tration of the intermediate $HMnO_3Cl^+$ which then reacts with Cl^- in a slow step.

$$HMnO_3Cl^+ + Cl^- \longrightarrow Cl_2 + HMnO_3$$

The above rate-determining step would involve the transfer of a Cl^+ from manganese to chloride ion, a process which resembles the bridge-transfer mechanism (inner-sphere mechanism) discovered by Taube and co-workers[7] for electron-transfer reactions of the metal complex ions. A two-electron transfer is suggested because manganese(V) has been detected in solution[8] and is in fact relatively stable in strongly basic solutions.[9] The possibility that the products of the slow step are manganese(VI) and Cl^{2-} cannot be excluded on the basis of kinetic data alone. It is interesting to note that permanganoyl chloride, MnO_3Cl, the conjugate base of the postulated kinetic intermediate $HMnO_3Cl^+$, has been prepared at low temperature.[10]

Effect of Ionic Strength.—A large salt effect is typical of ionic reactions. The effect of added inert electrolyte on the reaction rate was measured by using sodium perchlorate to vary the ionic strength of the reaction mixtures. Data showing the effect of ionic strength on k_6 are found in Table IV. This variation of k with ionic strength when plotted produces a curve resembling that of the activity coefficient of a strong electrolyte over a similar range of ionic strength.

TABLE IV

DEPENDENCE OF RATE ON IONIC STRENGTH AT 28.2°

Ionic strength, M	(Cl^-), M	(H^+), M	10^2k_6, M^{-5} sec^{-1}
2.00	0.109	2.0	1.20
2.50	0.109	2.0	1.95
3.00	0.109	2.0	4.35
3.50	0.109	2.0	5.80
1.50	0.400	0.5	0.95
1.00	0.400	0.5	0.48
0.50	0.400	0.4	1.18

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[7] H. Taube, H. Meyer, and R. L. Rich, *J. Am. Chem. Soc.*, **75**, 4118 (1953).

[8] H. Lux, *Z. Naturforsch.*, **1**, 281 (1946).

[9] H. H. Miller and L. B. Rogers, *Science*, **109**, 61 (1944).

[10] D. Michel and A. Doiwa, *Naturwissenschaften*, **53**, 129 (1966).

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The Crystal and Molecular Structure of Methyl Vanadate, $VO(OCH_3)_3$

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Methyl vanadate $VO(OCH_3)_3$ crystallizes in the monoclinic space group $P2_1/c$ with lattice constants $a = 8.73$, $b = 15.28$, and $c = 9.55$ A, $\beta = 97°$, $Z = 8$ molecules/unit cell. The vanadium is octahedrally coordinated, and the molecules form a linear polymer down the c axis of the crystal by the sharing of edges of the octahedra. Vanadium–oxygen distances can be grouped into five different groups: the short vanadyl oxygens with V–O distances of 1.51 and 1.57 A, single-bonded oxygens not involved in vanadium–vanadium bridging with V–O distances of 1.74 A, oxygens involved in weak vanadium–vanadium bridging with V–O distances of 1.84 and 1.86 A, oxygens involved in strong vanadium–vanadium bridging with V–O distances of 1.96 and 2.05 A, and the long vanadium–oxygen bonds of 2.2 and 2.3 A. Bonding of one polymer chain to adjacent ones is prevented by the presence of the methyl groups.

Introduction

The preparation and physical properties of a number of organic vanadates have been described by Cartan and Caughlan.[1] Several questions arose as a result of this preliminary study, among which were the interpretation of the dipole moments in terms of bond moments and reasons for the rather pronounced differences in color of the various organic vanadates. Since no structures were known, we decided at this time to determine the structures of several of the orthovanadates in order to answer some of the questions and to study the nature of the bonding around the vanadium atom. This is the first such structure to be reported in our more extensive program on the structures of organic vanadates.

Experimental Section

Preliminary work was done on methyl vanadate by Ryder.[2] He prepared crystals and showed them to be monoclinic but obtained an erroneous cell dimension and space group. He also determined the molecular weight ebulliometrically in carbon tetrachloride and obtained values of 307 and 284 in dilute solutions, indicating the existence of a dimer in this solvent.

Methal orthovanadate crystals used for this study were prepared by the addition of $VOCl_3$ to sodium methylate dissolved in excess methyl alcohol while cooling and stirring. The sodium chloride was removed by centrifuging and the excess alcohol was distilled. Upon cooling, crystals of methyl vanadate precipitated. These were easily recrystallized from methyl alcohol. The crystals were the shape of small needles and yellow in color. They quickly hydrolyzed in moist air and thus were enclosed in thin capillaries for examination. X-Ray and microscopic examination indicated generally poor-quality crystals, since all

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[1] F. Cartan and C. N. Caughlan, *J. Phys. Chem.*, **64**, 1756 (1960).

[2] W. A. Ryder, M.S. Thesis, Montana State University, 1957.

that were examined showed much mosaic character parallel to the *b* axis. All X-ray photographs taken showed considerable streaking along the reciprocal lattice lines. However, several small crystals were selected as suitable for an X-ray study.

The crystals are monoclinic with lattice dimensions $a = 8.73$, $b = 15.28$, $c = 9.55$ A, $\beta = 97°$. The measured density is 1.7 g/cc. Systematic extinctions are $0k0$, $k \neq 2n$, and $h0l$, $l \neq 2n$; thus the space group is $P2_1/c$. The number of molecules per unit cell is eight, which gives a calculated density of 1.68 g./cc.

Multiple-film Weissenberg photographs were taken for intensity measurements and 540 unique reflections were measured visually by comparing the reflections with a standard scale. Attempts were made to correct for the spot size, but the very pronounced streaking of the photographs made this difficult and inaccurate. Precession photographs were used only to correlate the layers for preliminary structure factor calculations and the initial Patterson map calculation.

Determination of the Structure

The three-dimensional Patterson showed only two large peaks on the Harker section. The attempt to interpret these as vanadium–vanadium Harker peaks produced a structure with certain unreasonable characteristics and one that would not refine below an R of 32%. It was thus considered unlikely that the structure was correct, even though we realized that the data were poor. Accordingly, after numerous attempts at solution from the Patterson failed, we tried the symbolic sign method of Karle and Karle.[3] The origin-determining and original symbolic signs are listed in Table I along with the E values.

TABLE I

Origin-determining and symbolic signs				E value	Final sign
5	3	1	+	3.53	+
3	2	3	+	3.47	+
−1	5	4	+	3.11	+
−3	2	1	a	2.59	−
−4	7	1	b	2.38	−
−5	2	1	c	1.94	+

All but one sign could be eliminated and, accordingly, two E maps were calculated and the correct structure was readily apparent from the one with a = (−). It is interesting to note that the E map with a = (+) was essentially the same as the incorrect structure we obtained from the misinterpretation of the Patterson map.

The initial E map located the vanadium and oxygen atoms and gave indication of the position of the carbons. A second Fourier was calculated which showed unequivocally all the atoms. The structure factor calculation with these positions gave an R of 24.6%. Three cycles of least-squares refinement using Busing, Martin, and Levy's program reduced the R to 16.8% (weighted $R = 18.8\%$), refining positional parameters and individual isotropic temperature factors. A final difference map showed no serious anomalies. In the refinement, a modified Hughes weighting scheme was used; *i.e.*, wt = 1 for $F_o < 4F_{\min}$; wt = $4F_{\min}/F_o$ for $F_o \geq 4F_{\min}$.[4]

The observed and calculated structure factors are listed in Table II, the positional parameters and B's are listed in Table III, and the bond distances and angles in Tables IV and V. Figures 1 and 2 show the structure in the unit cell, and Figure 3, the coordination around the vanadium in more detail.

Discussion of the Structure

Examination of the figures will show that the vanadium is octahedrally coordinated, with considerable distortion from a regular octahedron. The vanadium atoms are jointed together through oxygen bridges, O(3) and O(4) being the bridging atoms for the two more closely bound vanadiums. Figure 3 shows this bridge and also shows that apex oxygens O(9′) and O(10′) are symmetry related to equatorial oxygens O(9) and O(10) by the operation of the glide plane. The dimer units of Figure 3 are joined together down the *c* axis by sharing the edges of the octahedra through O(9′) and O(10), the entire second unit being related to the first by the glide plane. Thus, the molecules form a linear polymer down the *c* axis. Two vanadium–vanadium distances are observed, 3.18 A for V(1)–V(2) shown in Figure 3 and 3.40 A for V(2)–V(1′). Figure 2 shows the arrangement in the unit cell in projection indicating the manner in which the chains form.

Least-squares planes were calculated for the equatorial oxygens around the vanadium atoms. The best least-squares plane formed by O(3), O(4), O(5), and O(9) has the equation $-0.0685X + 0.9973Y + 0.0272Z = 2.4008$; and the plane formed by O(3), O(4), O(6), and O(10) has the equation $0.0833X + 0.9954Y - 0.0392Z = 3.2068$. X, Y, and Z are orthogonal axes formed by $X = x + z \cos \beta$, $Y = y$, $Z = z \sin \beta$, and the number to the right of the equal sign is the origin-to-plane distance in angstroms. For these two planes the sums of the square deviation of the atom from the planes are, respectively, 0.0302 and 0.02585 A^2. From these equations and the coordinates of the vanadium atoms, it was calculated that V(1) is 0.30 A below the plane of O(3), O(4), O(5), and O(9), and V(2) is 0.48 A below the plane of O(3), O(4), O(6), and O(10). The equation of the plane formed by all six oxygens—O(3), O(4), O(5), O(6), O(9), and O(10)—is $0.0085X + 0.9999Y - 0.061Z = 2.8066$. The sum of the square deviation of the atoms from the plane is 0.1425 A^2.

Comparison of this structure with other organic vanadates is not possible since no structures are known, but there is a marked similarity to the structures of inorganic vanadates. Pentavalent vanadium may be coordinated to four, five, or six oxygen atoms.[5–11] In the structure $Na_{2-x}V_6O_{15}$ reported by Wadsley,[5] the vanadium atoms are stated to be both five- and six-

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(3) I. L. Karle and J. Karle, *Acta Cryst.*, **16**, 969 (1964).

(4) E. W. Hughes, *J. Am. Chem. Soc.*, **63**, 1737 (1941).

(5) A. D. Wadsley, *Acta Cryst.*, **8**, 695 (1955).

(6) H. T. Evans, Jr., *U. S. Geol. Surv. Profess. Papers*, **320**, 91 (1959).

(7) A. Bystrom, K. A. Wilhelmi, and O. Brotzen, *Acta Chem. Scand.*, **4**, 1119 (1950).

(8) C. L. Christ, J. R. Clark, and H. T. Evans, Jr., *Acta Cryst.*, **7**, 801 (1954).

(9) H. G. Bachmann, R. R. Ahmed, and W. H. Barnes, *Z. Krist.*, **115**, 110 (1961).

(10) H. T. Evans, *ibid.*, **114**, 257 (1960).

(11) H. G. Bachmann and W. H. Barnes, *ibid.*, **115**, 215 (1961).

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $VO(OCH_3)_3$[a]

- 0 K 0		
4	1921	-1868
6	1457	2009
4 K - 0		
10	132	-148
11	133	-195
5 K - 0		
- 0	233	188
1	162	-119
2	241	-298
6	187	267
8 K - 0		
11	135	148
6 K - 0		
1	247	278
5	260	-270
7	245	238
7 K - 0		
- 0	248	-287
4	133	173
6	135	-161
8 K - 0		
1	212	-241
5	213	250
7	151	-117
9 K - 0		
- 0	531	338
2	154	-127
4	191	-195
6	177	233
10	131	-158
10 K - 0		
1	276	212
5	160	-178
- 0 K 1		
1	994	-629
2	1342	-901
3	943	771
4	796	736
5	512	-461
6	228	-193
7	188	-153
8	398	-481
9	425	520
10	290	376
1 K 1		
3	138	-124
4	138	93
5	145	166
6	113	-66
- 1 K 1		
1	1005	-704
2	1695	1358
3	595	624
4	323	-376
5	125	-113
7	163	-140
8	566	631
9	382	469
10	377	-465
12	165	-131
14	217	296
2 K 1		
2	466	302
4	348	285
8	256	-264
- 2 K 1		
1	340	440
3	290	-287
7	566	589
8	267	274
9	604	-652
11	204	-219
12	167	-128
13	321	390
15	167	-161
3 K 1		
5	220	-204
- 3 K 1		
2	979	-897
4	243	-183
6	532	537
8	590	-711
12	441	503
14	278	-303
4 K 1		
2	647	718
4	349	-379
8	493	514
10	269	-223
- 4 K 1		
1	764	-817
3	403	516
5	409	347
7	585	-584
9	450	480
11	297	241
13	362	-413
15	206	136
5 K 1		
1	531	-618
2	163	-230
3	891	968
5	254	-246
7	480	-588
9	504	604
13	306	-285
15	206	157
- 5 K 1		
2	527	605
4	179	-244
8	457	557
12	239	-271
14	174	194
6 K 1		
2	475	-567
3	157	-182
4	138	195
6	167	220
8	280	-379
- 6 K 1		
1	273	312
2	156	-181
3	269	-284
9	168	-260
9 - K 1		
2	237	-186
- 0 K 2		
3	1061	-512
5	408	413
7	428	-278
11	360	293
17	188	117
1 K 2		
1	267	268
2	603	-459
4	355	-538
5	108	-202
6	781	783
7	144	196
8	233	-143
10	493	-527
- 1 K 2		
4	195	-97
6	148	-97
8	285	211
2 K 2		
1	1516	1492
3	478	394
4	293	286
5	695	-738
6	206	-241
7	468	549
8	110	101
9	112	151
10	136	163
11	303	-364
17	123	-91
- 2 K 2		
0	323	-267
1	718	-603
3	449	-334
4	215	195
5	438	500
9	128	-153
11	118	192
3 K 2		
1	748	-812
2	342	400
3	175	-187
4	375	453
5	345	422
6	471	-615
7	375	-379
8	334	386
10	230	273
11	217	210
12	193	-243
- 3 K 2		
0	340	-344
1	190	172
2	203	214
4	190	200
5	203	-243
6	316	-370
7	150	174
10	219	277
4 K 2		
1	700	-722
2	365	-411
4	233	-262
5	385	430
6	530	648
7	493	-559
8	321	-375
10	277	-237
11	225	296
12	155	230
- 4 K 2		
0	170	255
1	148	164
4	120	-141
5	105	-70
5 K 2		
3	158	173
4	163	-161
5	318	-347
6	205	230
7	378	385
11	277	-265
12	123	135
13	118	116
- 5 K 2		
0	387	432
1	448	-508
1	448	-508
2	118	-144
4	110	-124
5	259	322
6	228	193
7	286	-291
11	206	218
6 K 2		
10	228	198
- 6 K 2		
0	983	-1038
1	315	-332
2	498	475
4	368	371
5	197	209
6	790	-725
7	185	-194
8	299	290
10	295	293
11	125	98
12	262	-247
7 K 2		
9	187	-166
- 7 K 2		
0	144	-142
1	791	705
3	145	119
5	537	-467
7	430	359
11	251	-239
- 8 K 2		
0	449	387
2	125	-102
4	185	-174
6	238	199
8	117	-48
10	142	-143
- 9 K 2		
1	201	-146
5	150	110
7	148	-104
- 0 K 3		
1	332	-343
2	203	192
3	173	120
4	175	165
5	104	111
6	105	-127
7	331	-412
9	411	458
11	156	162
12	215	-328
13	203	-287
14	171	213
15	149	156
18	119	-94
1 K 3		
1	203	-194
2	188	-264
3	154	-110
4	443	-353
5	151	200
6	109	139
7	129	-162
9	154	170
10	124	103
11	128	131
12	210	309
13	143	-160
14	170	-196
18	116	104
- 1 K 3		
1	1821	1165
2	1378	1028
3	1097	-954
4	168	-231
5	158	-89
6	218	-243
7	458	543
9	487	-714
10	175	-248
11	126	-32
12	186	-175
13	284	387
14	171	224
15	168	-212
18	104	-52
2 K 3		
1	922	871
2	343	-382
3	730	-746
7	292	306
9	535	-518
10	126	107
13	217	260
15	159	-127
- 2 K 3		
1	317	352
2	1307	-1014
3	294	-288
4	224	292
6	222	242
7	152	201
9	175	-244
10	154	220
12	277	316
14	152	-191
3 K 3		
2	989	1017
3	126	-106
4	660	-719
6	117	84
10	275	-299
12	173	-157
- 3 K 3		
1	317	-373
5	109	111
9	238	251
11	152	145
4 K 3		
1	432	-486
3	453	509
5	136	-171
9	152	202
- 4 K 3		
2	517	537
6	117	50
10	254	-194
5 K 3		
2	121	-140
6	128	-168
- 5 K 3		
5	182	190
9	152	-144
- 6 K 3		
2	338	371
3	146	-195
4	262	-308
6	131	-112
8	171	245
7 K 3		
2	133	-199
3	133	-167
4	133	148
7	129	126
9	122	-103
- 7 K 3		
1	194	180
2	203	-194
3	327	-376
4	194	229
5	164	153
7	189	193
8	152	-172
9	225	-234
13	140	88
8 K 3		
2	198	165
3	198	-155
4	182	-140
7	138	97
9	124	-96
- 8 K 3		
2	189	-131
3	180	150
8	141	-111
- 9 K 3		
2	164	113
8	152	138
-10 K 3		
1	129	96
3	171	-146
- 0 K 4		
2	559	351
4	330	-273
6	115	-64
8	268	308
10	327	-399
14	185	215
1 K 4		
1	217	-257
3	453	463
5	127	124
7	254	-311
9	166	239
11	134	-122
15	124	127
- 1 K 4		
1	1830	-1037
2	90	32
3	415	-266
4	106	79
5	868	754
6	132	-115
7	674	-553
9	272	-278
11	420	457
15	127	-142
17	139	124
2 K 4		
10	129	116
- 2 K 4		
0	1657	-1919
1	487	508
2	701	544
3	139	167
4	651	680
5	240	-244
6	734	-841
7	215	224
8	455	458
10	277	334
11	144	-126
12	332	-371
16	147	134
3 K 4		
1	308	377
4	117	133
5	178	-264
6	173	-199
7	173	122
- 3 K 4		
0	535	590
1	733	855
2	225	-235
4	110	-97
5	358	-435
6	303	362
7	570	620
8	206	-244
10	149	-119
11	219	-315
4 K 4		
1	409	-441
2	171	216
4	235	216
5	333	372
6	256	-333
7	284	-273
9	134	-95
10	173	176
11	187	203
- 4 K 4		
0	591	744
1	563	-639
2	257	-240
4	173	-208
5	276	283
6	314	365
7	330	-413
8	203	-221
10	144	-146
11	154	200
12	132	133
5 K 4		
1	180	-157
4	247	-220
5	129	87
6	244	198
10	152	-144
12	122	143
- 5 K 4		
0	651	-872
1	330	-439
2	193	201
4	288	324
5	196	234
6	303	-348
7	168	-226
8	164	171
10	173	197
6 K 4		
1	189	183
5	191	-163
7	203	149
11	196	-149
- 6 K 4		
1	300	302
3	105	90
5	174	-203
7	181	179
11	157	-164
7 K 4		
2	189	140
4	201	193
6	377	-279
8	157	85
10	235	168
8 K 4		
1	344	-303
5	296	250
7	244	-166
- 8 K 4		
1	132	113
5	159	-152
- 9 K 4		
0	180	167
4	149	-124
6	132	116
-10 K 4		
1	134	-77
5	134	96
- 0 K 5		
1	288	229
2	390	387
3	276	-336
4	192	-291
7	249	237
8	351	352
9	280	-288
13	148	119
1 K 5		
1	370	-380
2	259	315
3	282	330
7	261	-171
8	245	176
9	321	292
13	170	-129
- 1 K 5		
1	247	220
2	358	-284
3	362	-242
6	153	182
8	142	-119
2 K 5		
2	442	-468
4	232	175
8	232	-358
9	146	93
12	226	127
14	222	-171
- 2 K 5		
3	418	-360
4	179	-139
5	280	292
9	146	-155
3 K 5		
1	387	414
3	545	-552
5	306	191
7	397	343
9	304	-476
13	315	240
15	209	-142
- 3 K 5		
2	672	-818
3	150	-190
4	547	544
8	364	-330
10	276	238
14	136	-128
4 K 5		
2	543	664
4	170	-243
8	409	387
12	243	-208
14	228	184
- 4 K 5		
1	373	-413
3	638	696
5	183	-232
7	360	-377
9	345	394
13	200	-184
15	144	71
5 K 5		
1	170	-239
3	170	222
7	150	-186
9	168	157
13	138	-160
- 5 K 5		
2	379	428
4	164	-164
6	148	-180
8	304	318
12	185	-181
14	177	140
6 K 5		
8	166	-141
- 6 K 5		
1	146	211
3	146	-203
7	173	206
9	170	-221
13	177	184
- 7 K 5		
2	214	-194
8	196	-225
12	155	91
- 8 K 5		
2	148	148
7	134	-67
8	132	113
9	127	92

[a] Each group of numbers contains k, $10F_o$, $10F_c$.

TABLE III

POSITIONAL AND THERMAL PARAMETERS FOR $VO(OCH_3)_3$[a]

	x	y	z	B
V(1)	0.6643 (10)	0.1595 (8)	0.2066 (10)	4.51
V(2)	0.7717 (10)	0.1587 (8)	0.5374 (10)	3.40
O(3)	0.8498 (43)	0.1806 (21)	0.8572 (38)	3.76
O(4)	0.5896 (33)	0.1826 (18)	0.8920 (33)	3.86
O(5)	0.4688 (39)	0.1694 (27)	0.6259 (37)	4.20
O(6)	0.9650 (39)	0.1684 (24)	0.1096 (39)	4.35
O(7)	0.6853 (47)	0.0611 (25)	0.7101 (37)	5.20
O(8)	0.7478 (48)	0.0564 (27)	0.0407 (40)	5.51
O(9)	0.7888 (38)	0.1926 (23)	0.5750 (35)	4.82
O(10)	0.6515 (48)	0.1946 (26)	0.1744 (44)	5.73
C(11)	0.0130 (61)	0.1771 (36)	0.8453 (59)	6.03
C(12)	0.4141 (63)	0.1654 (37)	0.9206 (60)	5.19
C(13)	0.3497 (86)	0.1038 (47)	0.5767 (74)	7.29
C(14)	0.0698 (74)	0.0900 (36)	0.1763 (67)	5.77
C(15)	0.8929 (44)	0.1454 (26)	0.5105 (48)	3.75
C(16)	0.5574 (65)	0.1307 (36)	0.2426 (63)	6.09

[a] Numbers in parentheses are standard deviations and refer to least significant digits.

TABLE IV

INTERATOMIC DISTANCES[a]

Vanadium–vanadium	D, A
V(1)–V(2)	3.18 (2)
V(2)–V(1′)	3.40 (3)

Vanadium–oxygen	D, A
V(1)–O(3)	2.04 (6)
V(1)–O(4)	2.03 (4)
V(1)–O(5)	1.78 (5)
V(1)–O(7)	1.51 (5)
V(1)–O(9)	1.84 (5)
V(1)–O(10′)	2.25 (11)
V(2)–O(3)	1.96 (5)
V(2)–O(4)	2.06 (5)
V(2)–O(6)	1.74 (5)
V(2)–O(8)	1.58 (4)
V(2)–O(9)	2.30 (4)
V(2)–O(10)	1.86 (7)

Oxygen–carbon	D, A
O(3)–C(11)	1.44 (6)
O(4)–C(12)	1.54 (6)
O(5)–C(13)	1.47 (14)
O(9)–C(15)	1.36 (9)
O(6)–C(14)	1.59 (6)
O(10)–C(16)	1.48 (12)

Oxygen–oxygen	D, A
O(3)–O(4)	2.42 (5)
O(3)–O(6)	2.49 (7)
O(3)–O(8)	2.80 (6)
O(3)–O(9)	2.68 (6)
O(4)–O(5)	2.60 (7)
O(4)–O(8)	2.70 (9)
O(4)–O(10)	2.69 (7)
O(10)–O(6)	2.91 (8)
O(5)–O(9)	2.92 (6)

Apex-to-plane oxygens	D, A
O(7)–O(3)	2.61 (9)
O(7)–O(4)	2.78 (8)
O(7)–O(5)	2.56 (9)
O(7)–O(9)	2.61 (8)
O(10′)–O(5′)	2.63 (9)
O(10′)–O(4)	2.90 (7)
O(10′)–O(3)	2.99 (7)
O(10′)–O(9)	2.36 (9)
O(9′)–O(3)	2.94 (6)
O(9′)–O(4)	3.00 (8)
O(9′)–O(6)	2.62 (7)
O(8)–O(4)	2.70 (9)
O(8)–O(6)	2.57 (9)
O(8)–O(10)	2.66 (9)

[a] Numbers in parentheses are standard deviations and refer to least significant digits.

coordinated, although the five-coordinated vanadium could be described in terms of a highly distorted octahedron. In this, as well as in other similar structures, the octahedra are joined together into polymer chains by sharing edges and form zigzag ribbons down the structure. In the case of methyl vanadate, any cross bonding from one chain to another is prevented by the presence of the methyl groups since the carbon atoms will not coordinate with the oxygens and will not allow the oxygens to come close enough to coordinate with vanadium atoms in adjacent chains.

The vanadium–oxygen bond lengths suggest five different vanadium–oxygen bonds. There are two short bonds, *e.g.*, V(1)–O(7) and V(2)–O(8) (1.51 and

Table V

Bond Angles, Deg[a]

O(3)-V(1)-O(4)	73	O(6)-V(2)-O(10)	108
O(4)-V(1)-O(5)	86	O(10)-V(2)-O(4)	87
O(5)-V(1)-O(9)	107	O(4)-V(2)-O(3)	74
O(9)-V(1)-O(3)	87	O(3)-V(2)-O(6)	84
O(10')-V(1)-O(3)	88	O(9')-V(2)-O(6)	79
O(10')-V(1)-O(4)	86	O(9')-V(2)-O(10)	68
O(10')-V(1)-O(5)	80	O(9')-V(2)-O(4)	88
O(10')-V(1)-O(9)	70	O(9')-V(2)-O(3)	87
O(7)-V(1)-O(3)	93	O(8)-V(2)-O(6)	101
O(7)-V(1)-O(4)	102	O(8)-V(2)-O(10)	101
O(7)-V(1)-O(5)	102	O(8)-V(2)-O(4)	95
O(7)-V(1)-O(9)	102	O(8)-V(2)-O(3)	104
V(1)-O(4)-V(2)	102	V(2)-O(6)-C(14)	125
V(1)-O(3)-V(2)	105	V(2)-O(10)-C(16)	121
V(1)-O(4)-C(12)	126	V(2)-O(4)-C(12)	123
V(1)-O(5)-C(13)	132	V(2)-O(3)-C(11)	121
V(1)-O(9)-C(15)	131	O(8)-V(2)-O(9')	169
V(1)-O(3)-C(11)	130	O(7)-V(1)-O(10')	172

[a] Standard deviations for bond angles are approximately 1.0–2.0°.

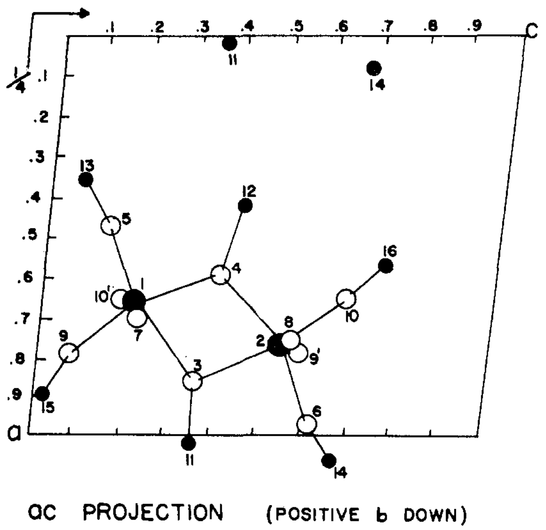

Figure 1.—*ac* projection of methyl vanadate (positive *b* down): •, carbon atoms; ○, oxygen atoms; ●, vanadium atoms.

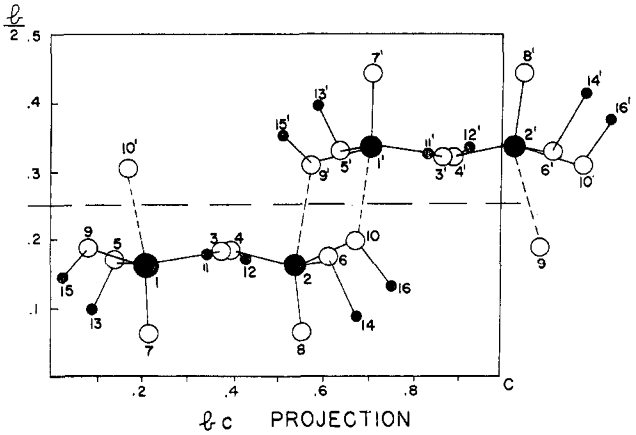

Figure 2.—*bc* projection of methyl vanadate.

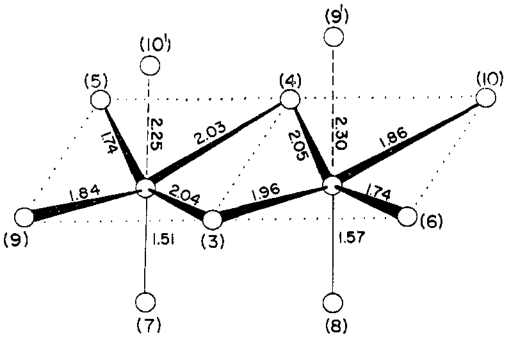

Figure 3.—Coordination around vanadium in methyl vanadate.

1.57 A), which are vanadyl bonds and presumably nearly double bonds.[10,11] The bonds from V(1) to O(9) and V(2) to O(10) are involved in somewhat weak vanadium–vanadium bridging and show distances of 1.84 and 1.86 A, whereas O(3) and O(4) are involved in the stronger bridging between V(1) and V(2) and show bond distances of 1.96 and 2.05 A. O(5) and O(6) do not appear to be involved in any bridging and give the bond distances of 1.74 A. V(1)–O(10)' and V(2)–O(9') are considerably longer than the others but are still short enough to be considered as weak vanadium–oxygen bonds.

These distances compare favorably with the V–O distances in inorganic vanadates. In $KVO_3 \cdot H_2O$, Christ, Clark, and Evans[8] obtained V–O distances from 1.63 to 1.99 A for pentacoordinated vanadium, whereas Wadsley[5] reported distances from 1.56 to 2.32 A for the octahedral coordinated vanadium. The bond distances in inorganic vanadates have been discussed in detail by Evans[10] and Bachmann and Barnes.[11]

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