The Crystal and Molecular Structure of Titanium Tetramethoxide

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Titanium tetramethoxide, empirical formula $Ti(OCH_3)_4$, crystallizes in the triclinic space group $P\bar{1}$; $a = 9.09$, $b = 10.62$, $c = 10.62$ Å; $\alpha = 101.2$, $\beta = 123.2$, $\gamma = 102.1°$ and $D_m = 1.496$ g.cm^{-3}. The structure has been solved by three-dimensional Patterson and Fourier syntheses and shown to consist of discrete tetrameric molecules, $Ti_4(OCH_3)_{16}$. Least-squares refinement reduced R to 0.139 for data consisting of 1285 reflexions from room temperature Cu $K\alpha$ Weissenberg photographs. The molecule consists of four titanium–oxygen octahedra surrounded by the terminal methyl groups, with methoxide oxygen bridges linking the titanium atoms. Titanium–oxygen bond lengths occur in several groups with their mean values ranging from 1.78 to 2.20 Å. The standard deviations of the atomic positions are, for titanium 0.01, oxygen 0.02 and carbon 0.04 Å excepting two carbon atoms with larger standard deviations of 0.10 Å due to partial hydrolysis of their methoxide groups.

Introduction

The interest shown in the structure, synthesis and properties of the titanium alkoxides has lead to efficient methods for their preparation (Dunn, 1959) and to crystal structure studies on titanium tetraethoxide (Ibers, 1963) and monomethyltriethyl titanate (Witters & Caughlan, 1965). These crystal structures show an arrangement of the titanium and oxygen atoms into a formally tetrameric unit, Ti_4O_{16}. By contrast titanium tetraethoxide and many similar compounds were originally reported to have trimeric molecules in solution (Caughlan, Smith, Katz, Hodgson & Crowe, 1951; Bradley, Mehrotra, Swanwick & Wardlaw, 1953) although evidence (Martin & Winter, 1963) has been subsequently presented that some tetramer is present in concentrated solutions of titanium tetraethoxide in benzene. In general, titanium alkoxides are probably tetrameric when crystalline but consist of predominantly lower polymeric forms in solution.

The simplest titanium alkoxide, titanium tetramethoxide, has a melting point of 216°C, which is much higher than many other titanium alkoxides (Dunn, 1959). Moreover in highly concentrated solutions in pure dry toluene almost 90% of the molecular entities present are tetramers. Thus this compound is a particularly stable member of the series, and with the high melting point as an indication of increased probability of locating the carbon atoms, a step not previously achieved in this class of compound (Ibers, 1963; Witters & Caughlan, 1965), it was decided to determine the crystal structure.

Preparation

The titanium tetramethoxide was synthesized by adding methanol to a solution of titanium tetrachloride in dry redistilled toluene, later saturating the solution with ammonia and distilling off the surplus methanol (Dunn, 1959). This gave a 64% yield of titanium tetramethoxide which was precipitated as transparent crystals with a slight brown tint. The compound was easily recrystallized from toluene on standing in the cold box of a refrigerator at $-5°C$ and the resulting crystals appear to remain stable indefinitely when stored under the mother liquor or in a desiccator. A sample made in 1955 gave identical X-ray powder patterns in 1955 and 1963 and the mass spectrum obtained in 1966 agreed with one made two years before.

Additional checks to determine that the crystals were not appreciably hydrolysed were made by using mass spectrometer and infrared data. Neither showed any evidence of hydrolysis. The only peak in the mass spectrum corresponding to a molecular weight greater than 100 and possibly due to a fragment from a partially hydrolysed molecule, $Ti(OCH_3)_2OH$ of M.W. 127, was shown to be probably derived from the fragment $Ti(OCH_3)_3H$ of M.W. 142 by electron impact causing the loss of CH_3. In an attempt to detect polymerization of the molecules a careful check was made of all peaks greater than 172, the M.W. of $Ti(OCH_3)_4$. No evidence of the tetramer, trimer or dimer was found at 688, 516 or 344. However, a peak at 312, equivalent to $Ti_2(OCH_3)_7(-H)$ was found, and from the small size of this peak it was expected that the dimer peak would not be observed above the background. Several other peaks, such as $Ti_2(OCH_3)_6$ and $Ti_2O(OCH_3)_5$ were found. The spectrum gave strong evidence for some polymerization of the tetramethoxide in the vapour phase and for the crystals being a very slightly hydrolysed or non-hydrolysed form of $[Ti(OCH_3)_4]_n$.

Infrared absorption spectra of the tetramethoxide taken both in the solid state and in a solution of carbon disulphide were very similar and it is likely that the same molecular species is present in both solid and solute. Some spectral lines were split, indicating the

presence of a polymer. All the peaks were consistent with those expected from $Ti_4(OCH_3)_{16}$.

Crystal mounting

Considerable precautions were necessary to protect the crystals from hydrolysis. Small crystals suitable for X-ray photography, usually rhombohedra or needles elongated along the [100] direction, were simply jammed into Lindemann glass capillary tubes since all adhesives used caused decomposition. The crystals were mounted in an atmosphere of very dry nitrogen after it was found that carbon dioxide also caused them to decompose.

Although the crystals were stable for long periods of time (1–2 months) in sealed tubes, any slow air leaks caused them to lose crystallinity quickly and become gels while still retaining their original shape. The crystal structure determination showed that hydrolysis was not suppressed completely, but there was no direct evidence of change in the crystals during photography.

Crystal data

The cell constants were determined from room temperature Cu $K\alpha$ oscillation and zero layer-line Weissenberg X-ray photographs.

The cell is triclinic with the following constants:

$$a= 9\cdot09 \pm 0\cdot02 \text{ Å} \qquad \alpha=101°13' \pm 12'$$
$$b=10\cdot62 \pm 0\cdot02 \qquad \beta=123°14' \pm 12'$$
$$c=10\cdot62 \pm 0\cdot02 \qquad \gamma=102°06' \pm 12'$$
$$V=774\cdot12 \text{ Å}^3 \qquad D_{meas}=1\cdot496 \text{ g.cm}^{-3}$$
$$Z=4 \qquad D_{calc}=1\cdot476 \text{ g.cm}^{-3}$$

The space group was shown to be the centrosymmetric group $P\bar{1}$ by the statistical test of Howells, Phillips & Rogers (1950) and hence the unit cell has two crystallographically independent $Ti(OCH_3)_4$ units. It was considered likely that these formed part of a centrosymmetric molecule $Ti_4(OCH_3)_{16}$, the contents of the entire unit cell.

Photography

The intensity measurements were taken from Cu $K\alpha$ X-ray diffraction photographs of crystals having a nearly cubic shape with an edge of approximately 0·2 mm. It was necessary to use Cu $K\alpha$ radiation as crystals suitable for Mo $K\alpha$ photography at room temperature could not be obtained (the largest crystals had dimensions of about 0·3 mm) and low temperature equipment was not available to us at the time. The high absorption of Cu radiation by the titanium atoms led to considerable errors in the observed structure factors and to a relatively heavy background. Data were collected out to about $\sin\theta=0\cdot90$ for the Cu sphere using the equi-inclination Weissenberg method. Within the effective sphere of reflection approximately 72% of the intensities were measured by visual com-

parison with a standard scale. After the Lorentz–polarization corrections were made the intensities were placed on a single (arbitrary) scale.

Determination of the structure

Patterson vector synthesis

The intensities were placed on an absolute scale and the overall isotropic temperature factor (B) found by using a slight modification of Wilson's (1942) method. A sharpened Patterson synthesis was then calculated in which the absolute intensities were modified by the function $(\sin\theta/\lambda) \exp(2B \sin^2\theta/\lambda^2)$ (Abrahamsson & Maslen, 1963). The origin peak was not removed. The other four titanium–titanium vector peaks were readily identified in the Patterson vector map, and the titanium atoms located. A subsequent attempt to use the Patterson superposition technique was abandoned as it led to a confusing set of peaks, probably due to the relatively large errors in the structure factors.

Determination of atom positions

The titanium atom coordinates were used to calculate a set of structure factors which showed an excellent trend of agreement with the observed structure factors, and gave an R value of 0·47 (where $R=(\Sigma|F_{obs}-|F_{calc}||)/\Sigma F_{obs}$). Two hundred of the largest structure factors that were sign-determined were used as input to an initial electron density map calculated with the Fortran program MUFR (White, 1966). Though much false detail appeared sixteen peaks were selected as possible sites for the oxygen and carbon atoms, and later analysis showed that the distorted octahedra of oxygen atoms surrounding each titanium atom had been correctly identified, but that only two carbon peaks had been found. The correct light atom (non-titanium) positions were distinguished from other Fourier peaks by the stability of their isotropic temperature factors when refined with their coordinates using the Fortran II least-squares refinement program ORFLS (Busing, Martin & Levy, 1962) adapted for the CDC 3600 computer. The function $\Sigma W(kF_o-|F_c|)^2$ was minimized and the atomic scattering factors were taken from International Tables for X-ray Crystallography (1962). An atom was rejected when an excessively large temperature factor was derived for it during several refinement cycles. The first four cycles clearly rejected the six false atoms and reduced R from 0·46 to 0·33.

A model constructed from transparent plastic sheets separated by foam plastic spacers now showed the Ti_4O_{16} tetrameric unit of four distorted octahedra. A straightforward sequence of Fourier and difference Fourier calculations interspersed with cycles of least-squares refinement, in which the reflexions were weighted individually, identified the remaining carbon atoms. The isotropic temperature factor refinement reduced R to 0·17 but did not resolve the two carbon atoms C(4) and C(5) properly from the oxygen atoms

Table 1. *Observed and calculated structure factors*

The three columns within each group contain the values of l (or k), $10F_o$ and $10F_c$. Reflexions indicated by an asterisk were given zero weight in the least-squares calculation.

	001	
1	*531	814
2	211	211
3	274	284
4	<36	09
5	<36	53
6	161	131
7	<36	29
8	<36	11
9	60	66
	011	
0	*571	836
1	*59	24
-1	*702	914
2	179	122
-2	66	58
3	251	252
-3	*944	1042
4	188	180
-4	*704	797
5	170	177
-5	187	180
6	227	189
-6	94	56
7	87	62
-7	<36	44
8	<36	35
-8	<36	13
-9	<36	36
-10	<36	46
	021	
0	400	467
1	194	142
-1	279	277
2	137	199
-2	68	46
3	259	334
-3	139	169
4	132	102
-4	*674	793
5	221	211
-5	500	482
6	103	119
-6	174	159
7	<36	44
-7	191	178
8	<36	49
-8	95	101
	031	
0	369	401
1	222	271
-1	439	519
2	237	261
-2	127	147
3	159	164
-3	48	25
4	157	166
-4	<36	09
5	<36	08
-5	238	207
6	138	133
-6	<36	29
7	81	82
-7	127	123
8	81	70
-8	212	192
9	64	92
-9	80	94
	041	
0	77	65
1	227	270
-1	449	487
2	<36	41
-2	105	106
3	205	229
-3	97	91
4	54	68
-4	237	208
5	252	251
-5	219	250
6	104	103
-6	151	148
7	<36	48
-7	<36	05
8	77	77
-8	126	87
-9	105	112
	051	
0	50	31
1	127	101
-1	*57	19
2	254	253
-2	90	120
3	96	86
-3	<36	32
4	208	186
-4	197	183
5	122	123
-5	391	384
6	<36	29
-6	209	201
7	59	49
	061	
0	137	199
1	293	276
-1	159	154
2	77	72
-2	76	66
3	69	56
-3	91	122
4	77	72
-4	<36	36
5	<36	52
-5	224	209
6	63	50
-6	71	71
-7	57	57
-8	118	117
-9	131	143
	071	
0	107	89
1	<36	21
-1	135	128
2	76	67
-2	248	244
3	<36	33
-3	232	241
4	91	76
-4	101	109
5	106	103
-5	<36	14
6	<36	08
-6	86	95
-7	70	63
-8	77	57
-9	109	112
	081	
0	107	92
1	141	132
-1	<36	38
2	48	60
-2	<36	49
3	66	62
-3	78	71
4	136	135
-4	46	39
5	47	57
-5	134	136
-6	160	197
-7	83	98
	091	
0	147	149
1	107	92
-1	*58	24
2	<36	03
-2	126	106
3	97	88
-3	137	145
4	50	67
-4	77	76
-5	109	91
-6	134	146
-7	51	62
-8	<36	18
-9	44	63
	0,10,1	
0	127	116
-1	102	82
-2	<36	34
-3	126	134
-4	99	117
-5	<36	15
-6	<36	15
-7	<36	28
-8	<36	31
-9	59	73
	0,11,1	
0	<36	27
-1	<36	49
-2	<36	27
-3	<36	50
-4	101	98
-5	<36	44
-6	<36	64
-7	81	90
	0,12,1	
0	37	32
-6	<36	19
	101	
0	*903	1356
1	*237	391
-1	458	659
2	118	114
-2	418	455
3	210	216
-3	277	292
4	121	95
-4	53	42
5	102	104
-5	86	73
6	<36	43
-6	259	245
7	100	87
-7	121	110
8	74	67
-8	<36	07
-9	136	128
-10	77	92
-11	<36	05
	111	
0	*325	511
1	105	72
-1	*514	693
2	95	70
-2	273	337
3	97	133
-3	*532	664
4	216	177
-4	708	764
5	100	94
-5	112	110
6	164	131
-6	137	124
7	139	139
-7	65	52
8	*45	19
-8	<36	40
-9	<36	43
-10	94	121
-11	52	31
	1-11	
0	*547	701
1	*442	562
-1	<36	42
2	382	407
-2	253	235
3	344	341
-3	280	285
4	518	533
-4	261	289
5	187	191
-5	50	35
6	<36	10
-6	298	267
7	<36	15
-7	<36	29
8	<36	20
-8	83	86
9	<36	20
-9	75	75
-10	<36	09
	121	
0	138	152
1	66	50
-1	71	88
2	375	415
-2	<36	25
3	543	544
-3	127	158
4	239	224
-4	*432	543
5	93	93
-5	396	420
6	108	118
-6	203	221
7	<36	15
-7	308	295
-8	<36	76
-9	<36	24
-10	<36	18
-11	<36	14
	1-21	
0	419	433
1	268	258
-1	229	205
2	55	43
-2	*268	154
3	97	123
-3	107	94
4	643	637
-4	<36	19
5	477	405
-5	208	194
6	<36	11
-6	77	88
7	117	133
-7	68	48
8	114	104
-8	66	61
9	<36	34
-9	92	79
-10	59	88
	131	
0	499	506
1	147	151
-1	*950	1156
2	348	393
-2	43	57
3	293	302
-3	92	127
4	<36	05
-4	112	87
5	<36	20
-5	254	272
6	<36	29
-6	66	58
7	<36	22
-7	237	209
-8	133	126
-9	<36	43
-10	62	52
-11	<36	50
	1-31	
0	196	259
1	*286	140
-1	200	222
2	397	348
-2	97	95
3	67	61
-3	122	112
4	120	83
-4	140	152
5	169	136
-5	<36	16
6	<36	21
-6	186	167
7	107	118
-7	<36	64
8	259	232
-8	77	77
9	59	86
-9	103	148
	141	
0	132	127
1	108	93
-1	*678	822
2	<36	29
-2	*422	534
3	117	96
-3	153	127
4	<36	54
-4	462	534
5	117	133
-5	189	190
6	<36	50
-6	56	36
7	<36	17
-7	<36	14
-8	47	53
-9	83	80
-10	<36	31
-11	62	68
	1-41	
0	84	79
1	61	59
-1	161	141
2	64	70
-2	65	83
3	119	117
-3	172	155
4	124	114
-4	<36	14
5	291	249
-5	322	318
6	77	68
-6	180	178
7	<36	06
-7	<36	45
8	144	124
-8	70	103
9	74	92
-9	41	51
	151	
0	<36	14
1	206	205
-1	70	65
2	224	242
-2	287	297
3	82	85
-3	145	155
4	108	106
-4	159	187
5	64	74
-5	432	499
6	<36	11
-6	195	176
-7	127	128
-8	82	78
-9	*37	08
-10	<36	19
-11	<36	48
	1-51	
0	88	64
1	134	144
-1	352	308
2	159	125
-2	312	259
3	65	34
-3	<36	24
4	268	230
-4	269	229
5	338	285
-5	234	225
6	64	81
-6	<36	41
7	<36	24
-7	<36	14
8	36	45
-8	<36	04
9	<36	08
	161	
0	76	77
1	190	156
-1	287	255
2	94	103
-2	211	227
3	48	58
-3	66	69
4	65	57
-4	39	39
5	<36	39
-5	266	262
6	60	59
-6	269	277
-7	<36	21
-8	107	119
-9	116	102
-10	61	44
	1-61	
0	226	231
1	250	237
-1	518	462
2	252	251
-2	145	121
3	114	71
-3	<36	06
4	<36	20
-4	47	60
5	137	130
-5	<36	12
6	<36	33
-6	<36	46
7	68	67
-7	<36	50
8	133	116
-8	42	58
9	102	99
	171	
0	47	75
1	<36	18
-1	177	157
2	83	89
-2	327	294
3	92	84
-3	180	171
4	71	69
-4	<36	39
5	78	86
-5	<36	33
-6	<36	19
-7	<36	32
-8	<36	44
-9	114	109
-10	83	82
	1-71	
0	214	172
1	70	58
-1	163	130
2	222	217
-2	<36	38
3	269	247
-3	117	118
4	<36	39
-4	107	101
5	128	129
-5	78	78
6	150	102
-6	<36	22
7	<36	39
-7	56	67
8	103	85
9	99	100
	181	
0	<36	07
1	107	119
-1	<36	40
2	79	82
-2	<36	47
3	82	66
-3	<36	44
4	92	112
-4	46	75
-5	199	177
-6	214	190
-7	108	105
-8	<36	11
-9	<36	12
-10	<36	32
	1-81	
0	138	135
1	34	44
-1	163	131
2	126	90
-2	<36	14
3	238	188
-3	82	85
4	130	122
-4	157	145
5	125	133
-5	56	67
6	167	153
-6	<36	24
7	<36	28
8	<36	07
9	<36	27
	191	
0	155	147
1	99	106
-1	<36	12
2	<36	15
-2	83	85
3	63	85
-3	68	65
-4	68	88
-5	68	106
-6	136	142
-7	<36	37
-8	<36	39
-9	71	64
-10	49	51
	1-91	
0	200	191
1	<36	38
-1	167	143
2	82	62
-2	<36	07
3	<36	58
-3	88	91
4	36	46
-4	67	80
5	96	64
6	117	109
7	79	64
8	<36	02
9	49	39
	1,10,1	
0	107	111
1	<36	29
-1	89	95
-2	<36	46
-3	115	121
-4	105	96
-5	<36	27
-6	<36	03
-7	<36	54
-8	58	73
-9	63	71
-10	70	63
	1,-10,1	
0	152	155
1	82	73
-1	45	45
2	68	68
-2	<36	28
3	166	144
-3	<36	17
4	95	90
5	47	26
6	<36	05
7	<36	16
8	<36	02
9	50	48
	1,11,1	
0	22	06
-1	<36	30
-2	<36	09
-3	83	75
-4	85	95
-5	<36	31
-6	<36	55
-7	87	93
-8	61	72
-9	<36	36
	1,-11,1	
0	54	50
1	76	85
-1	<36	06
2	<36	12
-2	<36	37
3	101	92
-3	40	57
4	119	117
5	43	34
6	58	48
7	<36	52
	1,12,1	
-7	53	72
	1,-12,1	
0	<36	36
1	<36	17
-1	<36	22
4	67	69
7	51	57
8	<36	46
	1,-13,1	
1	49	72
	201	
0	*279	175
1	113	110
-1	245	273
2	68	53
-2	*346	468
3	232	186
-3	167	184
4	39	48
-4	131	100
5	<36	17
-5	91	67
6	<36	44
-6	332	313
7	177	157
-7	237	202
8	67	76
-8	83	70
-9	137	144
-10	118	122
	211	
0	320	332
1	142	130
-1	276	342
2	46	42
-2	218	270
3	159	154
-3	*275	153
4	304	255
-4	209	205
5	<36	31
-5	<36	39
6	173	129
-6	98	113
7	124	129
-7	96	69
8	<36	22
-8	<36	08
-9	<36	38
-10	167	162
-11	55	72
	2-11	
0	256	270
1	257	246
-1	<36	81
2	156	169
-2	91	107
3	220	176
-3	248	249
4	304	261
-4	152	116
5	62	63
-5	266	215
6	<36	13
-6	394	371
7	43	27
-7	<36	43
8	52	36
-8	110	94
-9	77	66
-10	<36	02
	221	
0	54	48
1	158	156
-1	235	209
2	213	182
-2	<36	03
3	522	484
-3	331	318
4	221	197
-4	70	71
5	<36	43
-5	164	191
6	85	68
-6	106	86
-7	368	318
-8	85	106
-9	<36	53
-10	<36	12
-11	<36	38
	2-21	
0	273	263
1	<36	49
-1	115	152
2	140	134
-2	706	759
3	178	159
-3	62	79
4	454	377
-4	121	106
5	109	94
-5	172	167
6	<36	32
-6	77	62
7	133	95
-7	<36	19
8	68	53
-8	<36	08
-9	60	42
-10	70	72
	231	
0	401	388
1	<36	22
2	357	350
-2	79	96
3	223	226
-3	<36	19
4	36	53
-4	77	56
5	<36	16
-5	122	116
6	<36	22
-6	97	101
-7	305	265
-8	104	113
-9	<36	02
-10	107	114
-11	76	79
-1	569	626
	2-31	
0	430	474
1	355	354
-1	222	220
2	297	225
-2	146	191
3	44	55
-3	160	142
4	88	94
-4	<36	26
5	71	50
-5	<36	29
6	<36	09
-6	117	102
7	168	121
-7	89	74
8	140	128
-8	89	94
-9	119	140
-10	52	67
	241	
0	188	175
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2	<36	44
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3	*44	19
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4	<36	46
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5	<36	53
-5	201	208
6	67	57
-6	<36	12
-7	55	60
-8	<36	17
-9	<36	07
-10	107	81
-11	101	124
	2-41	
0	202	209
1	52	68
-1	<36	21
2	178	196
-2	112	77
3	103	99
-3	<36	16
4	250	276
-4	196	185
5	153	129
-5	310	325
6	<36	14
-6	255	234
7	<36	25
-7	<36	55
8	82	85
-8	134	122
-9	60	77
-10	<36	12
	251	
0	54	54
1	155	134
-1	101	101
2	165	140
-2	301	247
3	90	90
-3	100	108
4	<36	23
-4	240	255
5	73	65
-5	467	503
-6	275	247
-7	71	104
-8	186	144
-9	<36	29
-10	<36	20
-11	53	67
	2-51	
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1	94	94
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2	83	45
-2	342	343
3	<36	30
-3	<36	07
4	258	258
-4	285	282
5	204	171
-5	350	368
6	<36	35
-6	110	115
7	<36	43
-7	<36	09
8	<36	27
-8	*54	07
-9	<36	10
	261	
0	<36	16
1	88	74
-1	242	202
2	135	132
-2	288	269
3	<36	16
-3	<36	50
-4	65	53
-5	257	217
-6	345	373
-7	<36	23
-8	167	167
-9	110	111
-10	<36	21
-11	<36	06
	2-61	
0	88	86
1	243	232
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2	282	287
-2	310	302
3	<36	33
-3	<36	43
4	79	89
-4	160	157
5	60	61
-5	90	82
6	<36	35
-6	77	46
7	44	35
-7	80	92
8	91	80
-8	<36	57
	271	
0	<36	26
1	<36	31
-1	98	94
2	<36	12
-2	255	216
3	<36	23
-3	118	95
-4	92	81
-5	168	160
-6	<36	44
-7	<36	34
-8	78	65
-9	140	133
-10	82	86
	2-71	
0	277	284
1	*65	28
-1	393	387
2	254	252
-2	154	128
3	252	238
-3	<36	55
4	<36	08
-4	110	80
5	139	119
-5	89	88
6	64	76
-6	<36	42
7	<36	34
-7	68	86
8	79	66
-8	<36	42
9	63	54
	281	
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1	84	91
-1	<36	37
2	75	62
-2	45	43
-3	88	65
-4	<36	29
-5	177	149
	2-81	
0	76	72
1	<36	01
-1	<36	19
2	177	153
-2	<36	21
3	307	281
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4	138	171
-4	177	159
5	90	100
-5	82	65
6	109	119
-6	60	50
7	74	65
	291	
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1	80	95
-6	100	107
	2-91	
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1	88	77
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6	76	66
7	70	85
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5	<36	19
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6	<36	46
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7	61	101
-7	327	269
-8	154	136
-9	209	163
-10	156	121
	311	
0	83	62
1	41	65
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3	249	208
-3	268	247
4	153	148
-4	160	121
5	<36	03
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6	116	105
-6	258	215
-7	<36	23
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-9	<36	60
-10	151	127
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	3-11	
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1	72	92
-1	87	58
2	154	161
-2	289	266
3	247	265
-3	140	102
4	115	105
-4	58	42
-5	490	437
5	<36	14
6	<36	22
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7	<36	03
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-8	106	88
-9	54	58
	3k0	
2	215	165
-2	51	41
3	327	267
-3	278	273
4	125	120
-4	103	97
5	<36	06
-5	<36	43
6	<36	25
-6	81	81
7	<36	27
-7	257	270
8	<36	14
-8	116	128
9	<36	39
-9	174	166
-10	137	120
-11	62	63
-12	70	81
	401	
0	144	189
1	174	179
-1	91	120
-2	52	80
-3	300	307
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-5	<36	22
-6	51	59
-7	353	355
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-10	195	179
-11	58	57
	411	
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1	<36	18
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-2	37	44
3	154	130
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4	<36	54
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5	<36	19
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6	59	71
-6	259	242
-7	<36	07
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-10	132	126
-11	111	124
	4-11	
0	50	56
1	107	121
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3	138	130
-3	146	119
4	94	95
-4	<36	38
5	<36	21
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6	<36	37
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-8	<36	19
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2	282	233
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3	166	150
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5	<36	25
-5	119	114
6	<36	16
-6	215	217
7	<36	50
-7	180	185
-8	40	35
-9	159	158
-10	83	86
-11	59	47
-12	75	85
	501	
0	251	225
1	236	224
-1	77	99
-2	155	160
-3	70	101
-4	49	73
-5	198	161
-6	132	126
-7	348	293
-8	152	117
-9	245	197
-10	245	200
-11	85	66
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0	143	118
1	<36	77
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2	54	34
-2	99	111
3	<36	53
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4	<36	50
-4	230	233
-5	<36	10
-6	<36	39
-7	<36	10
-8	<36	01
-9	120	111
-10	121	124
-11	102	122
-12	<36	14
	5-11	
0	<36	19
1	247	234
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2	169	165
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3	<36	40
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4	114	85
-4	121	98
5	<36	13
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-6	436	391
-7	411	357
-8	<36	24
-9	217	156
-10	92	64
	5k0	
2	149	127
-2	87	74
3	108	97
-3	<36	12
4	<36	29
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-5	86	74
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-7	73	70
-8	102	106
-9	123	125
-10	66	67
-11	<36	27
-12	<36	24
	601	
0	266	236
1	161	162
-1	<36	34
-2	224	227
-3	182	170
-4	<36	04
-5	139	97
-6	194	214
-7	149	135
-8	<36	32
-9	237	204
-10	146	101
	611	
0	146	121
-1	92	94
-2	145	141
-3	435	421
-4	353	317
-5	<36	50
-6	<36	37
-7	<36	07
-8	52	46
-9	132	141
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-11	<36	11
-12	<36	56
	6-11	
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-1	<36	33
2	92	101
-2	68	96
3	<36	21
-3	227	210
-4	<36	39
-5	354	284
-6	245	229
-7	71	78
-8	224	159
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3	114	82
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4	<36	08
-4	<36	31
5	52	52
-5	<36	49
-6	139	158
-7	<36	39
-8	<36	72
-9	100	120
-10	80	79
-11	<36	23
-12	<36	04
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0	140	148
1	94	106
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-3	213	191
-4	89	80
-5	<36	18
-6	118	127
-7	<36	20
-8	131	102
-9	198	169
-10	<36	36
-11	73	80
-12	72	74
	711	
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-2	109	117
-3	241	243
-4	225	246
-5	<36	56
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-11	49	59
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	7-11	
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1	102	129
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-4	<36	39
-5	271	218
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-7	74	67
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	7k0	
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-4	<36	07
-5	<36	05
-6	108	103
-7	95	94
-8	<36	15
-9	93	118
-10	93	111
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1	<36	54
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-3	93	86
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-10	72	84
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-12	81	96
	8-11	
0	55	48
1	87	76
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	8k0	
2	<36	16
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3	<36	60
-3	<36	03
-4	<36	12
-5	<36	11
-6	79	54
-7	95	107
-8	<36	16
-9	58	73
-10	68	86
	901	
0	<36	24
-8	88	84
-9	136	128
-10	81	70
-11	<36	22
-12	42	26
	911	
-12	79	73
	9-11	
0	<36	24
-1	<36	32
-2	<36	34
-3	<36	13
-4	<36	22
-5	105	84
-6	159	126
-7	<36	20
-8	91	85
-9	101	56
	9k0	
-2	<36	20
-3	<36	04
-4	<36	10
-5	<36	26
-6	59	61
-7	64	86
	10,0,1	
-9	117	117
-10	77	94
	10,-1,1	
-2	<36	06
-3	<36	04
-4	<36	09
-5	63	56
-6	138	118
-7	<36	19
-8	102	95
-9	107	86
	11,0,1	
-9	64	68
-10	46	65
	11,-1,1	
-6	64	70

to which they are bonded. Allowance was made for the anomalous scattering of the titanium atoms but it made no significant difference to the R value.

Anisotropic refinement

Several cycles of least-squares refinement in which the titanium and oxygen atoms were given variable anisotropic temperature factors completed the structure determination. Initially an attempt was made to refine anisotropic temperature factors for the carbon atoms. This led to very elongated ellipsoids of vibration for five of the eight carbon atoms, two normal ellipsoids and one which did not refine realistically. It was therefore decided to give each carbon atom the

Table 2. *Positional and thermal parameters for the titanium, oxygen and carbon atoms*

The b_{ij} are defined by: $T = \exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)]$.
Estimated standard deviations $\times 10^{+4}$ are in brackets.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ti(1)	0·5117 (05)	0·2905 (03)	0·2914 (03)	0·0240 (07)	0·0102 (02)	0·0141 (03)	0·0054 (05)	0·0121 (04)	0·0013 (02)
Ti(2)	0·5171 (05)	0·6098 (03)	0·4060 (03)	0·0252 (07)	0·0107 (02)	0·0147 (03)	0·0086 (04)	0·0130 (04)	0·0060 (02)
O(1)	0·3654 (21)	0·5926 (13)	0·2035 (12)	0·0585 (51)	0·0271 (20)	0·0169 (16)	0·0284 (31)	0·0223 (27)	0·0150 (16)
O(2)	0·6981 (18)	0·7718 (09)	0·4887 (15)	0·0439 (41)	0·0092 (11)	0·0454 (31)	0·0107 (22)	0·0378 (32)	0·0116 (16)
O(3)	0·7011 (15)	0·2460 (11)	0·3048 (12)	0·0243 (28)	0·0145 (13)	0·0214 (18)	0·0064 (21)	0·0147 (21)	−0·0004 (13)
O(4)	0·3612 (17)	0·2836 (13)	0·0633 (13)	0·0351 (37)	0·0199 (17)	0·0225 (20)	0·0108 (27)	0·0195 (25)	0·0034 (16)
O(5)	0·3388 (15)	0·0904 (15)	0·2268 (12)	0·0184 (24)	0·0295 (22)	0·0182 (17)	0·0085 (25)	0·0117 (18)	−0·0026 (17)
O(6)	0·6570 (13)	0·5020 (08)	0·3812 (09)	0·0189 (22)	0·0091 (09)	0·0137 (12)	0·0049 (16)	0·0122 (15)	0·0042 (09)
O(7)	0·3667 (14)	0·6719 (09)	0·4648 (10)	0·0192 (24)	0·0130 (11)	0·0141 (13)	0·0089 (18)	0·0105 (16)	0·0065 (10)
O(8)	0·3965 (13)	0·4002 (08)	0·3588 (08)	0·0194 (23)	0·0092 (09)	0·0107 (11)	0·0062 (16)	0·0088 (15)	0·0030 (08)
C(1)	0·3035 (33)	0·5993 (22)	0·0530 (25)	0·0424	0·0224	0·0309	0·0120	0·0223	0·0101
C(2)	0·7705 (33)	0·8971 (22)	0·4829 (25)	0·0438	0·0232	0·0319	0·0124	0·0230	0·0104
C(3)	0·7252 (29)	0·1499 (19)	0·2162 (21)	0·0353	0·0187	0·0257	0·0100	0·0185	0·0084
C(4)	0·7790 (50)	0·7940 (50)	0·0790 (50)	0·0536	0·0284	0·0390	0·0152	0·0282	0·0128
C(5)	0·2170 (100)	0·9830 (100)	0·1330 (100)	0·0536	0·0284	0·0390	0·0152	0·0282	0·0128
C(6)	0·7921 (24)	0·5484 (15)	0·3526 (17)	0·0251	0·0133	0·0183	0·0071	0·0132	0·0060
C(7)	0·2305 (28)	0·7279 (18)	0·3776 (20)	0·0322	0·0170	0·0234	0·0091	0·0169	0·0077
C(8)	0·1568 (21)	0·3487 (13)	0·2432 (15)	0·0201	0·0106	0·0147	0·0057	0·0106	0·0048

Table 3. *Bond lengths and estimated standard deviations*

	Uncorrected bond lengths (Å)	σ	Corrected for thermal motion (Atoms riding) (Å)	σ
Oxygen atoms bonded to 1 titanium atom				
O(1)–Ti(2)	1·745	0·009	1·786	0·010
O(2)–Ti(2)	1·751	0·010	1·780	0·011
O(3)–Ti(1)	1·818	0·013	1·835	0·013
O(4)–Ti(1)	1·999	0·011	2·015	0·012
O(5)–Ti(1)	2·072	0·014	2·078	0·014
Oxygen atoms bonded to 2 titanium atoms				
O(6)–Ti(1)	2·054	0·008	2·048	0·008
O(6)–Ti(2)	1·963	0·010	1·959	0·010
O(7)–Ti(1′)	2·086	0·009	2·084	0·009
O(7)–Ti(2)	1·960	0·011	1·961	0·011
Oxygen atoms bonded to 3 titanium atoms				
O(8)–Ti(1)	2·202	0·010	2·196	0·010
O(8)–Ti(2)	2·138	0·008	2·134	0·009
O(8)–Ti(2′)	2·155	0·008	2·151	0·008
Oxygen–carbon bonds				
O(1)–C(1)	1·398	0·022	1·384	0·023
O(2)–C(2)	1·385	0·022	1·388	0·023
O(3)–C(3)	1·383	0·022	1·382	0·023
O(4)–C(4′)*	1·241	0·050	1·277	0·050
O(5)–C(5)*	1·152	0·100	1·186	0·100
O(6)–C(6)	1·435	0·019	1·446	0·019
O(7)–C(7)	1·420	0·021	1·438	0·021
O(8)–C(8)	1·494	0·016	1·500	0·016

* Carbon atoms belonging to partially hydrolysed methoxide groups.

temperature factor derived for it in the final cycle of isotropic least-squares refinement, and to hold it constant. After two more refinement cycles and inspection of Fourier and difference Fourier syntheses it was clear that the atoms C(4) and C(5) were in partially hydrolysed methoxide groups. By trial and error with a sequence of Fourier and difference Fourier syntheses the population parameters were estimated as 0·75 for C(4) and 0·50 for C(5). Their coordinates were also obtained and not varied in subsequent refinement cycles which now converged rapidly.

Table 1 lists the observed structure factors and the structure factors calculated after the final refinement cycle in which the variables were an overall scale factor, coordinates of all atoms except C(4) and C(5), and anisotropic thermal parameters for titanium and oxygen atoms. The largest parameter shift in the final refinement cycle was 30% of its standard deviation and the final R value was 0·139 for 1285 reflexions or 0·133 with the unobserved reflexions excluded. The weighting factor used was $1/F_{obs}^2$, with a maximum value of $1/(2·25F_{min})^2$ where F_{min} is the average minimum observable structure factor. Large reflexions with extinction effects and all unobserved reflexions calculating less than F_{min} were given zero weight. Unobserved reflexions calculating greater than F_{min} were treated as though $F_{obs}=F_{min}$. The final atomic coordinates and their standard deviations calculated by the least-squares refinement program are listed in Table 2. The bond lengths and bond angles within the molecule are given in Tables 3 and 4 respectively.

The mean separation of two atoms over their joint distribution cannot be calculated accurately as the correlation between their thermal displacements is not known. However, to improve on the uncorrected bond lengths the mean separation, assuming the lighter atom to be riding on the heavier atom, has also been calculated using the method of Busing & Levy (1964). The bond lengths, bond angles and standard deviations were all calculated from the atomic positional and thermal parameters and their standard deviations. The function and error program *ORFFE* (Busing, Martin & Levy, 1964) was used.

Fig. 1 shows the molecular structure and Fig. 2 the oxygen octahedra. Both Figures are computer-drawn stereoscopic views using the program *ORTEP* (Johnson, 1965) with the ellipsoids representing the volume in which there is 30% probability of including the atom. Anisotropic temperature factors were used for the titanium and oxygen atoms and isotropic temperature factors were used for the carbon atoms.

In an attempt to determine whether significant errors had been introduced because the carbon temperature factors had not been varied anisotropically a cycle of refinement was calculated varying positional and anisotropic thermal parameters for all atoms. The vibration parameters derived for the carbon atoms had standard deviations that were about twice those for the oxygen atoms and the ellipsoids were physically

Table 4. *Bond angles and estimated standard deviations*

Angle	θ	$\sigma(\theta)$
O(3)–Ti(1)–O(4)	99·6°	0·5°
O(3)–Ti(1)–O(5)	96·4	0·5
O(3)–Ti(1)–O(6)	94·7	0·5
O(3)–Ti(1)–O(7')	93·7	0·5
O(4)–Ti(1)–O(5)	94·2	0·5
O(4)–Ti(1)–O(6)	90·7	0·4
O(4)–Ti(1)–O(8)	94·5	0·4
O(5)–Ti(1)–O(8)	96·7	0·4
O(5)–Ti(1)–O(7')	89·2	0·4
O(6)–Ti(1)–O(8)	70·7	0·4
O(6)–Ti(1)–O(7')	83·2	0·3
O(8)–Ti(1)–O(7')	71·4	0·4
O(3)–Ti(1)–O(8)	159·9	0·4
O(4)–Ti(1)–O(7')	165·7	0·5
O(5)–Ti(1)–O(6)	166·9	0·5
O(1)–Ti(2)–O(2)	100·2	0·6
O(1)–Ti(2)–O(6)	97·7	0·5
O(1)–Ti(2)–O(7)	94·6	0·6
O(1)–Ti(2)–O(8)	94·5	0·5
O(2)–Ti(2)–O(6)	94·2	0·5
O(2)–Ti(2)–O(7)	99·0	0·5
O(2)–Ti(2)–O(8')	93·3	0·5
O(6)–Ti(2)–O(8)	73·8	0·4
O(6)–Ti(2)–O(8')	89·7	0·4
O(7)–Ti(2)–O(8)	89·6	0·4
O(7)–Ti(2)–O(8')	74·8	0·4
O(8)–Ti(2)–O(8')	74·0	0·3
O(1)–Ti(2)–O(8')	164·1	0·6
O(2)–Ti(2)–O(8)	162·3	0·5
O(6)–Ti(2)–O(7)	160·0	0·4
Ti(1)–O(6)–Ti(2)	112·8	0·5
Ti(1)–O(7')–Ti(2')	111·5	0·5
Ti(1)–O(8)–Ti(2)	100·9	0·4
Ti(1)–O(8)–Ti(2')	100·3	0·4
Ti(2)–O(8)–Ti(2')	106·0	0·3
C(1)–O(1)–Ti(2)	160·6	1·5
C(2)–O(2)–Ti(2)	152·4	1·3
C(3)–O(3)–Ti(1)	140·0	1·1
*C(4')–O(4)–Ti(1)	142·3	1·8
*C(5)–O(5)–Ti(1)	153·0	3·1
C(6)–O(6)–Ti(1)	117·1	0·8
C(6)–O(6)–Ti(2)	124·3	0·8
C(7)–O(7)–Ti(2)	125·7	1·0
C(7)–O(7)–Ti(1')	120·0	1·0
C(8)–O(8)–Ti(2)	114·7	0·7
C(8)–O(8)–Ti(1)	118·3	0·7
C(8)–O(8)–Ti(2')	114·6	0·7

* Carbon atoms belonging to partially hydrolysed methoxide groups.

reasonable except for that of C(6). A stereoscopic diagram of these results drawn by *ORTEP* showed that for the atoms other than C(6) the major axes of the vibration ellipsoids were in directions consistent with the molecular structure. However, this refinement made no significant difference to the coordinates of Table 2. Some refinement cycles using unit weighting were calculated, reflexions suffering from extinction effects and unobserved reflexions were treated as previously, and again the results were essentially those of the final refinement. The contributions of the hydrogen atoms to the calculated structure factors were ignored throughout.

Results and discussion

The crystal structure of titanium tetramethoxide consists of discrete tetrameric molecules $Ti_4(OCH_3)_{16}$. Each

molecule has a crystallographic centre of symmetry as well as an apparent mirror plane of symmetry not implied by the space group. In Fig. 1 the viewing direction is nearly parallel to the mirror plane, the mean plane of the atoms C(8), O(8), Ti(1), O(3), C(3) and their centrosymmetric pairs. The titanium atoms are octahedrally coordinated to six oxygen atoms and linked through methoxide oxygen bridges. The four titanium–oxygen octahedra which may be seen in Fig. 2 share either two or three edges; the pair of atoms O(8) and O(8′) are common vertices to three octahedra and two other pairs, O(6) and O(6′), and O(7) and O(7′), are common vertices to two octahedra.

As may be seen in Fig. 1 it is not meaningful to describe the molecular structure in terms of the em-

pirical formula $Ti(OCH_3)_4$. Agreeing with this, solutions of the tetramethoxide in dry toluene at moderate concentrations were found to contain 88% tetrameric molecules. Even at low concentrations the solutions still contained 60% tetrameric molecules, with 27% monomers and only very small percentages of dimer or trimer.

The two crystallographically independent titanium atoms have different coordinations of methoxide oxygen bridges and methoxide groups; Ti(2) is linked by four methoxide oxygen bridges to three titanium atoms while Ti(1) is linked by three bridges to two titanium atoms. Two of the singly coordinated methoxide groups are coordinated to Ti(2) and three to Ti(1). The Ti(1) atoms are not as centrally bonded within the molecule
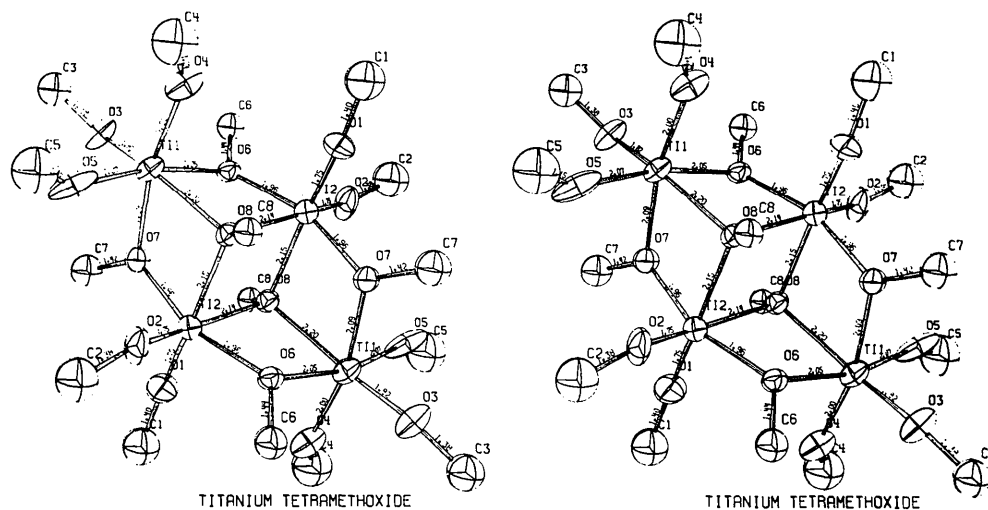

Fig. 1. A stereoscopic pair of drawings of the molecule viewed almost perpendicularly to the plane of the titanium atoms and almost parallel to the apparent mirror plane of symmetry.
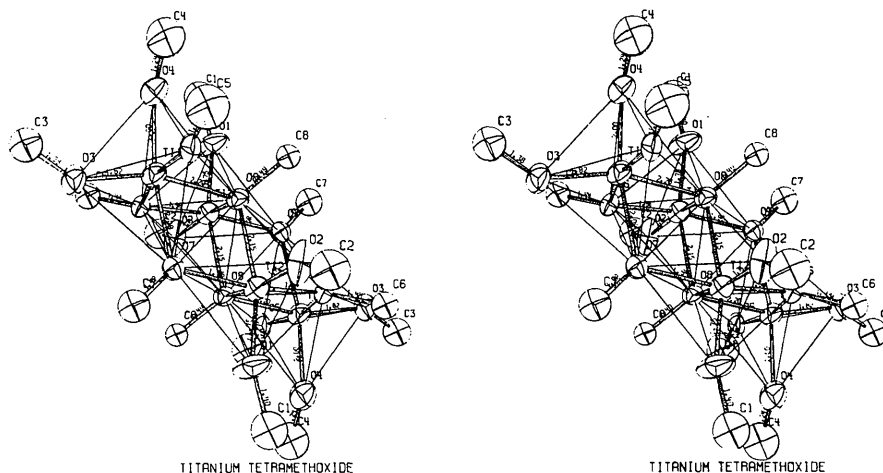

Fig. 2. A stereoscopic pair of drawings of the molecule with the titanium–oxygen octahedra outlined.

as the Ti(2) atoms, and have slightly more pronounced anisotropic thermal vibrations. As would be expected, the partially hydrolysed methoxide groups are coordinated to them. As no oxygen deficiency was found in the molecule the hydrolysed methoxide groups have apparently been replaced by hydroxide groups.

The expected upper limits of error in the bond lengths and angles, estimated as three times the standard deviation (σ) calculated by the least-squares analysis, are 0·03 Å for titanium–oxygen bonds and 0·06 Å for oxygen–carbon bonds, 1·4° for Ti–O–Ti or O–Ti–O angles and 3·0° for Ti–O–C angles. The high value of 3σ allows for the random errors and those caused by absorption and extinction effects. The difference between the angles O(3)–Ti(1)–O(4) and O(3)–Ti(1)–O(5) and that between the lengths O(4)–Ti(1) and O(5)–Ti(1) are both about 6σ, which is a significant deviation from mirror symmetry. These comparisons involve both O(4) and O(5) of the partly hydrolysed methoxide groups. The bond lengths and angles which include the partly present atoms C(4) and C(5) have limits of error about four times as large as those quoted for the other carbon atoms, and little significance can be attached to them.

The titanium–oxygen bond lengths may be grouped conveniently into the six categories of Table 5. In general the more titanium atoms coordinated to an oxygen atom the longer are its titanium–oxygen bonds, and where bonds are from oxygen atoms with the same titanium coordination a bond length to Ti(1) is always longer than an equivalent bond length to Ti(2), though it does not seem probable that there are simply two effective coordination radii for the titanium atoms. The titanium–oxygen bonds of O(6) and O(7) have an average bond length to Ti(1) 0·11 Å greater than that to Ti(2), a significant difference as $\sigma = 0·010$ Å for these bonds. The bonds to Ti(1) from O(4) and O(5) are significantly longer than the similar bonds from the oxygen atoms of non-hydrolysed groups, the mean difference being 0·27 Å. These long bonds from Ti(1) are apparently due to the hydrolysis as the bond length O(3)–Ti(1) is much shorter. The range of titanium–oxygen bond lengths, 1·75 to 2·20 Å, is considerable, and the four octahedra of the basic Ti_4O_{16} units are appreciably distorted. Faces that would be parallel in a regular octahedron are inclined to each other at up

to 12°. Both Ibers (1963) and Witters & Caughlan (1965) who found the titanium and oxygen atom positions in titanium tetraethoxide and monomethyltriethyltitanate reported the octahedral arrangement of the oxygen atoms in the tetramer and observed a similar range of Ti–O bond lengths.

The carbon–oxygen bond lengths in the non-hydrolysed methoxide groups vary from 1·38 to 1·39 Å when the oxygen is bonded to one titanium atom, 1·44 to 1·45 Å when the oxygen is bonded to two titanium atoms and it is 1·50 Å when the oxygen is bonded to three titanium atoms. The average distance between each carbon atom and its four nearest neighbours, 3·90 Å, is the expected van der Waals separation for methyl groups. The minimum separation of 3·77 Å occurs between C(2) and C(6). Intermolecular packing is similarly efficient with 3·90 Å the average close approach between carbon atoms. The shortest intermolecular approach not involving a hydrolysed carbon is 3·67 Å from O(3) to C(6'), while the minimum intermolecular approach is 3·53 Å between C(5) and C(5'). The close packing of the methyl groups appears to influence the Ti–O–C bond angles. For methoxide groups which are coordinated to only one titanium atom the Ti–O–C angles vary between 140·0° and 160·6°, a range of 20·6°, while the angles which include the doubly and triply coordinated methoxide groups vary by 8·6° and 3·7° respectively. These latter groups are much more rigidly held in position by titanium–oxygen bonds and not easily distorted from position by steric effects.

The thermal vibrations of the oxygen atoms are largest in directions normal to their bonds. The root mean square thermal displacements of the oxygen atoms have minimum values of about 0·18 Å but the maximum value depends on the oxygen–titanium coordination number. The oxygen atoms coordinated to one titanium atom have maximum thermal displacements varying from 0·34 Å for O(3) to 0·44 Å for O(5). The maximum thermal displacements of O(6) and O(7) which are coordinated to two titanium atoms are 0·23 and 0·25 Å respectively while O(8), which has tetrahedral coordination to C(8) and three titanium atoms, has a maximum thermal displacement of 0·23 Å and these three oxygen atoms have nearly isotropic thermal motion. The refined anisotropic thermal parameters of the carbon atoms did not define an ellipsoid for C(6), and for C(5) in the half hydrolysed methoxide group, the major axis of its highly elongated ellipsoid was calculated to be in the direction of the O(5) atom.

Table 5. *Titanium–oxygen bond lengths*

(Atoms riding, mean $\sigma = 0·010$)

Number of titanium atoms bonded to oxygen	Oxygen – Ti(1) bond length (Å)	Oxygen – Ti(2) bond length (Å)
1	1·84 2·02 (1·98) 2·08	1·79 1·78 (1·78)
2	2·05 (2·07) 2·08	1·96 (1·96) 1·96
3	2·20 (2·20)	2·13 (2·14) 2·15

Professor R. L. Martin and Dr G. Winter of the University of Melbourne for their continuing interest in this project and for many helpful discussions. Dr Winter measured the density of the crystals and also did the cryoscopic analysis. The calculations were done on the C.S.I.R.O. Computing Network and arranged through the Melbourne Computing Centre with excellent cooperation from their staff.

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The Structure of Na4Mn4Ti5O18

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$Na_4Mn_4Ti_5O_{18}$, formed at 1200°C by crystallization from the composition $NaMnTiO_4$, is orthorhombic, with unit-cell dimensions $a = 9.268$, $b = 26.601$, $c = 2.888$ Å. Mn^{3+} and Ti^{4+} atoms occupy octahedral positions, while the coordination of another Mn^{3+} is a rectangular pyramid. In this structure, groups of octahedra, joined by extensive edge and corner sharing, are linked together by the five-coordinated Mn^{3+} to leave a series of tunnels for the sodium ions. One of these is a single tunnel similar to that found in calcium ferrite; the other is a much larger one and contains sites for four sodium ions, only half of which are filled. The chemical composition was deduced from this structure analysis.

Introduction

An investigation of a group of alkali-transition metal oxides of the form $NaA^{3+}B^{4+}O_4$ (Reid, Wadsley & Sienko, 1967) has shown that many of them, including $NaScTiO_4$, $NaScZrO_4$, $NaScHfO_4$, $NaFeSnO_4$, $NaScSnO_4$ and $NaFeTiO_4$ prepared below their melting points, are isomorphous with calcium ferrite. Another compound close to these in overall stoichiometry, $Na_{0.9}Fe_{0.9}Ti_{1.1}O_4$, formed a related structure, the outstanding features of which were greater edge sharing of the octahedra, and the formation of double tunnels to accommodate the sodium atoms (Mumme & Reid, 1968).

Attempts to make additional compounds isomorphous with these were unsuccessful. '$NaAlTiO_4$' formed $Na_2Ti_7O_{15}$ together with other unidentified phases (Wadsley & Mumme, 1968) while '$NaCoTiO_4$' and '$NaNiTiO_4$' each formed a number of heteropolytypes containing more or less sodium, and having layer structures with close similarities to α-$NaFeO_2$ (Mumme, Reid & Wadsley, 1968). In all of these there were obvious and gross changes of composition. $NaMnTiO_4$, however, prepared by solid state reaction appeared to form a unique congruently melting single phase. The ideal composition of it, $Na_4Mn_4Ti_5O_{18}$, was derived from this structural analysis.

Experimental

Well formed prismatic crystals of $Na_4Mn_4Ti_5O_{18}$ were originally prepared by melting the composition '$NaMnTiO_4$' at 1200°C. The weight loss from 5 grams of sample, a mixture of TiO_2, sodium oxalate and MnO_2 held in a platinum dish, was only 0.3% greater than the expected weight loss for total conversion of Mn^{4+} to Mn^{3+}.

The approximate lattice parameters were determined from single-crystal photographs and were used to index the powder diffractometer data, which had been col-