bar{11}$	<28	15
9	1	$\bar{10}$	146	146
9	1	$\bar{9}$	61	- 58
9	1	$\bar{8}$	35	21
9	1	$\bar{7}$	74	74
9	1	$\bar{6}$	82	- 89
9	1	$\bar{5}$	53	- 49
9	1	$\bar{4}$	147	-161
9	1	$\bar{3}$	58	52
9	1	$\bar{2}$	<25	6
9	1	$\bar{1}$	<25	20
9	1	0	168	170
9	1	1	39	- 36
9	1	2	58	64
9	1	3	52	- 48
9	1	4	85	- 91
9	1	5	27	27
9	1	6	116	-107
9	1	7	49	- 28
9	1	8	112	-100
9	1	9	<28	8
9	1	10	89	82
9	1	11	32	- 40
9	1	12	151	146
9	1	13	37	34
9	1	14	66	70
11	1	$\bar{14}$	159	185
11	1	$\bar{13}$	27	- 31
11	1	$\bar{12}$	126	124
11	1	$\bar{11}$	<26	7
11	1	$\bar{10}$	47	- 39
11	1	$\bar{9}$	<28	- 16
11	1	$\bar{8}$	180	-186
11	1	$\bar{7}$	97	98
11	1	$\bar{6}$	144	-169
11	1	$\bar{5}$	<28	- 12
11	1	$\bar{4}$	40	36
11	1	$\bar{3}$	49	38
11	1	$\bar{2}$	98	103
11	1	$\bar{1}$	<28	9
11	1	0	104	97
11	1	1	<28	19
11	1	2	20	21
11	1	3	67	- 75
11	1	4	168	-161
11	1	5	<28	6
11	1	6	48	- 55
11	1	7	<27	- 13
11	1	8	70	70
11	1	9	<25	6
11	1	10	113	118
11	1	11	<20	- 15
11	1	12	51	53
13	1	$\bar{12}$	114	-117
13	1	$\bar{11}$	26	22
13	1	$\bar{10}$	133	-125
13	1	$\bar{9}$	<24	2
13	1	$\bar{8}$	72	- 63
13	1	$\bar{7}$	62	55
13	1	$\bar{6}$	138	136
13	1	$\bar{5}$	47	- 31
13	1	$\bar{4}$	226	217
13	1	$\bar{3}$	<27	13
13	1	$\bar{2}$	94	77
13	1	$\bar{1}$	59	- 48
13	1	0	108	-100
13	1	1	<27	18
13	1	2	209	-213
13	1	3	65	- 52
13	1	4	113	-108
13	1	5	43	36
13	1	6	84	83
13	1	7	<22	2
13	1	8	103	104
15	1	$\bar{8}$	129	149
15	1	$\bar{7}$	<19	14
15	1	$\bar{6}$	110	122
15	1	$\bar{5}$	37	- 29
15	1	$\bar{4}$	46	- 36
15	1	$\bar{3}$	<22	18
15	1	$\bar{2}$	173	-178
15	1	$\bar{1}$	27	- 7
15	1	0	168	-165
15	1	1	79	75
15	1	2	26	25
15	1	3	24	- 29
15	1	4	119	132
15	1	5	39	41
0	2	0	230	345
0	2	1	97	- 96
0	2	2	189	216
0	2	3	61	- 53
0	2	4	164	-150
0	2	5	67	42
0	2	6	190	-185
0	2	7	<21	- 7
0	2	8	188	-179
0	2	9	<25	2
0	2	10	136	141
0	2	11	75	67
0	2	12	155	166
0	2	13	<30	- 26
0	2	14	128	117
0	2	15	<28	6
0	2	16	45	- 37
0	2	17	67	- 68
0	2	18	92	-105
2	2	$\bar{18}$	22	23
2	2	$\bar{17}$	<22	14
2	2	$\bar{16}$	45	36
2	2	$\bar{15}$	<28	11
2	2	$\bar{14}$	126	118
2	2	$\bar{13}$	<30	23
2	2	$\bar{12}$	<29	6
2	2	$\bar{11}$	40	- 38
2	2	$\bar{10}$	101	-103
2	2	$\bar{9}$	<25	22
2	2	$\bar{8}$	212	-213
2	2	$\bar{7}$	42	- 31
2	2	$\bar{6}$	63	- 52
2	2	$\bar{5}$	<17	2
2	2	$\bar{4}$	179	164
2	2	$\bar{3}$	171	-138
2	2	$\bar{2}$	199	230
2	2	$\bar{1}$	46	- 45
2	2	0	185	-203
2	2	1	30	- 26
2	2	2	168	-158
2	2	3	88	- 67
2	2	4	245	-246
2	2	5	120	102
2	2	6	36	- 28
2	2	7	101	90
2	2	8	173	158
2	2	9	60	52
2	2	10	226	251
2	2	11	41	46
2	2	12	<30	18
2	2	13	76	- 65
2	2	14	147	-147
2	2	15	<27	7
2	2	16	187	-202
4	2	$\bar{18}$	70	92
4	2	$\bar{17}$	52	53
4	2	$\bar{16}$	118	124
4	2	$\bar{15}$	25	21
4	2	$\bar{14}$	64	50
4	2	$\bar{13}$	21	- 14
4	2	$\bar{12}$	121	-153
4	2	$\bar{11}$	<29	20
4	2	$\bar{10}$	61	- 61
4	2	$\bar{9}$	<26	19
4	2	$\bar{8}$	75	- 65
4	2	$\bar{7}$	48	- 38
4	2	$\bar{6}$	131	130
4	2	$\bar{5}$	55	45
4	2	$\bar{4}$	180	175
4	2	$\bar{3}$	124	-106
4	2	$\bar{2}$	97	79
4	2	$\bar{1}$	44	28
4	2	0	110	-107
4	2	1	113	- 86
4	2	2	90	- 63
4	2	3	32	- 25
4	2	4	59	49
4	2	5	147	133
4	2	6	249	272
4	2	7	<24	- 15
4	2	8	45	36
4	2	9	39	- 39
4	2	10	49	- 39
4	2	11	<30	5
4	2	12	185	-187
4	2	13	<29	- 14
4	2	14	108	-107
4	2	15	44	37
4	2	16	47	34
6	2	$\bar{17}$	34	- 33
6	2	$\bar{16}$	56	- 53
6	2	$\bar{15}$	<26	5
6	2	$\bar{14}$	125	-133
6	2	$\bar{13}$	36	- 31
6	2	$\bar{12}$	195	-185
6	2	$\bar{11}$	<29	20
6	2	$\bar{10}$	<29	18
6	2	$\bar{9}$	74	74
6	2	$\bar{8}$	142	151
6	2	$\bar{7}$	< 25	9
6	2	$\bar{6}$	182	194
6	2	$\bar{5}$	<23	1
6	2	$\bar{4}$	< 22	- 10
6	2	$\bar{3}$	141	-138
6	2	$\bar{2}$	140	-140
6	2	$\bar{1}$	<20	2
6	2	0	243	-279
6	2	1	<21	8
6	2	2	26	14
6	2	3	<22	2
6	2	4	81	84
6	2	5	17	3
6	2	6	71	53
6	2	7	< 26	14
6	2	8	75	- 74
6	2	9	42	- 41
6	2	10	69	- 67
6	2	11	<30	15
6	2	12	97	- 76
6	2	13	69	66
6	2	14	104	97
6	2	15	26	33
6	2	16	76	87
8	2	$\bar{16}$	132	-153
8	2	$\bar{15}$	<23	24
8	2	$\bar{14}$	61	- 51
8	2	$\bar{13}$	59	51
8	2	$\bar{12}$	82	69
8	2	$\bar{11}$	80	81
8	2	$\bar{10}$	260	300
8	2	$\bar{9}$	<29	17
8	2	$\bar{8}$	90	87
8	2	$\bar{7}$	49	- 38
8	2	$\bar{6}$	110	-107
8	2	$\bar{5}$	< 26	- 11
8	2	$\bar{4}$	217	-238
8	2	$\bar{3}$	25	- 19
8	2	$\bar{2}$	105	-110
8	2	$\bar{1}$	56	60
8	2	0	46	45
8	2	1	<25	6
8	2	2	227	232
8	2	3	<26	- 16
8	2	4	164	160
8	2	5	103	-102
8	2	6	41	30
8	2	7	51	- 2
8	2	8	193	-184
8	2	9	<30	- 10
8	2	10	50	- 41
8	2	11	67	55
8	2	12	55	41
8	2	13	49	50
8	2	14	95	100
10	2	$\bar{15}$	27	30
10	2	$\bar{14}$	125	133
10	2	$\bar{13}$	<24	17
10	2	$\bar{12}$	95	91
10	2	$\bar{11}$	49	- 49
10	2	$\bar{10}$	<29	8
10	2	$\bar{9}$	<29	3
10	2	$\bar{8}$	197	-189
10	2	$\bar{7}$	<30	1
10	2	$\bar{6}$	161	-168
10	2	$\bar{5}$	<29	7
10	2	$\bar{4}$	81	- 85
10	2	$\bar{3}$	71	76
10	2	$\bar{2}$	185	231
10	2	$\bar{1}$	<29	15
10	2	0	159	165
10	2	1	71	- 79
10	2	2	61	54
10	2	3	58	- 63
10	2	4	134	-165
10	2	5	62	- 69
10	2	6	195	-205
10	2	7	87	95
10	2	8	81	- 80
10	2	9	<27	28
10	2	10	114	125
10	2	11	<23	21
10	2	12	96	106
12	2	$\bar{12}$	45	- 41
12	2	$\bar{11}$	49	- 50
12	2	$\bar{10}$	44	- 44
12	2	$\bar{9}$	24	18
12	2	$\bar{8}$	93	- 98
12	2	$\bar{7}$	49	60
12	2	$\bar{6}$	69	69
12	2	$\bar{5}$	50	43
12	2	$\bar{4}$	155	153
12	2	$\bar{3}$	<29	12
12	2	$\bar{2}$	150	148
12	2	$\bar{1}$	51	- 40
12	2	0	100	- 87
12	2	1	51	- 34
12	2	2	142	-138
12	2	3	36	24
12	2	4	113	-117
12	2	5	<27	6
12	2	6	86	83
12	2	7	44	40
12	2	8	128	120
12	2	9	45	- 45
12	2	10	124	143
14	2	$\bar{10}$	65	- 72
14	2	$\bar{9}$	53	61
14	2	$\bar{8}$	<21	5
14	2	$\bar{7}$	28	34
14	2	$\bar{6}$	103	105
14	2	$\bar{5}$	< 24	- 10
14	2	$\bar{4}$	<25	6
14	2	$\bar{3}$	<25	2
14	2	$\bar{2}$	<25	1
14	2	$\bar{1}$	<25	3
14	2	0	141	-144
14	2	1	<25	8
14	2	2	61	- 62
14	2	3	40	33
14	2	4	47	41
14	2	5	<20	- 8
14	2	6	106	121
1	3	$\bar{17}$	57	63
1	3	$\bar{16}$	<24	4
1	3	$\bar{15}$	69	59
1	3	$\bar{14}$	119	110
1	3	$\bar{13}$	51	54
1	3	$\bar{12}$	231	247
1	3	$\bar{11}$	115	-110
1	3	$\bar{10}$	<28	24
1	3	$\bar{9}$	<26	- 28
1	3	$\bar{8}$	135	-119
1	3	$\bar{7}$	74	- 60
1	3	$\bar{6}$	205	-182
1	3	$\bar{5}$	50	54
1	3	$\bar{4}$	<16	13
1	3	$\bar{3}$	<14	12
1	3	$\bar{2}$	160	182
1	3	$\bar{1}$	61	- 58
1	3	0	129	148
1	3	1	94	- 88
1	3	2	24	- 28
1	3	3	50	- 58
1	3	4	179	-168
1	3	5	105	- 87
1	3	6	211	-186
1	3	7	147	142
1	3	8	46	30
1	3	9	<26	28
1	3	10	111	125
1	3	11	<29	- 20
1	3	12	95	82
1	3	13	51	- 48
1	3	14	108	-105
1	3	15	<26	13
1	3	16	83	- 85
3	3	$\bar{17}$	41	43
3	3	$\bar{16}$	151	164
3	3	$\bar{15}$	32	- 37
3	3	$\bar{14}$	85	86
3	3	$\bar{13}$	<29	- 27
3	3	$\bar{12}$	97	- 83
3	3	$\bar{11}$	50	- 47
3	3	$\bar{10}$	187	-207
3	3	$\bar{9}$	65	61
3	3	$\bar{8}$	126	-115
3	3	$\bar{7}$	<23	20
3	3	$\bar{6}$	40	49
3	3	$\bar{5}$	141	137
3	3	$\bar{4}$	345	371
3	3	$\bar{3}$	87	- 81
3	3	$\bar{2}$	142	139
3	3	$\bar{1}$	144	-160
3	3	0	140	-136
3	3	1	67	- 61
3	3	2	263	-254
3	3	3	125	116
3	3	4	211	-194
3	3	5	62	63
3	3	6	67	64
3	3	7	110	96
3	3	8	158	150
3	3	9	<28	22
3	3	10	101	102
3	3	11	<29	5
3	3	12	51	43
3	3	13	58	- 59
3	3	14	108	-116
5	3	$\bar{16}$	38	37
5	3	$\bar{15}$	49	- 61
5	3	$\bar{14}$	110	-114
5	3	$\bar{13}$	29	34
5	3	$\bar{12}$	125	-129
5	3	$\bar{11}$	< 29	21
5	3	$\bar{10}$	<29	5
5	3	$\bar{9}$	93	99
5	3	$\bar{8}$	195	216
5	3	$\bar{7}$	36	- 32
5	3	$\bar{6}$	212	203
5	3	$\bar{5}$	129	-118
5	3	$\bar{4}$	87	85
5	3	$\bar{3}$	147	-123
5	3	$\bar{2}$	245	-245
5	3	$\bar{1}$	<20	4
5	3	0	225	-235
5	3	1	20	- 17
5	3	2	146	-118
5	3	3	175	145
5	3	4	224	181
5	3	5	35	- 24
5	3	6	216	207
5	3	7	38	- 38
5	3	8	66	58
5	3	9	65	- 72
5	3	10	100	- 98
5	3	11	29	- 38
5	3	12	151	-170
5	3	13	<27	26
5	3	14	88	- 90
5	3	15	68	80
5	3	16	50	72
7	3	$\bar{16}$	69	- 82
7	3	$\bar{15}$	27	- 29
7	3	$\bar{14}$	94	-100
7	3	$\bar{13}$	75	72
7	3	$\bar{12}$	<29	- 25
7	3	$\bar{11}$	<29	30
7	3	$\bar{10}$	121	114
7	3	$\bar{9}$	<29	4
7	3	$\bar{8}$	88	95
7	3	$\bar{7}$	44	- 42
7	3	$\bar{6}$	120	-107
7	3	$\bar{5}$	45	42
7	3	$\bar{4}$	114	- 91
7	3	$\bar{3}$	<28	28
7	3	$\bar{2}$	139	-130
7	3	$\bar{1}$	101	94
7	3	0	94	78
7	3	1	<25	23
7	3	2	219	202
7	3	3	26	11
7	3	4	187	184
7	3	5	135	131
7	3	6	79	- 75
7	3	7	50	- 52
7	3	8	180	-191
7	3	9	<29	33
7	3	10	159	-157
7	3	11	91	94
7	3	12	<26	29
7	3	13	<23	25
7	3	14	122	126
9	3	$\bar{14}$	37	- 44
9	3	$\bar{13}$	66	74
9	3	$\bar{12}$	99	90
9	3	$\bar{11}$	<28	21
9	3	$\bar{10}$	119	117
9	3	$\bar{9}$	<29	- 13
9	3	$\bar{8}$	<30	20
9	3	$\bar{7}$	36	- 35
9	3	$\bar{6}$	70	- 71
9	3	$\bar{5}$	<29	14
9	3	$\bar{4}$	40	- 45
9	3	$\bar{3}$	<28	5
9	3	$\bar{2}$	73	71
9	3	$\bar{1}$	20	22
9	3	0	132	146
9	3	1	125	-133
9	3	2	<29	- 20
9	3	3	<29	- 17
9	3	4	41	- 35
9	3	5	42	- 50
9	3	6	158	-177
9	3	7	<29	18
9	3	8	78	- 70
9	3	9	47	41
9	3	10	62	59
9	3	11	50	50
9	3	12	87	118
9	3	13	34	- 38
11	3	$\bar{12}$	93	105
11	3	$\bar{11}$	57	- 58
11	3	$\bar{10}$	54	- 52
11	3	$\bar{9}$	<27	- 22
11	3	$\bar{8}$	131	-129
11	3	$\bar{7}$	<28	1
11	3	$\bar{6}$	140	-131
11	3	$\bar{5}$	110	93
11	3	$\bar{4}$	<29	22
11	3	$\bar{3}$	<29	6
11	3	$\bar{2}$	116	123
11	3	$\bar{1}$	<29	27
11	3	0	78	72
11	3	1	<29	- 26
11	3	2	<29	- 28
11	3	3	<29	8
11	3	4	61	- 45
11	3	5	<28	- 12
11	3	6	78	- 78
11	3	7	62	54
11	3	8	69	74
11	3	9	< 22	- 14
11	3	10	60	61
13	3	$\bar{10}$	124	-156
13	3	$\bar{9}$	44	42
13	3	$\bar{8}$	39	- 44
13	3	$\bar{7}$	29	31
13	3	$\bar{6}$	87	86
13	3	$\bar{5}$	69	69
13	3	$\bar{4}$	158	156
13	3	$\bar{3}$	32	- 36
13	3	$\bar{2}$	102	99
13	3	$\bar{1}$	46	- 46
13	3	0	64	- 56
13	3	1	67	- 58
13	3	2	154	-159
13	3	3	42	41
13	3	4	50	- 30
13	3	5	<22	10
13	3	6	43	44
15	3	$\bar{3}$	38	- 38
15	3	$\bar{2}$	100	-117
15	3	$\bar{1}$	<18	24
15	3	0	102	-116
15	3	1	45	53
0	4	0	200	226
2	4	0	71	- 63
4	4	0	57	- 60
6	4	0	91	- 85
8	4	0	141	144
10	4	0	208	211
12	4	0	<44	9
14	4	0	74	- 77
1	5	0	99	97
3	5	0	30	- 21
5	5	0	184	-195
7	5	0	94	79
11	5	0	94	73
13	5	0	64	- 64
0	6	0	195	161
2	6	0	42	- 13
4	6	0	126	-107
6	6	0	101	- 91
8	6	0	71	48
10	6	0	114	100
1	7	0	121	102
3	7	0	<44	12
5	7	0	136	-123
7	7	0	30	24
0	8	0	101	95
2	8	0	10	27

Table III

Interatomic Distances (Å.)

(A) Within the ZrO_8 Polyhedra[a]

M–A (σ 0.02)		M–B (σ 0.02)	
$Zr–O_1$	2.09_0	$Zr–O_1$	2.15_7
$Zr–O_2$	2.23_8	$Zr–O_5$	2.17_3
$Zr–O_4$	2.26_1	$Zr–O_8$	2.22_0
$Zr–O_6$	2.22_0	$Zr–O_9$	2.19_0
Av.	2.20_2	Av.	2.18_5
$Zr(C_2O_4)_4^{4-}$	2.230	$Zr(C_2O_4)_4^{4-}$	2.168

a (σ 0.04)		*m* (σ 0.04)	
$O_1–O_2$	2.77	$O_1–O_1$	2.34 ± 0.06
$O_4–O_6$	2.78	$O_2–O_9$	2.50 ± 0.04
Av.	2.78	$O_4–O_8$	2.49
HSM	2.63	$O_5–O_6$	2.63
MF	2.57	Av.	2.49
$Zr(C_2O_4)_4^{4-}$	2.570	HSM	2.63
		MF	2.57
		$Zr(C_2O_4)_4^{4-}$	2.563

g (σ 0.04)		*b* (σ 0.04)	
$O_1–O_4$	2.74	$O_1–O_8$	3.00
$O_1–O_5$	2.64	$O_2–O_5$	3.24
$O_1–O_6$	2.82	$O_5–O_9$	3.16
$O_1–O_8$	2.62	$O_8–O_9$	3.42
$O_2–O_5$	2.82	Av.	3.21
$O_2–O_8$	2.67	HSM	3.29
$O_4–O_9$	2.76	MF	3.27
$O_6–O_9$	2.72	$Zr(C_2O_4)_4^{4-}$	3.19
Av.	2.72		
HSM	2.63		
MF	2.72		
$Zr(C_2O_4)_4^{4-}$	2.735		

(B) Within the Sulfate Groups (σ_{S-O} 0.03, σ_{O-O} 0.04)

$S_1–O_2$	1.46_2	$S_2–O_4$	1.43_6
$S_1–O_3$	1.45_0	$S_2–O_5$	1.49_3
Av.	1.45_6	$S_2–O_6$	1.47_9
		$S_2–O_7$	1.43_6
		Av.	1.46_1
$O_2–O_2$	2.38	$O_4–O_5$	2.35
$O_2–O_3$	2.34	$O_4–O_6$	2.37
$O_2–O_3$	2.36	$O_4–O_7$	2.37
$O_3–O_3$	2.48	$O_5–O_6$	2.42
Av.	2.39	$O_5–O_7$	2.43
		$O_6–O_7$	2.41
		Av.	2.39

(C) O–O Distances < 3.20, Which Do Not Belong to a ZrO_8 Polyhedron or a Sulfate Group (σ 0.04)

$O_1–O_3$	2.80	$O_6–O_6$	2.81
$O_1–O_7$	2.96	$O_7–O_8$	2.71
$O_2–O_7$	3.12	$O_7–O_9$	2.72
$O_3–O_8$	2.75	$O_8–O_8$	3.18
$O_3–O_9$	2.75		

[a] Notations according to Hoard and Silverton[11] of Figure 2.

Each zirconium has an eightfold coordination (two hydroxide oxygens, four sulfate oxygens, and two water oxygens) with the bonds directed from the zirconium toward the vertices of a dodecahedron with triangular faces (the same coordination as in $Mo(CN)_8^{4-}$.[10] The interatomic distances in this coordination polyhedron and in the sulfate groups are listed in Table III. The distances in the ZrO_8 polyhedron (*cf.* Figure 2) are divided into six groups (M–A, M–B, *a*, *b*, *g*, and *m*) in accordance with the nomenclature of Hoard and Silverton for the $\bar{4}2m$ symmetry of the ideal $Mo(CN)_8^{4-}$ coordination.[11] Hoard and Silverton have recently discussed the stereochemistry of discrete eight coordination. Using their parameters and the average value of the M–A and M–B bonds (2.194 Å.) the oxygen–oxygen distances in the ZrO_8 polyhedron have been calculated for two models: (1) hard sphere-model (HSM) and (2) most favorable (MF) coordination which gives the greatest average orbital strength (2.981) using sp^3d^4 hybrid orbitals.[11,12] These calculated bond lengths are compared with the observed values in Table III; also included in the table are the observed values in the $Zr(C_2O_4)_4^{4-}$ polyhedron.[13]

The interatomic distances connecting the two trapezoids that make up the dodecahedron agree reasonably well with the MF distances and those observed in $Zr(C_2O_4)_4^{4-}$. The *a* distances are significantly longer than the values calculated for both models whereas three of the four *m* distances are significantly shorter than the HSM value but roughly comparable to the MF value. The main distortion of the polyhedron is within the trapezoids and is presumably caused by the formation of the double hydroxide bridge across one of the *m* edges and the linking of the polyhedron through sulfate groups into a three-dimensional network. The dimerization of the Zr–O polyhedrons usually occurs over one of the *m* edges when a dodecahedral coordination is a link in a polymeric complex (*cf.* the $(ZrF_6)_n^{2n-}$ ion in K_2ZrF_6.[14]

The two shortest of the Zr–O bonds, 2.09 Å. (of the M–A type) and 2.16 Å. (of the M–B type), are formed by the Zr and O_1 ($= OH^-$) atoms. As is to be expected, the Zr bonds to the double hydroxide bridge are the strongest Zr–O bonds in the structure.

The O–O distance in the hydroxide bridge is very short, only 2.34 ± 0.06 Å. This seems to be significant for other $M–(OH)_2–M$ arrangements. Distances of 2.36, 2.39, and 2.44 Å. have been found in $Zr(OH)_2SO_4$-(I) and $Zr(OH)_2(NO_3)_2(H_2O)_4$ (to be published). Johansson[15] found 2.40 Å. for the OH–OH bridges in $Al_2(OH)_2(H_2O)_{10}(SO_4)_2 \cdot 2H_2O$ and the corresponding selenate. He also found 2.34 Å. for similar bridges in $NaAl_{13}O_4(OH)_{24}(H_2O)_{12}(SeO_4)_4(H_2O)_x$.[16]

Comparison of the Structures of Several Basic Zirconium Salts

(A) **ZrO_2–SO_3–H_2O System.**—A series of three basic sulfates can be separated as hydrolysis products from 2–3 *M* neutral zirconium sulfate solutions at varying temperatures. The crystal structure determinations of

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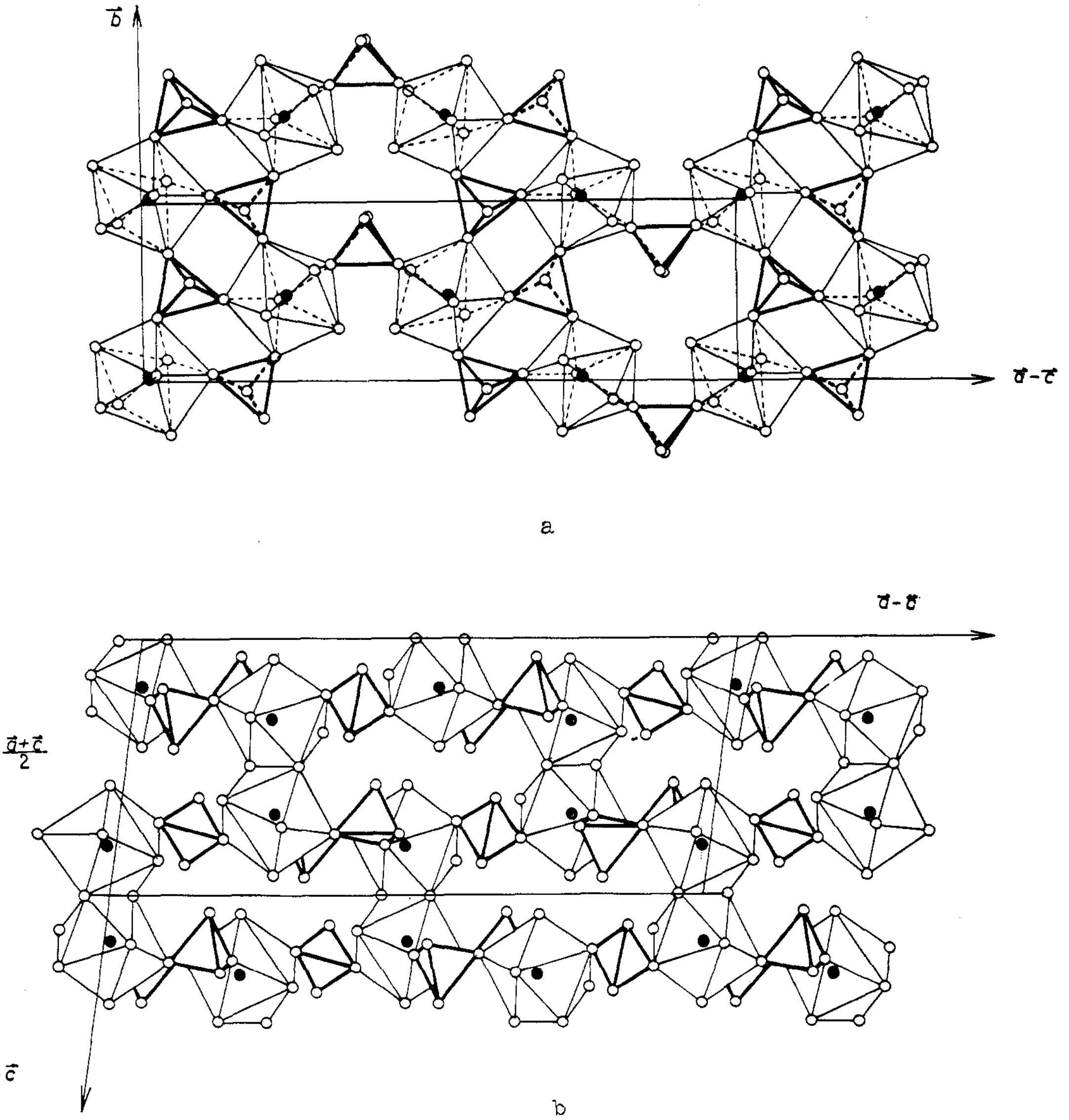

Figure 1.—(a) The structure of $Zr_2(OH)_2(SO_4)_3(H_2O)_4$, viewed along the $\vec{a}+\vec{c}$ direction of the structure. (b) The structure of $Zr_2(OH)_2(SO_4)_3(H_2O)_4$, viewed along the $\vec{b}$ direction of the structure. (● = Zr, ○ = oxygen; heavy lines connect oxygen atoms in SO_4^{2-} groups and light lines connect oxygen atoms in ZrO_8 polyhedra.)

these salts show increasing polymerization of the zirconium ion in the condensed phase with increasing temperature.

$Zr(SO_4)_2(H_2O)_4$.—The neutral salt is a layer structure with zirconium having an eightfold coordination of four sulfate oxygens with four water molecules in the form of an antiprism.[17] Each zirconium atom is connected by sulfate groups to four other zirconium atoms in the layer, and the layers are held together by hydrogen bonds.

$Zr_2(OH)_2(SO_4)_3(H_2O)_4$.—In this basic sulfate which crystallizes at 100°, two of the water molecules in the coordination sphere around zirconium are replaced by hydroxide bridges. Geometrically, the structure is still composed of layers with each zirconium connected to four others by sulfate groups but with entirely different symmetry. The Zr–O coordination has changed from an antiprism to the dodecahedral $Mo(CN)_8^{4-}$ type, and the zirconium and hydroxide ions are in the form of dimers with the formula $Zr_2(OH)_2^{6+}$.

$Zr(OH)_2SO_4$(I).—At approximately 200° a second basic salt, isomorphous with $Th(OH)_2SO_4$ and $U(OH)_2SO_4$,[18,19] crystallizes.[2b] In this salt all of the water molecules coordinated to zirconium are replaced by hydroxide groups, and the zirconium and hydroxide ions form infinite zigzag chains with the composition $(Zr(OH)_2)_n^{2n+}$. The chains are held together by sulfate groups with each sulfate group connecting three chains. The zirconium–oxygen coordination, however, has changed back to an antiprismatic one.

$Zr(OH)_2SO_4$(II).—This basic zirconium sulfate which separates at 300° (*cf.* Table I) has the same composition and almost the same lattice parameters as the one obtained at 200° except that it has a slight distortion to monoclinic symmetry so that the space group is $P2_1/n$

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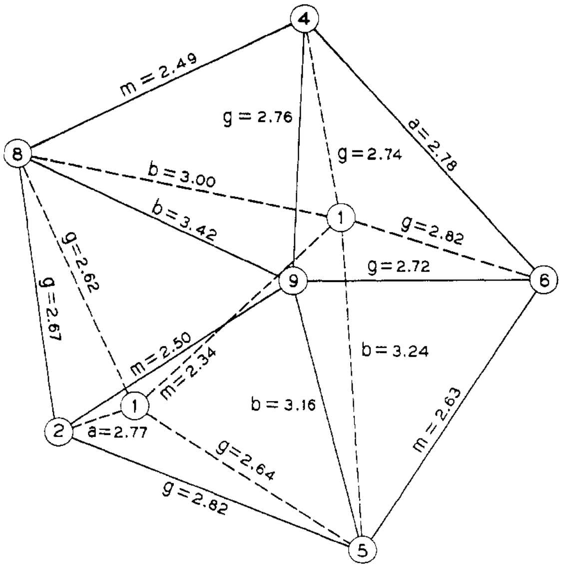

Figure 2.—The coordination of oxygen atoms around zirconium in $Zr_2(OH)_2(SO_4)_3(H_2O)_4$. The distances that should be equal according to the ideal $\bar{4}2m$ symmetry of the $Mo(CN)_8{}^{4-}$ coordination are marked according to Hoard and Silverton.[11]

instead of Pnma. Patterson projections show that the zirconium and sulfur positions are very similar, and the difference between the two compounds might be that the oxygen coordination of zirconium has changed. However, the crystals are mostly twinned, and a complete structure determination will not be reported until a three-dimensional refinement has been made.

Table IV

Complexes and Interatomic Distances in Zirconium Basic Salts

Salt	Ref.	Complex	Coord. no.	Symmetry	Zr–Zr, Å.	Zr–O, Å.	Av. Zr–O, Å.	O–O, Å.
$Zr_2(OH)_2(SO_4)_3(H_2O)_4$	...	$Zr_2(OH)_2{}^{6+}$	8	Dodecahedron	3.55	2.09–2.26	2.194	2.34–3.42
$Zr(OH)_2SO_4(I)$	...	$(Zr(OH)_2)_n{}^{2n+}$	8	Antiprism	3.58	2.14–2.28	2.19	2.38–2.89
$Zr_4(OH)_6(CrO_4)_5(H_2O)_2$	20	$(Zr_4(OH)_6CrO_4)_n{}^{8n+}$	7	Pentagonal pyramid	3.60	1.97–2.21	2.14	2.55–3.04
$Zr(OH)_2(NO_3)_2(H_2O)_4$		$(Zr(OH)_2NO_3(H_2O)_2)_n{}^{n+}$	8	Dodecahedron	3.57	2.12–2.37	2.21	2.39–3.32
$ZrOCl_2(H_2O)_8$ $ZrOBr_2(H_2O)_8$	21	$Zr_4(OH)_8(H_2O)_{16}{}^{8+}$	8	Antiprism	3.57	2.09–2.37	2.24	
ZrO_2	23	...	7			2.04–2.26	2.16	2.52–3.03
$Zr(SO_4)_2(H_2O)_4$	17	...	8	Antiprism		2.176–2.183	2.180	2.531–2.859
$Na_4Zr(CrO_4)\cdot 3H_2O$	24	$Zr(CrO_4)_4{}^{4-}$	8	Dodecahedron		2.144–2.244	2.199	2.563–3.19
Zirconium(IV) tetrakis-acetylacetonate	13		8	Antiprism		2.181–2.217	2.198	2.590–2.812

From the description above it may be noted that (1) as the mole ratio of $ZrO_2:SO_3$ changes from 1:2 to 1:1 in this series, the number of sulfate groups bonded to each zirconium remains constant at four, (2) there is a tendency to form linear zirconium complexes containing double hydroxide bridges, and (3) the changing symmetry of the zirconium coordination in this series of salts supports the theory presented by Hoard and Silverton that the energetics of direct bonding interactions differ very little for dodecahedral $Mo(CN)_8{}^{4-}$ and the antiprismatic configurations and that the choice between them is usually determined by other factors.[11]

(B) Other Basic Zirconium Salts. $Zr_4(OH)_6(CrO_4)_5(H_2O)_2$.—In this laboratory, the system ZrO_2–CrO_3–H_2O has been studied and the structure of $Zr_4(OH)_6(CrO_4)_5(H_2O)_2$ investigated.[20] The structure is built up of infinite chains of zirconium atoms bonded by hydroxide ions and chromate oxygens in the ratio 3:1 so that there is a double oxygen bridge between every pair of zirconium atoms. The resulting chains have the over-all composition $(Zr_4(OH)_6CrO_4)_n{}^{8n+}$. The zirconium atoms are coordinated to seven oxygen atoms in the shape of an almost regular pentagonal bipyramid.

$Zr(OH)_2(NO_3)_2(H_2O)_4$.—The crystals of this basic nitrate contain infinite zigzag chains bonded by double hydroxide bridges.[2b] The chains are more isolated in this crystal than in any of the basic salts discussed above as they are connected only by hydrogen bonds. The chains have the composition $(Zr(OH)_2NO_3(H_2O)_2)_n{}^{n+}$, and each zirconium atom is coordinated to eight oxygen atoms in the form of a dodecahedron with triangular faces.

$ZrOCl_2(H_2O)_8$, $ZrOBr_2(H_2O)_8$.—The zirconium atoms in these structures investigated by Clearfield and Vaughan[21] form finite complexes with four zirconiums at the corners of a slightly distorted square joined by hydroxide double bridges. The formula of the complex is $Zr_4(OH)_8(H_2O)_{16}{}^{8+}$, and the Zr–O coordination is eightfold in the shape of an antiprism. The results of X-ray diffraction studies on aqueous solutions of $ZrOCl_2(H_2O)_8$ and $HfOCl_2(H_2O)_8$ have been shown to be compatible with the existence of the above tetrameric complex in the solutions.[22]

The different complexes and coordinates of zirconium in the basic salts studied to date are summarized in Table IV. Also, the range and average Zr–Zr, Zr–O, and O–O interatomic distances in these salts are listed. For comparison the distances in ZrO_2,[23] $Zr(SO_4)_2(H_2O)_4$,[17] $Na_4Zr(C_2O_4)\cdot 3H_2O$,[24] and zirconium(IV) tetrakis(acetylacetonate)[13] have been given.

In summary it may be noted that the structure of all the basic zirconium salts reported to date have double hydroxide bridges as the bonding unit. No zirconyl

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groups were found, in agreement with the recent review by Clearfield.[25] In the sulfate, chromate, and nitrate systems there appears to be a tendency to form linear complexes. The predominant coordination number of zirconium in these salts is eight, and the ZrO_8 polyhedra have either the symmetry of a dodecahedron ($Mo(CN)_8^{4-}$) or an antiprism.

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Structure of Manganese(II) Croconate, $C_5O_5Mn(H_2O)_3$, a One-Dimensional Coordination Polymer

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A three-dimensional single crystal X-ray examination of $C_5O_5Mn(H_2O)_3$ has established its detailed stereochemical relationship to that of the isostructural copper(II) and zinc(II) croconates which possess significant structural differences. Crystals of $C_5O_5Mn(H_2O)_3$ are orthorhombic with eight formula species in a unit cell of symmetry Pbca and of dimensions $a = 12.07$ Å., $b = 8.20$ Å., $c = 15.63$ Å. A mixed anisotropic–isotropic least-squares refinement has produced final discrepancy factors of $R_1 = 8.2\%$ and $R_2 = 10.0\%$ for the data collected photographically with Mo Kα radiation. The polymeric structure is composed of infinite chains formed by the linkage of each manganese(II) to two adjacent oxygens of one croconate ring and to a single oxygen of another croconate ring such that only two nonadjacent oxygens per croconate are not manganese-coordinated. Each manganese(II) of similar localized environment is coordinated to six oxygens by the attachment of three waters. A comparison of the structural features of manganese(II) croconate with those of the homologous copper(II) and zinc(II) compounds is made.

Introduction

Recent X-ray studies[2] of the isostructural copper(II) and zinc(II) croconates not only have shown the overall structure of the first-row divalent transition metal croconates (which possess nearly identical powder patterns[3]) to consist of polymeric chains but also have revealed important differences in their detailed stereochemistry. In addition to a marked distortion of the oxygen environment for the six-coordinated d^9 copper(II) as contrasted to the more regular environment of the d^{10} zinc(II), the geometries of the croconate rings in the two metal complexes are different. The D_{5h} symmetry of the "free" electron-delocalized croconate dianion,[4] $C_5O_5^{2-}$, is essentially retained in copper(II) croconate, whereas in zinc(II) croconate the croconate ring of *idealized* C_{2v} symmetry is related to that of the localized α-enediol, croconic acid. In order to obtain further experimental evidence concerning the extent of the Jahn–Teller effect in determining the stereochemistry of this homologous series of oxygen-coordinated divalent metal ions, a three-dimensional X-ray investigation of the high-spin d^5 manganese(II) croconate (which like the zinc(II) electronic configuration does not exhibit Jahn–Teller instability) was carried out. The preparation and characterization of these transition metal complexes of general formula $C_5O_5M(H_2O)_3$ (where M = Mn, Fe, Co, Ni, Cu, and Zn) are given by West and Niu.[3]

Experimental Section

Crystals of $C_5O_5Mn(H_2O)_3$ were generously made available by Professor R. C. West and Dr. H. Y. Niu of the University of Wisconsin. Lattice parameters were obtained from *hk*0 and 0*kl* photographs with a NaCl-calibrated precession camera. Multiple-film equi-inclination Weissenberg photographs were obtained with Zr-filtered Mo Kα radiation for nine reciprocal levels, *h*0*l* through *h*8*l*. A total of 807 observed, independent maxima were measured by visual estimation with a calibrated set of intensities and then corrected for Lorentz-polarization effects. The crystal utilized for collecting the Weissenberg intensity data was sufficiently small ($\mu R_{max} < 0.5$) that absorption corrections were not made.

Results

Unit Cell and Space Group.—Crystals of $C_5O_5Mn(H_2O)_3$ are orthorhombic with lattice parameters $a =$

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[1] Alfred P. Sloan Research Fellow, 1963–1965.

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[3] R. West and H. Y. Niu, *J. Am. Chem. Soc.*, **85**, 2586 (1963).

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