transformed to a Cartesian system, and the view is along the vector from the yttrium ion to the center of the quadrilateral O(3)–O(6)–O(7)–O(8). The distances and angles of this polyhedron are listed in Table IV. In addition to distortions in lengths and angles, the O(1)–O(5)–O(4)–O(9) quadrilateral is folded about the O(1)–O(4) diagonal.

In spite of the deviations from $\bar{8}$2m symmetry, the average parameters for this polyhedron agree well with those calculated by Hoard and Silverton for minimization of the ligand repulsive energy.[10] In the notation of Hoard and Silverton, we have $l = 1.270$, $s = 1.195$, $l/s = 1.064$, and $\theta = 57.1°$, as compared with their values 1.258, 1.190, 1.057, and 57.3°.

The distortion of the polyhedron can be attributed to the presence of two chemically different ligands bonded to the same central metal atom. The geometric constraints of the bidentate acetylacetonate groups *vs.* the monodentate water molecules undoubtedly contribute to the deformation, as does the difference in the mutual repulsion of the two ligands.

[10] J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963).

CONTRIBUTION FROM THE CHEMISTRY DIVISION, RESEARCH DEPARTMENT,
U. S. NAVAL ORDNANCE TEST STATION, CHINA LAKE, CALIFORNIA

Crystal Structure of Potassium Permanganate

BY GUS J. PALENIK[1]

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Potassium permanganate forms deep purple, orthorhombic crystals with $a = 9.105$, $b = 5.720$, and $c = 7.425$ A. The space group is Pnma and there are four molecules per unit cell. 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 4.6% for the 561 observed reflections used in the analysis. After a correction for libration, the three independent Mn–O distances are 1.622, 1.625, and 1.634 A. The average Mn–O distance in the ion is 1.629 ± 0.008 A. The average O–Mn–O angle is 109.4 ± 0.7°. Therefore, the permanganate ion can be described as a manganese atom surrounded by four oxygen atoms at the corners of a regular tetrahedron.

Introduction

Manganese is unique in that it forms three oxy anions: permanganate, manganate, and hypomanganate. They are all tetrahedral MnO_4 ions with a charge of −1, −2, and −3, respectively. The permanganate ion has been the subject of several papers[2] discussing the electronic structure of the ion. It is generally agreed that the extra electrons in the manganate and hypomanganate ions occupy an antibonding orbital. The Mn–O bond should therefore lengthen in going from permanganate to manganate to hypomanganate. A study of these ions should provide a comparison of the effect of the antibonding electrons on the size and shape of the MnO_4 tetrahedron.

The crystal structure of potassium permanganate was originally studied by Mooney,[3] who reported the ion to be "a nearly regular tetrahedron" with Mn–O distances of 1.68, 1.52, 1.58, and 1.58 A, the average distance being 1.59 A. More recently Ramaseshan, Venkatesan, and Mani,[4] in the course of studying anomalous dispersion with zonal data, reported Mn–O distances of 1.56, 1.56, 1.54, and 1.54 A with an average of 1.55 A. Since neither previous study was sufficiently precise to detect small changes in bond distances, a redetermination of the crystal structure of potassium permanganate was undertaken.

Collection and Reduction of the X-Ray Data

Crystals were grown by slowly cooling a warm aqueous solution of potassium permanganate in a dewar. A crystal was cleaved to give a parallelepiped of approximately 0.15 × 0.15 × 0.15 mm. The crystal was mounted on a glass fiber with the $\bar{b}$ axis parallel to the fiber axis and dipped in liquid nitrogen to minimize extinction effects.

The unit cell and intensity measurements were carried out with the General Electric single-crystal orienter, using molybdenum radiation (α_1 0.70926, α_2 0.71354 A). The unit cell dimensions were determined using a very narrow beam. The α_1–α_2 doublet could be resolved for values greater than about 27°, and the average values from these measurements are: $a = 9.105 \pm 0.005$, $b = 5.720 \pm 0.003$, $c = 7.425 \pm 0.004$ A. The reported density[5] is 2.703 g cm^{-3}, and the value calculated for four molecules per unit cell is 2.714 g cm^{-3}.

A wide beam was used for the intensity measurements which were made with a scintillation counter. A linear amplifier–pulse height selector combination together with a zirconium filter provided almost mono-

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[1] Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada.

[2] (a) H. Basch, A. Viste, and H. B. Gray, *J. Chem. Phys.*, **44**, 10 (1966); (b) L. Oleari, G. de Michelis, and L. di Sipio, *Mol. Phys.*, **10**, 111 (1966), and references therein.

[3] R. C. L. Mooney, *Phys. Rev.*, **37**, 1306 (1931).

[4] S. Ramaseshan, K. Venkatesan, and N. V. Mani, *Proc. Indian Acad. Sci.*, **A46**, 95 (1957).

[5] "Handbook of Chemistry and Physics," 44th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1963, p 632.

chromatic 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 609 reflections with $2\theta \leq 60.0°$. A 20-sec count was made for each reflection. Five standard reflections were counted periodically with ten values being obtained during the course of the intensity measurements. The standard deviation of each of the five reflections was less than or equal to the expected value based on counting statistics. Reflections of the type $0kl$ with $k + 1 = 2n + 1$ and $hk0$ with $h = 2n + 1$, required by the space group Pnma to be absent, were measured and used to derive a background curve. The 561 reflections which were greater than or equal to 1.2 times the background count were considered to be observed reflections. Those reflections which were less than 1.2 times the background were entered as -0.1 times the background count. Under the conditions of the intensity measurements, the α_1–α_2 doublet could be measured, and no correction for the splitting was applied. The reduction of these data to a set of observed amplitudes on an arbitrary scale was carried out in the usual manner.

Solution and Refinement of the Structure

Initial positional parameters for the Mn and K atoms were obtained from the structure of perchloric acid monohydrate,[6] which is isomorphous with potassium permanganate. A difference Fourier was calculated to obtain the oxygen atom positions. Two successive observed Fourier syntheses reduced the conventional R factor ($R = \Sigma|(|F_o| = |F_c|)|/\Sigma|F_o|$) to 21.4%. At this point further refinement was carried out by least-squares methods.

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^- Ion Are Also Given[a]

	Uncorrected			Libration corrected		
Atom	x (σ_x)	y (σ_y)	z (σ_z)	x	y	z
Mn	43,835 (7)	25,000[b]	19,182 (9)	43,834	25,000[b]	19,181
K	31,872 (11)	25,000[b]	65,871 (15)			
O(1)	31,416 (52)	25,000[b]	3,944 (67)	31,250	25,000[b]	3,713
O(2)	59,941 (50)	25,000[b]	10,452 (78)	60,156	25,000[b]	10,319
O(3)	42,047 (33)	2,038 (61)	31,567 (44)	42,033	1,747	31,782

[a] All values are $\times 10^5$. [b] Value determined by the symmetry 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	591 (10)	2184 (29)	1050 (15)	0[b]	27 (12)	0[b]
K	623 (13)	3365 (46)	1249 (20)	0[b]	−90 (21)	0[b]
O(1)	1347 (62)	4213 (181)	1700 (84)	0[b]	−1496 (115)	0[b]
O(2)	1014 (50)	4510 (201)	2358 (102)	0[b]	1435 (134)	0[b]
O(3)	1125 (35)	2417 (97)	1922 (62)	−185 (95)	−288 (60)	1088 (112)

[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.

Using individual isotropic temperature factors, five least-squares cycles in which the full matrix was computed reduced R to 9.7%. Anisotropic temperature factors for each atom were introduced, and five least-squares cycles produced an R of 4.6%. The largest shift in any parameter after the last cycle was less than 1×10^{-5}, and the refinement was considered complete.

The final positional parameters are given in Table I together with the estimated standard deviations obtained from the inverse matrix. 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.

The weighting scheme used in the least-squares refinement was: $\sqrt{w} = 1$ if $F_o \leq 8.0$ and $\sqrt{w} = 8.0/F_o$ if $F_o > 8.0$. The scattering factors for manganese, potassium, and oxygen were taken from the "International Tables."[7] The scattering factor for neutral manganese calculated using the TFD model was used since the net charge on the manganese ion was calculated by Ballhausen and Gray[8] to be 0.66.

Discussion of the Structure

The Permanganate Ion.—The bond distances and angles in the permanganate ion were calculated using the positional parameters obtained from the least-squares refinement. These distances and angles are given in Table IV. Using the standard deviations for the positional parameters obtained from the least-squares refinement, the errors in bond lengths are 0.005 A for Mn–O and K–O bonds and 0.007 A for O–O bonds. The corresponding error in the O–Mn–O angles is 0.6°. The average of the four Mn–O bond distances is 1.607 ± 0.005 A, with all the Mn–O bonds being equal within the experimental error. The average O–Mn–O angle is 109.4 ± 0.6°, with all of the angles being equal within experimental error.

The only other tetrahedral manganese(VII) compound that can be compared with permanganate is the isoelectronic MnO_3F molecule. From microwave measurements[9] the Mn–O distance was determined to be 1.586 ± 0.005 A. The difference between the two Mn–O distances is possibly significant.

The thermal parameters obtained from the least-squares refinement were analyzed to determine the magnitude and orientation of the vibration ellipsoids.

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(6) F. S. Lee and G. B. Carpenter, *J. Phys. Chem.*, **63**, 279 (1959).

(7) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 201.

(8) C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," W. A. Benjamin, Inc., New York, N. Y., 1964, pp 123–128.

(9) A. Javan and A. Engelbrecht, *Phys. Rev.*, **96**, 649 (1954).

TABLE III

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

K= 0,L=-0		
2	438	402
4	384	-357
6	296	-265
8	668	-662
10	111	-55
12	89	73
K= 0,L= 1		
1	269	-244
2	476	437
3	156	-141
4	1119	1167
6	276	270
7	112	105
8	90	-86
9	-11	12
10	77	-76
11	85	82
12	242	-242
K= 0,L= 2		
0	801	-911
1	504	-487
2	528	-509
3	199	181
4	69	57
5	40	-40
6	283	268
7	470	-452
8	331	323
9	121	126
10	101	107
11	99	105
12	30	-17
K= 0,L= 3		
1	45	46
2	422	-406
3	657	644
4	432	-408
5	360	-353
6	89	-93
7	149	-150
8	30	28
9	60	-54
10	83	95
11	211	-211
12	51	51
K= 0,L= 4		
0	217	-246
1	271	268
2	134	126
3	275	268
4	143	94
5	233	215
6	80	-75
7	270	254
8	40	43
9	99	-106
10	71	-69
11	123	-127
K= 0,L= 5		
1	201	-190
2	132	129
3	212	-200
4	389	-443
5	53	39
6	60	56
7	144	138
8	58	63
9	172	176
10	46	-53
11	101	101
K= 0,L= 6		
0	450	495
1	91	-98
2	49	41
3	203	-205
4	58	-56
5	184	-186
6	23	15
7	48	-45
8	225	-235
9	28	24
10	30	-33
K= 0,L= 7		
1	190	187
2	199	197
3	58	-61
4	325	332
5	63	60
6	82	82
7	111	-110
8	40	-44
9	108	-108
K= 0,L= 8		
0	270	-286
1	133	-131
2	150	-151
3	77	70
4	29	-9
5	103	105
6	125	126
7	85	-85
8	154	160
K= 0,L= 9		
1	35	-35
2	147	-152
3	84	87
4	136	-135
5	46	-39
6	100	-102
K= 0,L=10		
0	66	53
1	48	46
2	134	135
3	25	26
K= 1,L=-0		
2	850	1009
4	38	-24
6	597	615
8	126	125
10	313	-317
12	66	-65
K= 1,L= 1		
0	512	-570
1	91	90
2	800	-849
3	63	-66
4	29	21
5	217	-224
6	565	561
7	30	-28
8	138	138
9	43	-37
10	184	182
11	61	59
12	48	45
K= 1,L= 2		
1	806	825
3	350	-343
4	433	-427
5	104	97
6	279	-258
7	283	-270
8	-11	-7
9	242	-241
10	157	156
11	77	75
12	76	77
K= 1,L= 3		
0	94	98
1	364	-359
2	203	192
3	529	504
4	62	57
5	585	570
6	59	-56
7	97	-95
8	142	-136
9	67	62
10	86	-99
11	138	-135
12	-11	-0
K= 1,L= 4		
1	492	-489
2	-10	-3
3	44	-37
4	223	210
5	19	-8
6	74	-69
7	251	238
8	39	-43
9	270	268
10	59	56
11	23	12
K= 1,L= 5		
0	192	-213
1	151	-148
2	309	298
3	427	-422
4	20	10
5	306	-296
6	245	-232
7	49	-47
8	113	109
9	49	45
10	70	-72
11	110	114
K= 1,L= 6		
1	214	228
2	343	339
3	130	128
4	30	29
5	59	-55
6	171	164
7	169	-166
8	31	28
9	124	-118
10	141	-147
K= 1,L= 7		
0	137	-145
1	188	182
2	200	-199
3	77	82
4	31	-28
5	55	53
6	148	147
7	119	120
8	88	91
9	67	-66
K= 1,L= 8		
1	20	4
2	169	-170
3	149	-154
4	160	-161
5	133	128
6	126	-123
7	25	25
8	21	10
K= 1,L= 9		
0	177	197
1	56	-55
2	97	99
3	40	40
4	-11	-0
5	56	55
6	71	-70
K= 1,L=10		
1	63	-63
2	23	14
3	-11	1
K= 2,L=-0		
0	953	-1215
2	95	91
4	58	43
6	81	-81
8	431	449
10	75	80
12	22	-16
K= 2,L= 1		
1	435	444
2	209	203
3	145	140
4	510	-516
5	252	-256
6	181	-185
7	168	-172
8	48	-41
9	17	-22
10	-11	-10
11	53	-52
12	192	198
K= 2,L= 2		
0	230	231
1	612	611
2	174	160
3	293	294
4	70	70
5	194	198
6	54	-45
7	315	316
8	207	-209
9	188	-191
10	105	-106
11	116	-123
12	-11	-13
K= 2,L= 3		
1	505	-513
2	180	183
3	543	-535
4	219	212
5	509	505
6	70	64
7	287	290
8	-11	5
9	69	72
10	58	-57
11	142	145
K= 2,L= 4		
0	146	158
1	410	-415
2	117	-112
3	567	-552
4	58	-53
5	339	-327
6	85	82
7	175	-173
8	37	-40
10	53	50
11	142	147
K= 2,L= 5		
1	404	394
2	200	-201
3	198	191
4	273	285
5	165	-157
6	53	-44
7	228	-220
8	-11	-18
9	168	-171
10	60	65
K= 2,L= 6		
0	238	-269
1	124	136
2	34	31
3	284	282
4	-11	-3
5	219	218
6	89	-86
7	29	30
8	179	175
9	51	-51
10	44	42
K= 2,L= 7		
1	194	-194
2	70	-69
3	41	41
4	200	-202
5	40	-36
6	72	-66
7	117	114
8	-11	1
K= 2,L= 8		
0	144	165
1	120	116
2	90	90
3	50	-51
4	38	33
5	90	-91
6	62	62
7	64	64
K= 2,L= 9		
1	-11	4
2	94	97
3	73	-73
4	85	84
5	52	53
K= 2,L=10		
0	28	-29
1	55	-55
2	112	-106
K= 3,L=-0		
2	475	-504
4	16	16
6	393	-418
8	102	-113
10	201	220
K= 3,L= 1		
0	207	226
1	18	-16
2	455	467
3	139	136
4	31	34
5	180	183
6	330	-339
7	-11	2
8	90	-98
9	-11	12
10	146	-150
11	49	-50
K= 3,L= 2		
1	583	-583
2	255	256
3	171	176
4	236	248
6	192	192
7	230	230
8	-11	22
9	180	187
10	109	-110
11	55	-60
K= 3,L= 3		
0	101	-105
1	126	130
2	129	-128
3	452	-442
4	35	-32
5	429	-435
6	39	46
7	71	74
8	103	104
9	24	-18
10	69	73
11	115	114
K= 3,L= 4		
1	426	425
2	-11	-10
3	35	34
4	166	-164
5	38	-38
6	43	44
7	214	-215
8	31	38
9	205	-209
10	35	-36
K= 3,L= 5		
0	157	174
1	121	121
2	186	-179
3	344	337
4	34	-25
5	248	242
6	146	143
7	39	35
8	83	-81
9	48	-45
10	61	58
K= 3,L= 6		
1	174	-184
2	206	-207
3	99	-100
4	-11	0
5	60	53
6	130	-123
7	133	133
8	33	-34
9	97	93
K= 3,L= 7		
0	77	85
1	130	-128
2	138	139
3	57	-60
4	29	29
5	43	-43
6	102	-98
7	95	-93
8	64	-65
K= 3,L= 8		
1	21	-13
2	112	117
3	109	111
4	117	116
5	86	-83
6	99	95
K= 3,L= 9		
0	134	-148
1	32	34
2	77	-75
3	46	-43
4	-11	-0
K= 4,L=-0		
0	851	946
2	186	194
4	102	-108
6	131	-137
8	352	-359
10	40	-51
K= 4,L= 1		
1	102	-95
2	205	200
3	94	-90
4	523	529
5	81	82
6	135	148
7	60	61
8	42	-42
9	-11	15
10	52	-52
11	45	49
K= 4,L= 2		
0	384	-400
1	230	-213
2	215	-215
3	34	-24
4	24	22
5	58	-59
6	138	139
7	217	-217
8	185	190
9	69	75
10	65	66
K= 4,L= 3		
1	104	104
2	179	-176
3	290	284
4	190	-186
5	175	-177
6	61	-66
7	97	-106
8	-11	11
9	52	-49
10	59	57
K= 4,L= 4		
0	75	-81
1	151	153
2	76	71
3	174	166
4	71	33
6	54	-54
7	152	145
8	18	22
9	60	-63
10	35	-35
K= 4,L= 5		
1	143	-138
2	49	54
3	117	-111
4	209	-210
5	34	38
6	25	23
7	95	94
8	26	31
9	105	106
K= 4,L= 6		
0	235	258
1	42	-47
2	28	30
3	119	-120
4	29	-26
5	116	-115
6	-11	-0
7	32	-31
8	136	-135
K= 4,L= 7		
1	101	103
2	109	106
3	29	-27
4	195	191
5	32	31
6	58	54
7	69	-62
K= 4,L= 8		
0	160	-171
1	69	-67
2	95	-94
4	-11	-2
5	61	57
K= 4,L= 9		
1	18	-14
K= 5,L=-0		
2	353	354
6	223	227
8	-11	25
10	151	-149
K= 5,L= 1		
0	226	-238
1	25	30
2	289	-288
3	42	-45
4	18	11
5	85	-86
6	234	237
7	-11	-7
8	87	90
9	-11	-18
K= 5,L= 2		
1	208	202
2	198	-191
3	66	-64
4	168	-175
5	48	48
6	116	-117
7	103	-98
8	-11	1
9	107	-111
K= 5,L= 3		
0	90	95
1	74	-79
2	75	77
3	176	166
4	-11	9
5	206	206
6	33	-39
7	-11	-14
8	65	-68
9	23	28
K= 5,L= 4		
1	184	-182
3	-11	-21
4	65	68
5	-11	-10
6	17	-19
7	108	104
8	-11	-10
K= 5,L= 5		
0	24	-30
1	40	-47
2	114	114
3	154	-155
4	-11	-1
5	136	-131
6	106	-103
7	36	-33
K= 5,L= 6		
1	94	102
2	152	150
3	58	59
4	42	40
5	35	-31
6	77	75
K= 5,L= 7		
0	93	-94
1	71	75
2	105	-103
3	45	48
4	-11	-2
5	38	32
K= 5,L= 8		
1	-11	-8
2	90	-87
K= 6,L=-0		
0	284	-277
2	42	-46
4	-11	4
6	-11	12
8	153	152
K= 6,L= 1		
1	75	78
2	27	-25
3	50	52
4	189	-180
5	59	-60
6	65	-68
7	49	-50
8	-11	-7
K= 6,L= 2		
0	117	119
1	143	131
3	103	98
4	-11	12
5	72	71
6	28	-30
7	84	90
8	80	-81
K= 6,L= 3		
1	145	-142
2	47	50
3	141	-135
4	57	57
5	131	126
6	30	33
7	103	101
K= 6,L= 4		
0	31	37
1	112	-115
2	29	-31
3	163	-159
4	-11	-13
5	116	-113
6	26	25
7	64	-64
K= 6,L= 5		
1	136	136
2	31	-32
3	65	64
4	90	85
5	64	-58
K= 6,L= 6		
0	100	-99
1	37	41
2	-11	-7
3	104	101
4	-11	1
K= 7,L=-0		
2	104	-100
4	38	-33
6	102	-97
K= 7,L= 1		
0	51	55
1	-11	4
2	99	97
3	59	53
4	-11	16
5	54	52
6	77	-72
K= 7,L= 2		
1	132	-128
2	55	59
3	-11	14
4	62	57
5	-11	11
K= 7,L= 3		
0	44	-44
1	-11	-5
2	33	-32
3	136	-127
4	-11	-4
5	120	-115
K= 7,L= 4		
1	132	128
2	-11	-1
3	-11	16
4	38	-38
K= 7,L= 5		
0	30	32
1	35	36
K= 8,L=-0		
0	140	141
K= 8,L= 1		
1	-11	-22

TABLE IV

DISTANCES AND ANGLES IN THE PERMANGANATE ION

	Uncorrected	Libration corrected
	A	
Mn–O(1)	1.600	1.622
Mn–O(2)	1.603	1.625
Mn–O(3)	1.612	1.634
O(1)–O(2)	2.642	2.677
O(1)–O(3)	2.621	2.661
O(2)–O(3)	2.614	2.652
O(3)–O(3)′	2.627	2.657
	Deg	
O(1)–Mn–O(2)	111.1	111.0
O(1)–Mn–O(3)	109.4	109.6
O(2)–Mn–O(3)	108.8	108.9
O(3)–Mn–O(3)′	109.2	109.0

The results of the analysis are presented in Table V. The mean-square displacements for the Mn atom are approximately equal, indicating that the vibrations are nearly isotropic. The smallest O atom vibrations are almost parallel with the corresponding Mn–O bond. The angles are 5.0, 8.5, and 8.7° for O(1), O(2), and O(3), respectively.

The permanganate ion can be considered as a rigid body, and the method given by Cruickshank[10] was used to calculate libration corrections. The corrected parameters are given in Table I, and the distances and angles calculated using these parameters are presented in Table IV. The average Mn–O bond distance has increased to 1.629 A, but the average O–Mn–O angle is still 109.4°. The correction for the bond length is over 3 standard deviations and clearly indicates the need for using thermal corrections in the bond distances. The uncertainty in the corrected distance

TABLE V

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

Atom	$(r^2)^{1/2\,a}$	Direction cosines[b]		
Mn	190	0	−10000	0
	171	−1010	0	−9949
	157	−9949	0	1010
O(1)	279	−7664	0	6424
	264	0	−10000	0
	161	−6424	0	−7664
O(2)	285	−5347	0	−8450
	273	0	10000	0
	164	−8450	0	5347
O(3)	250	−3408	4652	8170
	213	−9398	−1934	−2819
	183	−0268	8638	−5031
K	236	0	10000	0
	187	−1691	0	9856
	161	−9856	0	−1691

[a] Values times 10^3, in A. [b] Values times 10^4 (cosines are given with respect to *a*, *b*, *c*).

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

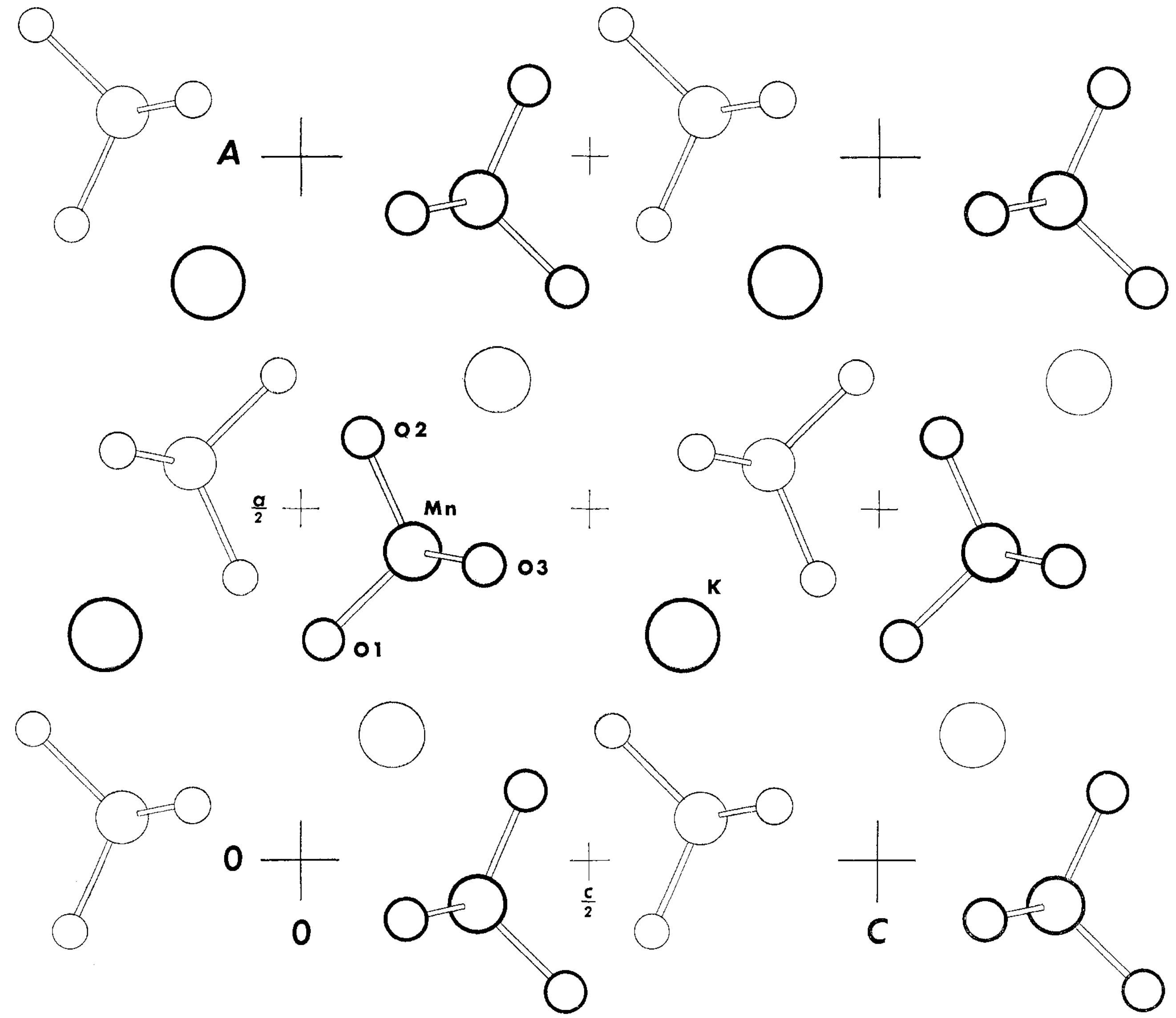

Figure 1.—An (010) projection of the structure of potassium permanganate illustrating the ionic packing.

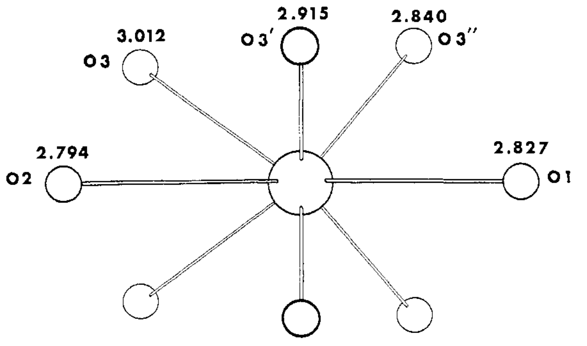

Figure 2.—The coordination of oxygen atoms around the potassium ion. The K···O distance is given above the oxygen atom.

arises in part from the approximations involved in the rigid-body analysis. If one assumes a standard deviation of 0.008 A, the Mn–O distances in MnO_3F and MnO_4^- are significantly different.

The Molecular Packing.—An illustration of the molecular packing is given in Figure 1. The coordination polyhedron of oxygen atoms around the potassium ion is illustrated in Figure 2. The oxygen atoms form an irregular Archimedes antiprism around the potassium ion. A survey of other potassium salts indicated that the coordination polyhedron of oxygen atoms around a potassium ion is rarely regular and

Table VI

Intermolecular Distances[a]

x_i–x_j	Molecule	Distance, A
K–O(3)	A (000)	3.005
K–O(1)	A (001)	2.810
K–O(2)	B $(\bar{1}00)$	2.773
K–O(3)	D (101)	2.831
K–O(3)	E (000)	2.911
O(1)–O(2)	D (100)	3.143
O(1)–O(3)	E (000)	3.080
O(3)–O(3)	D (101)	3.076
O(3)–O(3)	C $(0\bar{1}0)$	3.060
O(1)–O(2)	B (000)	3.290
O(2)–O(3)	B $(\bar{1}00)$	3.246

[a] x_i 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: $^1/_2 - x, \bar{y}, ^1/_2 + z$. The numerals after the molecular designation give the unit-cell translations in the order a, b, c.

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.

CONTRIBUTION FROM THE CHEMISTRY DIVISION, RESEARCH DEPARTMENT,
U. S. NAVAL ORDNANCE TEST STATION, CHINA LAKE, CALIFORNIA

Crystal Structure of Potassium Manganate

BY GUS J. PALENIK[1]

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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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(1) Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada.

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