rarely the same in any two cases. The lack of a regular coordination polyhedron around a potassium ion suggests that the molecular packing in most potassium salts is determined by the larger anion.

To investigate the intermolecular packing in more detail, all intermolecular distances less than 4.0 A were calculated. All intermolecular K···O distances less than 3.23 A and all O···O distances less than 3.48 A are tabulated in Table VI. The K···O distances are in the same range, 2.62–3.20 A, as those found in other salts. The O···O contacts of 3.060–3.143 A are in agreement with nonbonded O···O contacts in a number of different compounds. The intermolecular distances support the hypothesis that the packing is determined mainly by the permanganate ions.

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Crystal Structure of Potassium Manganate

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Potassium manganate obtained from the reduction of potassium permanganate forms black, acicular, orthorhombic crystals. The space group is Pnma and there are four molecules in the unit cell of dimensions $a = 7.667$, $b = 5.895$, and $c = 10.359$ A. The intensity data were measured using an automatic diffractometer and molybdenum radiation. The structure was refined by least-squares methods with anisotropic thermal parameters for each atom. The final residual (R) was 5.8% for the 687 observed reflections used in the analysis. The three independent Mn–O distances, after a correction for libration, are 1.647, 1.669, and 1.661 ± 0.008 A. The average Mn–O bond distance in the ion is 1.659 A. The average O–Mn–O angle is 109.5 ± 0.7°. Within the experimental error, the distances are all equal and the angles are all equal to the value expected for a regular tetrahedron. The increase of 0.030 A in the Mn–O bond length compared to the value in the permanganate ion is in agreement with the molecular orbital representation of the manganate ion.

Introduction

The three oxyanions of manganese, permanganate, manganate, and hypomanganate, offer a unique system for studying the effects of antibonding electrons on bond distances and angles in a simple ion. A precise determination of the crystal structure of potassium permanganate was carried out recently,[2] and the study of the potassium manganate ion is given below.

The axial ratios for potassium manganate were measured in 1831 by Mitscherlich,[3] who also reported that K_2MnO_4, K_2SO_4, K_2SeO_4, and K_2CrO_4 were isomorphous. Recently, Herbstein[4] determined the unit cell dimensions and space group from oscillation and Weissenberg photographs, but he made no attempt to obtain any molecular parameters or the Mn–O bond distance.

Experimental Section

Potassium manganate was prepared by the method reported by Scholder and Waterstradt.[5] The small, well-formed crystals produced during the reaction were used without recrystallization. Weissenberg photographs confirm the results given by Herbstein.[4] A second crystal with dimensions of 0.053 × 0.058 × 0.155 mm was used for the intensity measurements. The crystal was mounted on a thin glass fiber with the long dimension of the crystal (the $\bar{b}$ axis) parallel to the fiber axis. The crystal was dipped in liquid nitrogen to minimize extinction effects. The crystal was aligned on a General Electric single-crystal orienter with the $\bar{b}$ axis parallel to the ϕ axis of the orienter.

The unit cell dimensions were measured on the orienter using a narrow beam, 0.75° take-off angle, of molybdenum radiation (α_1 0.70926 and α_2 0.71354 A). The α_1–α_2 doublet could be resolved for 2θ values greater than 27° and the average dimensions are: $a = 7.667 \pm 0.004$, $b = 5.895 \pm 0.003$, $c = 10.359 \pm 0.005$ A. These values are in good agreement with the dimensions reported by Herbstein.[4] The density reported by Gosser[6] is 2.778 g cm^{-3}, and the value calculated for four molecules per unit cell is 2.796 g cm^{-3}. A take-off angle of 3.75°, which produces a wide beam, was used in the intensity measurements made with a scintillation counter. A linear amplifier–pulse height selector combination and a zirconium filter were used to approximate monochromatic radiation. The diffractometer was automated by the Datex Corp. and was controlled by a prepunched paper tape. The stationary counter–stationary crystal technique was employed in measuring 1490 reflections with $2\theta \leq 60.0°$. A 20-sec count was made for each reflection. Four standard reflections were counted after every 75 reflections to monitor the crystal alignment and beam stability and to check for any radiation damage. An analysis of the 21 standard values measured before, during, and after the intensity measurements did not reveal any significant change in the intensities of the four standard reflections.

Reflections of the type $0kl$ with $k + l = 2n + 1$ and $hk0$ with $h = 2n + 1$, required by the space group Pnma to be absent, were measured and used to derive a background curve. Equivalent reflections were averaged and then the background correction was made. Of the 740 independent reflections, the 687

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(3) J. W. Mellow, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 12, Longmans, Green and Co., London, 1932, p 285.

(4) F. H. Herbstein, *Acta Cryst.*, **13**, 357 (1960).

(5) R. Scholder and H. Waterstradt, *Z. Anorg. Allgem. Chem.*, **277**, 172 (1954).

(6) P. Groth, "Chemische Kristallographie," Vol. 2, Engelmann, Leipzig, 1908, p 351.

reflections which were greater than or equal to 1.2 times the background were considered as observed reflections. The 53 unobserved reflections were entered as −0.1 times the background count. Under the experimental conditions used in the intensity measurements, the α_1–α_2 doublet could be measured, and no correction for the splitting was made. The reduction of the intensity measurements to a set of observed structure amplitudes on an arbitrary scale was made in the usual manner.

Refinement of the Structure

Initial position parameters for all atoms were obtained from the structure of β-K_2SO_4[7] which is isomorphous with K_2MnO_4. A total of five least-squares cycles using individual isotropic thermal parameters reduced the usual residual R ($R = \Sigma|(|F_o| - |F_c|)|/\Sigma|F_o|$) to 0.083. Individual anisotropic thermal parameters were introduced and six least-squares cycles reduced R to 0.058. The largest shift in any parameter after the last cycle was less than 1×10^{-5}, and the refinement was considered to be complete.

The final positional parameters together with their estimated standard deviations obtained from the inverse matrix are given in Table I. The anisotropic thermal parameters are given in Table II, also with their estimated standard deviations. The set of observed and calculated structure factors on an absolute scale is given in Table III.

TABLE I

THE FINAL POSITIONAL PARAMETERS OBTAINED FROM THE LEAST-SQUARES REFINEMENT AND THEIR ESTIMATED STANDARD DEVIATIONS. THE LIBRATION-CORRECTED PARAMETERS FOR THE MnO_4^{2-} ION ARE ALSO GIVEN[a]

	Uncorrected			Libration corrected		
Atom	x (σ_x)	y (σ_y)	z (σ_z)	x	y	z
Mn	22,946 (11)	25,000[b]	42,058 (56)	22,945	25,000[b]	42,057
O(1)	1,659 (69)	25,000[b]	41,677 (47)	1,475	25,000[b]	41,673
O(2)	30,122 (76)	25,000[b]	57,172 (39)	30,183	25,000[b]	57,252
O(3)	30,584 (54)	2,227 (65)	34,773 (9)	30,667	2,046	34,713
K(1)	16,338 (19)	25,000[b]	8,698 (15)			
K(2)	−1,217 (17)	25,000[b]	69,855 (14)			

[a] All values are $\times 10^5$. [b] Value determined by the symmetry of the space group.

TABLE II

FINAL THERMAL PARAMETERS ($\times 10^5$) WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mn	578 (15)	925 (25)	447 (8)	0[b]	−14 (14)	0[b]
O(1)	665 (68)	2,478 (184)	773 (53)	0[b]	16 (93)	0[b]
O(2)	1,129 (76)	2,004 (158)	484 (41)	0[b]	−72 (91)	0[b]
O(3)	1,378 (62)	1,333 (95)	856 (38)	189 (131)	432 (81)	−583 (104)
K(1)	766 (22)	1,365 (39)	684 (14)	0[b]	105 (26)	0[b]
K(2)	653 (19)	1,446 (37)	491 (12)	0[b]	−13 (22)	0[b]

[a] The temperature factor is of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] Value required by the symmetry of the space group.

All the least-squares refinements were carried out using the full matrix. The weighting scheme used was: $\sqrt{w} = 1$ if $F_o \leq 20.0$ and $\sqrt{w} = 20.0/F_o$ if $F_o > 20.0$. The scattering factors for manganese, potassium, and oxygen were taken from the "International Tables."[8] The scattering factor for neutral manganese calculated using the TFD model was used since the effective charge on the manganese atom is probably quite low.

Discussion of the Structure

The Manganate Ion.—The bond distances and angles presented in Table IV were calculated using the final set of positional parameters obtained from the least-squares refinement. The estimated standard deviations for the positional parameters were used to calculate the errors in the bond distances, which are 0.005 A for Mn–O and K–O distances and 0.007 A for O–O distances. The four Mn–O bonds are equal within the experimental error and the average Mn–O bond is 1.646 ± 0.005 A. The expected error in the O–Mn–O angle is 0.6° and the six O–Mn–O angles are equal within this error, the average angle being 109.5 ± 0.6°.

The magnitude and orientation of the vibration ellipsoid of an atom were obtained from an analysis of the thermal parameters. The mean-square displacements and direction cosines are tabulated in Table V. The vibrations of the two potassium ions are not strongly anisotropic. In the case of K(1), two of the mean-square displacements are approximately equal, with the third one about 20% higher. For K(2), a similar situation exists except that the third displacement is about 20% lower. The smallest oxygen displacements are approximately parallel to the corresponding Mn–O bond. The angles between the smallest vibration and the corresponding Mn–O bond are 2° 37′, 8° 36′, and 9° 37′ for O(1), O(2), and O(3), respectively.

The manganate ion was assumed to be a rigid body and libration corrections for the positional parameters were calculated following the method given by Cruickshank.[9] The libration-corrected parameters are given in Table I, and the distances and angles calculated using these parameters are presented in Table IV. It is interesting to note that the libration corrections for the manganate ion averaged 0.013 A compared to an average of 0.022 A for the permanganate ion.[2] The small value for the manganate ion corresponds to stronger electrostatic forces in the case of the doubly charged ion. The average Mn–O distance has increased to 1.659 A, with an assumed error of ±0.008 A. The standard deviation has been increased by 0.003 A to take into account any errors introduced by the assumptions in the rigid-body treatment.

A comparison of the Mn–O bond lengths in the permanganate and manganate ions is informative. Both ions are tetrahedral with the average uncorrected Mn–O distance of 1.607 ± 0.005 A in MnO_4^- and 1.646 ± 0.005 A in MnO_4^{2-}. The difference of 0.039 A is definitely significant.

A more valid comparison might be between the average libration-corrected distances of 1.629 ± 0.008 A in MnO_4^- and 1.659 ± 0.008 A in MnO_4^{2-}. The difference of 0.030 A is certainly significant. It can be

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(7) M. T. Robinson, *J. Phys. Chem.*, **62**, 925 (1958).

(8) "International Tables for X-ray Crystallography," Vol. II, The Kynoch Press, Birmingham, England, 1962, p 201.

(9) D. W. J. Cruickshank, *Acta Cryst.*, **9**, 757 (1956); *ibid.*, **14**, 896 (1961).

TABLE III

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES ON AN ABSOLUTE SCALE (×10) FOR POTASSIUM MANGANATE

H= 0,K= 0		
2	394	393
4	815	-899
6	762	-797
8	687	-674
10	347	316
12	298	278
14	220	201
H= 1,K= 0		
1	74	-74
2	559	565
3	310	309
4	164	-149
5	454	-455
6	34	-25
7	297	290
8	49	36
9	64	-59
10	159	-148
11	69	-62
12	98	-88
13	120	116
14	67	50
H= 2,K= 0		
0	766	-833
1	290	-294
2	771	-856
3	644	-672
4	630	646
5	476	-484
6	596	593
7	207	202
8	88	77
9	385	370
10	149	142
11	60	53
12	351	-351
13	69	-51
14	122	-118
H= 3,K= 0		
1	809	-878
2	497	-515
3	617	645
4	385	-383
5	51	-38
6	80	61
7	270	267
8	144	140
9	55	-28
10	248	221
11	130	-122
12	78	74
13	55	40
H= 4,K= 0		
0	874	957
1	-19	-1
2	60	-65
3	599	641
4	105	-73
5	450	469
6	207	-197
7	273	-257
8	381	-375
9	295	-288
10	185	175
11	127	-127
12	62	51
13	76	66
H= 5,K= 0		
1	129	-131
2	658	690
3	63	59
4	464	479
5	136	-126
6	141	129
7	364	354
8	401	-391
9	70	-53
10	283	-284
11	123	-116
12	27	14
H= 6,K= 0		
0	412	405
1	209	-209
2	207	-206
3	279	-281
4	60	-46
5	283	-283
6	93	81
7	59	56
8	79	-70
9	298	282
10	128	138
11	43	36
12	95	-81
H= 7,K= 0		
1	184	180
2	187	-184
3	218	224
4	429	-444
5	420	-411
6	49	40
7	120	-121
8	187	184
9	-19	-17
10	149	156
11	83	76
H= 8,K= 0		
0	192	186
1	113	-105
2	72	-56
3	125	131
4	60	57
5	92	94
6	60	-63
7	42	-48
8	143	-148
9	38	11
H= 9,K= 0		
1	353	-394
2	139	134
3	82	96
4	57	5[illegible]
5	183	181
6	110	115
7	322	313
8	112	-129
H=10,K= 0		
0	50	38
1	167	-162
2	135	-136
3	87	-83
4	60	51
5	70	-72
H= 0,K= 1		
1	255	-234
3	1253	-1630
5	462	-450
7	580	563
9	313	301
11	357	345
13	182	-183
H= 1,K= 1		
1	579	569
2	296	-286
3	122	111
4	565	566
5	295	-287
6	267	-273
7	307	-316
8	141	128
9	170	-167
10	36	-11
11	72	74
12	118	-123
13	162	164
14	90	85
H= 2,K= 1		
0	493	-488
1	806	878
2	346	-341
3	283	277
4	286	272
5	194	193
6	399	391
7	26	8
8	67	62
9	496	-503
10	106	-99
11	27	6
12	127	-140
13	29	11
14	29	-25
H= 3,K= 1		
1	664	-669
2	-19	-0
3	33	36
4	431	448
5	323	321
6	379	-384
7	441	433
8	33	16
9	95	79
10	38	12
11	167	-165
12	31	-17
13	146	-143
H= 4,K= 1		
0	501	512
1	180	179
2	99	106
3	536	-551
4	169	-163
5	215	-207
6	298	-290
7	206	-211
8	149	-143
9	32	12
10	163	167
11	232	236
12	106	98
13	57	-58
H= 5,K= 1		
1	597	610
2	86	86
3	109	108
4	568	571
5	575	-587
6	122	-119
7	335	-344
8	40	-37
9	45	-33
10	124	-138
11	173	188
12	119	-131
H= 6,K= 1		
0	116	-112
1	208	210
2	228	-228
3	145	-134
4	130	128
5	60	57
6	224	230
7	151	197
8	37	20
9	155	-155
10	-19	6
11	34	32
H= 7,K= 1		
1	306	-303
2	444	-446
3	95	89
4	157	-158
5	135	133
6	173	-182
7	250	254
8	269	260
9	27	-28
10	175	187
H= 8,K= 1		
0	130	136
1	88	89
2	70	-59
3	220	-231
4	60	39
5	112	-111
6	-18	-2
7	85	93
8	102	-112
9	39	-5
H= 9,K= 1		
1	38	33
2	258	270
4	401	431
5	143	-152
6	85	-83
7	32	7
H=10,K= 1		
0	52	-43
1	152	159
2	148	-155
3	72	78
4	68	62
5	57	64
H= 0,K= 2		
0	1264	-1883
2	599	-578
4	271	249
6	963	1034
8	687	652
10	472	-434
12	236	-219
14	177	-153
H= 1,K= 2		
1	244	220
2	258	239
3	483	-478
4	281	-272
5	396	389
6	179	-176
7	151	-150
8	196	198
9	-18	14
10	115	121
11	36	34
12	-18	14
13	87	-86
14	-17	-15
H= 2,K= 2		
0	126	96
1	628	629
2	819	892
3	650	669
4	255	-242
5	124	123
6	741	-773
7	128	-119
8	102	-99
9	251	-244
10	34	-27
11	100	-103
12	277	295
13	49	37
H= 3,K= 2		
1	401	375
2	200	193
3	120	-114
4	490	507
5	56	40
6	-17	11
7	442	-430
8	229	-232
9	108	112
10	190	-186
11	149	155
12	52	-41
13	91	-86
H= 4,K= 2		
0	725	-733
1	396	-383
2	-18	13
3	662	-670
4	38	33
5	134	-115
6	233	226
7	167	158
8	316	324
9	168	165
10	164	-176
11	174	188
12	32	-31
13	43	-53
H= 5,K= 2		
1	325	318
2	664	-671
3	345	-339
4	427	-418
5	133	131
6	87	-76
7	167	-175
8	361	340
9	36	-29
10	225	246
11	57	77
12	26	2
H= 6,K= 2		
0	236	-218
1	378	367
2	163	160
3	298	295
4	68	-53
6	28	-24
7	-16	3
8	95	92
9	204	-210
10	143	-166
11	73	-82
H= 7,K= 2		
1	247	-236
2	308	302
3	103	-101
4	356	346
5	360	362
6	95	-96
7	46	64
8	112	-111
9	54	58
10	132	-141
H= 8,K= 2		
0	304	-296
1	65	56
2	87	88
3	117	-123
4	29	30
5	61	-56
6	-18	-8
7	35	20
8	111	119
9	37	-11
H= 9,K= 2		
1	346	362
2	207	-207
3	85	-90
4	-19	3
5	152	-155
6	72	-72
7	305	-298
H=10,K= 2		
0	42	28
1	128	133
2	99	105
3	69	64
4	93	-87
H= 0,K= 3		
1	-19	13
3	1027	1123
5	495	465
7	520	-491
9	297	-278
11	289	-267
13	159	150
H= 1,K= 3		
1	310	-296
2	163	160
3	225	-213
4	350	-346
5	248	255
6	216	221
7	304	307
8	141	-139
9	91	96
10	-16	10
11	54	-65
12	101	110
13	121	-126
H= 2,K= 3		
0	469	455
1	543	-535
2	204	207
3	270	-266
4	249	-256
5	251	-251
6	263	-260
7	43	38
8	53	-56
9	414	447
10	54	62
11	-18	-19
12	117	132
13	-18	-5
H= 3,K= 3		
1	495	475
2	132	121
3	51	26
4	374	-387
5	297	-280
6	283	278
7	405	-378
8	26	25
9	63	-67
10	29	-24
11	146	141
12	-18	3
H= 4,K= 3		
0	545	-525
1	148	-137
2	64	-60
3	450	434
4	194	191
5	176	175
6	192	195
7	171	-181
8	127	131
9	-17	-7
10	109	-118
11	192	-200
12	106	-102
H= 5,K= 3		
1	517	-498
2	136	-126
3	75	-70
4	421	-403
5	475	485
6	104	113
7	268	279
8	31	-5
9	34	32
10	114	129
11	148	-158
H= 6,K= 3		
0	149	150
1	207	-205
2	180	169
3	92	88
4	142	-131
5	37	-26
6	154	-165
7	193	-138
8	-18	-27
9	118	126
10	-18	-18
H= 7,K= 3		
1	303	285
2	410	401
3	114	-106
4	129	120
5	121	-116
6	159	153
7	188	-204
8	214	-214
9	-18	10
H= 8,K= 3		
0	131	-132
1	39	-51
2	47	50
3	207	198
4	30	-29
5	80	69
6	45	1
7	65	-68
8	100	105
H= 9,K= 3		
1	44	-41
2	227	-230
3	47	-52
4	376	-371
5	127	125
6	57	66
H=10,K= 3		
0	48	30
1	140	-150
H= 0,K= 4		
0	1246	1556
2	226	213
4	474	-434
6	529	-517
8	465	-439
10	248	236
12	212	199
H= 1,K= 4		
1	-17	-29
2	289	282
3	185	175
4	-17	39
5	279	-276
6	-18	9
7	161	168
8	-17	-13
9	41	-33
10	98	-111
11	27	-41
12	59	-68
H= 2,K= 4		
0	443	-432
1	192	-181
2	517	-491
3	355	-356
4	363	363
5	243	-249
6	434	432
7	128	121
8	49	57
9	230	252
10	84	88
11	35	42
12	253	-261
H= 3,K= 4		
1	383	-367
2	339	-322
3	320	322
4	295	-297
5	53	-50
6	-18	30
7	175	168
8	111	119
9	-18	-36
10	164	167
11	78	-83
12	64	58
H= 4,K= 4		
0	564	553
1	41	48
2	-18	-30
3	424	407
4	43	-44
5	268	274
6	127	-134
7	171	-169
8	240	-261
9	196	-206
10	117	126
11	92	-100
H= 5,K= 4		
1	119	-114
2	480	458
3	65	62
4	335	322
5	87	-89
6	89	86
7	231	245
8	281	-280
9	-19	-25
10	193	-212
H= 6,K= 4		
0	239	226
1	160	-154
2	153	-149
3	190	-187
4	32	-14
5	194	-182
6	63	65
7	31	33
8	35	-43
9	198	207
H= 7,K= 4		
1	163	153
2	160	-153
3	164	152
4	348	-318
5	326	-307
6	-19	32
7	95	-101
8	136	136
H= 8,K= 4		
0	154	147
1	70	-68
2	43	-43
3	95	104
4	36	36
5	92	73
6	61	-42
H= 9,K= 4		
1	303	-293
2	104	100
3	70	68
H= 0,K= 5		
1	187	-180
3	740	-739
5	215	-195
7	293	280
9	180	177
11	260	244
H= 1,K= 5		
1	288	279
2	175	-170
3	-18	-14
4	231	232
5	137	-143
6	141	-133
7	139	-146
8	66	74
9	108	-119
10	-19	3
11	44	48
H= 2,K= 5		
0	180	-182
1	475	458
2	188	-176
3	267	245
4	102	107
5	107	111
6	240	246
7	-17	5
8	43	45
9	300	-321
10	65	-75
11	35	-24
H= 3,K= 5		
1	363	-354
2	-19	20
3	47	41
4	166	173
5	189	183
6	208	-218
7	261	249
8	29	44
9	44	60
10	-18	4
H= 4,K= 5		
0	269	256
1	79	73
2	108	102
3	301	-291
4	69	-72
5	117	-116
6	218	-226
7	110	116
8	96	-100
9	-18	13
10	116	124
H= 5,K= 5		
1	341	332
2	-16	-4
3	70	69
4	359	332
5	329	-344
6	62	-64
7	216	-223
8	38	-41
9	27	-20
H= 6,K= 5		
0	44	-51
1	118	115
2	157	-151
3	66	-63
4	62	63
5	64	58
6	156	169
7	82	87
8	-17	17
H= 7,K= 5		
1	209	-192
2	279	-270
3	-19	32
4	124	-121
5	109	99
6	108	-113
H= 8,K= 5		
0	104	98
1	72	74
2	-18	-23
3	144	-136
4	-17	19
H= 0,K= 6		
0	701	-708
2	172	-176
4	150	138
6	448	422
8	340	324
10	236	-221
H= 1,K= 6		
1	-17	45
2	43	-38
3	160	-155
4	133	-130
5	174	175
6	80	-81
7	56	-72
8	92	92
9	-18	11
H= 2,K= 6		
0	144	155
1	192	193
2	367	349
3	245	252
4	138	-150
5	71	76
6	368	-365
7	61	-72
8	58	-64
9	121	-132
H= 3,K= 6		
1	123	121
2	148	152
3	108	-95
4	242	252
5	50	56
6	-19	10
7	178	-172
8	116	-128
9	52	51
H= 4,K= 6		
0	312	-322
1	137	-136
2	-18	7
3	325	-308
4	-18	15
5	77	-85
6	102	109
7	96	101
8	159	175
H= 5,K= 6		
1	156	142
2	338	-321
3	145	-131
4	224	-220
5	46	54
6	29	-44
7	96	-110
H= 6,K= 6		
0	94	-94
1	174	163
2	109	100
3	146	145
4	-18	-27
5	54	63
H= 7,K= 6		
1	152	-144
2	175	159
3	71	-63
H= 0,K= 7		
1	-18	8
3	443	434
5	234	224
7	247	-220
H= 1,K= 7		
1	97	-104
2	67	71
3	83	-95
4	100	-105
5	110	112
6	93	95
7	160	152
H= 2,K= 7		
0	173	195
2	74	82
3	154	-166
4	112	-115
5	141	-149
6	108	-110
7	29	36
H= 3,K= 7		
1	192	197
2	71	76
3	-19	20
4	144	-157
5	139	-136
6	100	109
H= 4,K= 7		
0	249	-266
1	54	-53
2	-18	-38
3	193	187
4	98	105
5	75	84
H= 5,K= 7		
1	240	-225
2	53	-61
3	-17	-28
H= 0,K= 8		
0	484	476
2	83	88
H= 1,K= 8		
1	-18	-8
2	105	96
3	64	70
H= 2,K= 8		
0	148	-157
1	76	-81
2	196	-197

TABLE IV

DISTANCES AND ANGLES IN THE MANGANATE ION

	Uncorrected	Libration corrected
	A	
Mn–O(1)	1.633	1.647
Mn–O(2)	1.655	1.669
Mn–O(3)	1.648	1.661
O(1)–O(2)	2.706	2.729
O(1)–O(3)	2.689	2.713
O(2)–O(3)	2.677	2.699
O(3)–O(3′)	2.685	2.705
	deg	
O(1)–Mn–O(2)	110.8	110.8
O(1)–Mn–O(3)	110.1	110.2
O(2)–Mn–O(3)	108.3	108.3
O(3)–Mn–O(3′)	109.1	109.0

noted that the assumptions involved in the rigid-body treatment are about the same for these two similar ions, and therefore the difference between the two distances will be more precise than the actual individual values.

The increase in the Mn–O bond distance of 0.030 A in the manganate ion is in agreement with its molecular orbital description. The extra electron in MnO_4^{2-} goes into the first excited orbital, which is a mixture of

TABLE V

ROOT MEAN-SQUARE DISPLACEMENTS, $(r^2)^{1/2}$, AND THEIR DIRECTION COSINES RELATIVE TO THE CRYSTALLOGRAPHIC AXES OF THE PRINCIPAL AXES OF THE THERMAL VIBRATION ELLIPSOIDS

Atom	$(r^2)^{1/2}$ [a]	Direction cosines ($\times 10^4$) with respect to *a*, *b*, *c*		
Mn	156	−0396	0000	9992
	131	−9992	0000	−0396
	128	0000	10000	0000
O(1)	209	0000	−10000	0000
	205	−0145	0000	−9999
	141	−9999	0000	0145
O(2)	188	0000	10000	0000
	184	−9822	0000	1876
	161	−1876	0000	−9822
O(3)	233	5152	−2085	8313
	194	8234	3894	−4127
	139	2377	−8971	−3723
K(1)	194	−1424	0000	−9898
	155	0000	10000	0000
	150	−9898	0000	1424
K(2)	163	−0360	0000	9994
	160	0000	−10000	0000
	139	−9994	0000	−0360

[a] Values × 10^3, in A.

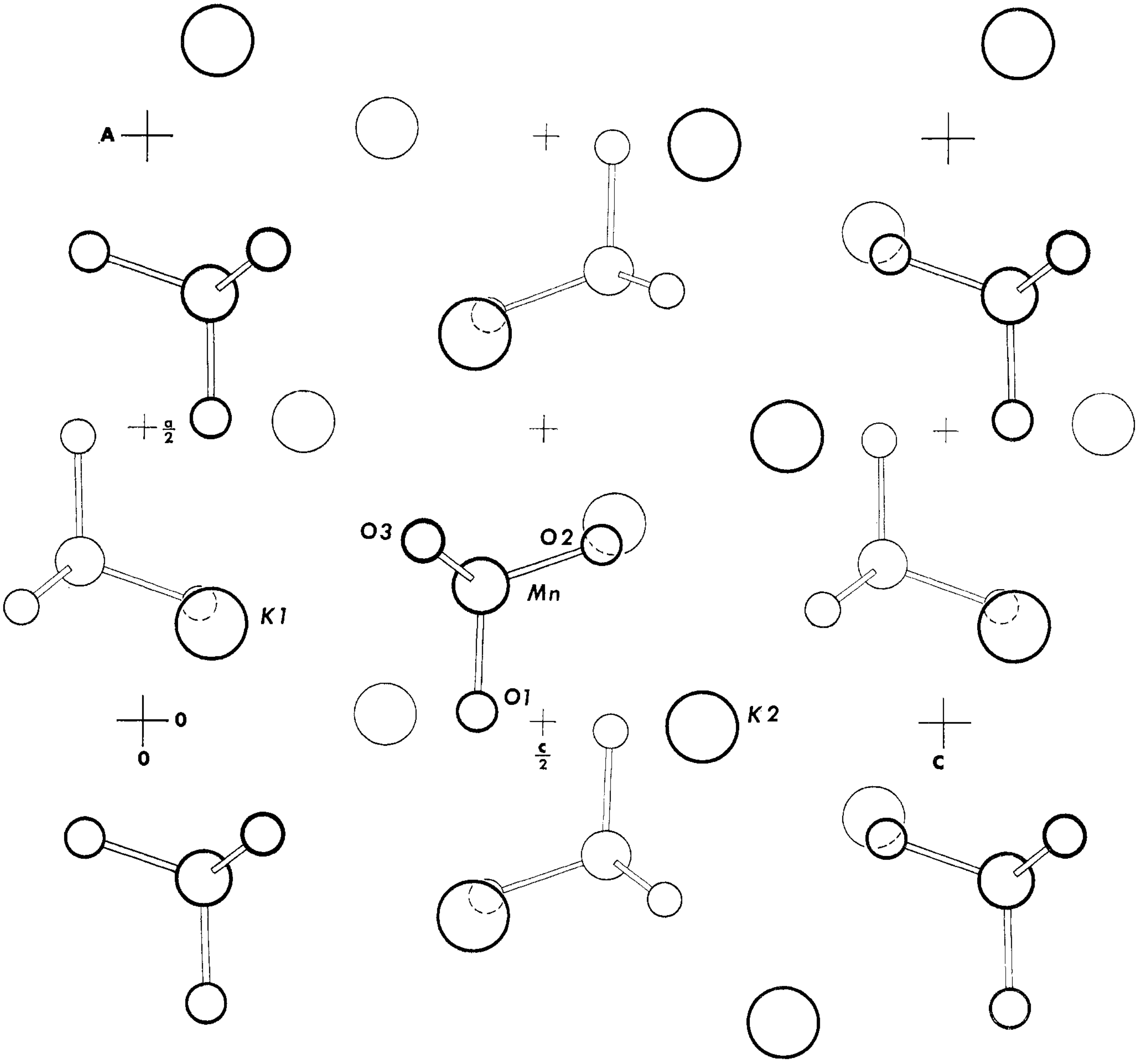

Figure 1.—An (010) projection of the structure of potassium manganate illustrating the ionic packing.

metal and ligand orbitals, and therefore should affect the bond length.

The only other ion which was studied in two different oxidation states with the same geometrical shape is bis(1,2-dicyanoethylene-1,2-dithiolato)nickel. X-Ray diffraction studies of this ion in the -2[10a] and -1[10b] states have been carried out, but the differences in the bond lengths in the two ions were considered marginally significant. In this case the extra electron is located mainly on the nickel atom and hence has little effect on the ligand bond lengths. In direct contrast are the effects in MnO_4^- and MnO_4^{2-} where the electron is involved with the ligands and the Mn–O bond lengths increase.

The Molecular Packing.—In simple one-to-one ionic solids, the crystal packing is determined to a large extent by the relative sizes of the two ions. Since there are two cations per anion in potassium manganate, a more complex structure was anticipated. An illustration of the arrangement of the ions in the unit cell is given in Figure 1, from which it is seen that the arrangement is indeed not a simple one.

All intermolecular distances less than 4.0 A were calculated. In Table VI all K···O contacts less than 3.3 A and all O···O contacts less than 3.5 A are tabulated. The coordination polyhedron of each potassium ion is different both as to the number of and distance from the surrounding oxygen atoms. In the case of K(2), there are six oxygen atoms less than 2.9 A away from the potassium ion, two at 2.719 A, two at 2.804 A, one at 2.739 A, and one at 2.767 A. These oxygen

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(10) (a) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 605 (1965); (b) C. J. Fritchie, Jr., *Acta Cryst.*, **20**, 107 (1966).

TABLE VI

INTERMOLECULAR DISTANCES[a]

x_i–x_j	Molecule	Distance, A
K(1)–O(1)	B(000)	2.690
K(1)–O(2)	B($\bar{1}$00)	3.230
K(1)–O(2)	E(100)	2.963
K(1)–O(3)	E(110)	2.961
K(1)–O(3)	B($\bar{1}$00)	3.130
K(1)–O(3)	A(000)	3.208
K(2)–O(1)	A(000)	2.027
K(2)–O(1)	D(011)	3.180
K(2)–O(2)	A(000)	2.739
K(2)–O(2)	B($\bar{1}$01)	2.767
K(2)–O(3)	C(001)	2.804
K(2)–O(3)	E(111)	2.719
O(4)–O(4)	D(001)	3.423
O(4)–O(6)	B($\bar{1}$00)	3.442
O(5)–O(6)	D(101)	3.499
O(5)–O(6)	E(111)	3.365
O(6)–O(6)	C(0$\bar{1}$0)	3.189

[a] x_1 is in the molecule A and x_j in the molecule specified after x_j. The molecules are located as follows: A: x, y, z; B: $1/2 + x, 1/2 - y, 1/2 - z$; C: $x, 1/2 - y, z$; D: $\bar{x}, \bar{y}, \bar{z}$; E: $-1/2 - x, -1/2 + y, -1/2 + z$.

atoms form a distorted octahedron around the potassium ion K(2). The coordination polyhedron is completed by three other longer contacts, one at 2.927 A and two at 3.180 A. However, in the case of K(1) there is only one oxygen atom less than 2.9 A away from the ion, at 2.690 A. The next nearest oxygen atoms around K(1) are two at 2.961 A and two at 2.963 A. The coordination is completed by five additional oxygen atoms, two at 3.130 A, two at 3.208 A, and one at 3.20 A. The complexity of the coordination polyhedra around the two ions is similar to that found in other potassium salts where the K···O distances range from 2.62 to 3.20 A.

The coordination of oxygen atoms around the two cations cannot be explained on the basis of anion–anion contacts. A survey of the O···O intermolecular distances tabulated in Table VI reveals only one distance (3.189 A) which could represent van der Waals contact. In all other cases the O···O distances are too long. Therefore, the crystal packing must be determined mainly by the cation–anion contacts.

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The Crystal Structure of Hydroxylamine-O-sulfonic Acid

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The crystal structure of hydroxylamine-O-sulfonic acid (H_2NOSO_3H) was determined from Weissenberg and precession single-crystal X-ray diffraction patterns. The diffraction patterns indicated that the crystals were orthorhombic, but satisfactory agreement with the visually observed intensity data was obtained only by assuming that the crystals were monoclinic and twinned on (001) or (100). This assumption led to a structure in which the oxygen atoms are located in a distorted tetrahedral fashion about the sulfur atom at distances of 1.42, 1.46, 1.47, and 1.68 A (average error = ±0.03 A); the oxygen atom involved in the long S–O bond is also bonded to a nitrogen atom at 1.48 A. The structure is compatible with the zwitterion form of the acid found from previous nmr studies of Richards and Yorke.[1] The crystal structure results should be considered corroborative rather than determinative of the zwitterion form.

Introduction

The determination of the structure of hydroxylamine-O-sulfonic acid, H_2NOSO_3H, was begun some 10 years ago at this laboratory in conjunction with a study of some hydroxylaminesulfonic acids and their salts.[2,3] The compounds are generally unstable, but H_2NOSO_3H was stable enough to form crystals. When it became apparent that the structure of H_2NOSO_3H could not be solved without assuming crystal twinning, the computations proved too involved for more than a rough determination of the structure in 1956. Recently there has been some interest in related structures.[4-6] On this basis it seemed worthwhile to undertake a three-dimensional refinement of H_2NOSO_3H using the original intensity data and employing the more elegant computational methods offered by modern computers.

Experimental Details

Hydroxylamine-O-sulfonic acid was prepared by the method of Sommer, Schulz, and Nassau.[7] The powdery product was recrystallized from water under reduced pressure at 0°. Single crystals were sealed in glass capillaries and examined by X-ray diffraction. The crystal constants are $a = 6.395 \pm 0.017$ A, $b = 10.707 \pm 0.010$ A, $c = 5.050 \pm 0.007$ A, and $\beta = 90.0 \pm 0.2°$. The X-ray density for four molecules per unit cell is 2.17 g/cm^3 which is in excellent agreement with the experimental value of 2.17 g/cm.[3]

Intensity data were taken including 0*kl* through 3*kl* and *hk*0 Weissenberg films and *h*0*l* precession films. The relative intensities were estimated visually using a calibrated strip. Lorentz

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(1) R. E. Richards and R. W. Yorke, *J. Chem. Soc.*, 2821 (1959).
(2) R. F. Belt, Ph.D. Theisis, University of Iowa, 1956.
(3) R. F. Belt and N. C. Baenziger, *J. Am. Chem. Soc.*, **79**, 316 (1957).
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(6) C. Pascard-Billy, *ibid.*, **18**, 829 (1965).
(7) F. Sommer, O. Schulz and M. Nassau, *Z. Anorg. Allgem. Chem.*, **147**, 142 (1925).