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The Crystal and Molecular Structure of Dichlorodiphenoxytitanium(IV)

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Dichlorodiphenoxytitanium(IV) crystallizes in space group $P2_1/n$ with $a = 9.82$ A, $b = 14.01$ A, $c = 9.84$ A, $\beta = 94° 50'$, and $z = 4$. Attempts to solve the structure from the Patterson failed, but direct sign determination by symbolic addition was used successfully. The final R value for 1275 reflections is 6.1%. Dichlorodiphenoxytitanium(IV) is dimerically located around the center of symmetry, the two titaniums being joined with oxygen bridges, each titanium being pentacoordinated in the form of a trigonal bipyramid. The two chlorine atoms and an oxygen atom form the equatorial plane. One of the oxygens joining titanium to the phenyl ring has a bond angle of 167° and two short bonds, indicating probable sp hybridization. The other oxygen is probably using sp^2 hybrid orbitals, since it is bonded to carbon and two titaniums with bond angles near 120°. Titanium–oxygen distances are 1.744, 1.910, and 2.122 A. The two titanium–chlorine distances are 2.219 and 2.209 A, and the two carbon–oxygen distances are 1.359 and 1.422 A. The red color of the crystal is probably due to delocalized electrons in the C_6H_5OTi group or splitting of d energy levels of titanium due to the five ligands.

Introduction

Preliminary crystal structures have been reported for two organic compounds of titanium, tetraethyl titanate by Ibers[1] and monomethyltriethyl titanate by Witters and Caughlan.[2] Each of these compounds has been shown to be tetrameric in the crystalline state, the titanium atom exhibiting octahedral coordination. Apparent molecular weights indicate that the alkoxides are trimeric in benzene solutions.[3,4] A striking difference is observed in the appearance of chlorophenoxytitanium in that a deep red color is exhibited, in contrast to the colorless alkoxides. In connection with structural studies of organic compounds of titanium, we became interested in knowing whether or not titanium would show octahedral coordination in these chlorophenoxide compounds and why the marked difference in color existed. Thus, an X-ray crystal structure analysis was started, in the hope of understanding the unusual characteristics.

Experimental Section

Crystals of $TiCl_2(OC_6H_5)_2$ were prepared by heating $TiCl_3(OC_6H_5)$ in a closed container at 120–150° and 1 mm pressure. The $TiCl_3(OC_6H_5)$ disproportionates, liberating $TiCl_4$, and crystals of $TiCl_2(OC_6H_5)_2$ collect on the walls on the container.

The $TiCl_3(OC_6H_5)$ was prepared by a method first described by Luchinskii and Altmann,[5] which was used by Crowe and Caughlan[6] to obtain purified crystals. This method consists of slowly mixing cold dilute solutions of phenol in petroleum ether and chloroform with a similar solution of titanium tetrachloride. Upon distilling the solvent and cooling, crystals of $TiCl_3(OC_6H_5)$ are obtained.

Crystals of $TiCl_2(OC_6H_5)_2$ have a deep red color and are somewhat unstable in moist air although they hydrolyze much less readily than either $TiCl_4$ or the simple titanium alkoxides. Several crystals were sealed in Pyrex capillaries and one was selected for the X-ray study. Its approximate dimensions were 0.2 × 0.2 × 1 mm. This crystal exhibited $P2_1/n$ symmetry as indicated by lattice parameters and systematic extinction, *i.e.*, $k \neq 2n$ for the $0k0$ zone and $h + l \neq 2n$ for the $h0l$ zone; $a = 9.821 \pm 0.003$ A, $b = 14.006 \pm 0.004$ A, $c = 9.836 \pm 0.003$ A, and $\beta = 94° 50' \pm 10'$. The density was measured on another crystal by flotation and was 1.49 g/cm^3, compared to 1.50 g/cm^3 calculated for four molecules per unit cell. The linear absorption coefficient for Mo Kα radiation is 10.34 cm^{-1}.

The data were collected using a General Electric single-crystal orienter and spectrogoniometer equipped with a scintillation counter for detector. Independent reflections were collected by the 2θ-scan technique (moving crystal–moving counter method) using 100-sec scans and reading the background for 50 sec on each side of the peak. The scan rate in 2θ was 2°/min; the take-off angle 4°. Zirconium-filtered molybdenum radiation was used; 2600 reflections were collected, of which 1175 were treated as observed. The data were corrected for the Lorentz-polarization factor using an IBM 1620 computer. No absorption correction was applied, since for this size crystal the effects are negligible using Mo Kα radiation. For structure factor calculations, form factors used were from the literature.[7] Anomalous terms of the form factors were not used.

Structure Determination

The first attempt to solve the structure was from a three-dimensional Patterson map.[8] The Harker section showed peaks of correct weight and relative position to provide reasonable positions for the titanium and chlorine atoms. A partial structure factor calculation provided phases from which Fouriers were calculated in order to locate the remaining atoms. A minimum function was calculated from a sharpened Patterson. This indicated reasonable oxygen positions consistent with those from the Fourier. Using the indicated titanium, two chlorine, and two oxygen positions for a partial structure factor calculation, an R factor of 50% was obtained. The three-dimensional Fourier from these phases showed badly distorted phenyl rings. Numerous attempts were made to refine this structure, all of which failed to reduce the R factor

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(1) J. A. Ibers, *Nature*, **197**, 686 (1963).

(2) R. D. Witters and C. N. Caughlan, *ibid.*, **205**, 1312 (1965).

(3) C. N. Caughlan, H. S. Smith, W. Katz, W. Hodson, and R. W. Crowe, *J. Am. Chem. Soc.*, **73**, 5652 (1951).

(4) D. C. Bradley, R. C. Mehrotra, J. D. Stanwick, and W. J. Wardlaw, *J. Chem. Soc.*, 2025 (1953).

(5) G. P. Luchinskii and E. S. Altmann, *Z. Anorg. Allgem. Chem.*, **225**, 321 (1935).

(6) R. W. Crowe and C. N. Caughlan, *J. Am. Chem. Soc.*, **72**, 1694 (1950).

(7) J. A. Ibers, International Tables for Crystallography, Kynoch Press, Birmingham, England, 1962, Vol. III, Table 3.3 1A.

(8) All programs used except the least-squares refinement are from the Montana State University Crystallographic Program Library written for IBM 1620 Model II by C. N. Caughlan, C. T. Li, G. W. Svetich, K. D. Watenpaugh, and R. D. Witters.

below 35%. Also, numerous attempts were made to reinterpret the Patterson, all of which led to essentially the same conclusion.

At this point we decided to try the symbolic sign determination method described by Karle and Karle.[9] Accordingly, the structure factors were normalized using the absolute scale factor and temperature factor from a Wilson plot.[10] Computer programs for normalization of structure factors and computing relationships are available in our library.[8]

Initially, three origin-determining signs and four symbolic signs were assigned (Table I). The Σ_2 relations defined by $sE_{\vec{h}} \sim s\sum_{k} E_{\vec{k}} \cdot E_{\vec{h}-\vec{k}}$ were computed for 242 normalized structure factors exceeding 1.4. As the relationships were built up, all the symbolic signs were eliminated except c. Subsequently, 230 signs were assigned with only one arbitrary choice. Using these two possible sets of signs, two three-dimensional E maps were computed. The correct structure was immediately apparent in the E map using c = (−). Upon checking the signs after refinement, all the signs proved to be correct.

TABLE I

INITIAL CHOICE OF SIGNS

h, k, l	Sign	E	h, k, l	Sign	E
0, 5, 2	+	1.83	−3, 9, 1	a	2.93
2, 8, 1	+	2.48	2, 2, 4	b	2.27
−3, 1, 6	+	2.99	9, 2, 2	c	3.86
			−3, 1, 1	d	2.86

The x and y positions of the titanium and two chlorines were the same as those obtained from the Patterson function. The z coordinates of the titanium and two chlorines were interchanged. This had the effect of moving the $TiCl_2$ groups closer together along the c axis in the incorrect structure. However, this completely changed the interpretation of some of the peaks in the Patterson, even though giving approximately the same peak heights. The peak which caused the most difficulty in the Patterson was interpreted as a double weight Ti–Ti Harker peak, but actually was four Cl–Cl interactions located in approximately the same place. The same Ti–Cl vectors could be explained with both the correct and incorrect structure. Much of this difficulty was caused because the titanium and the chlorines in the centrosymmetrically related positions had the same y coordinate, causing multiple-weight peaks.

Refinement started with all atoms at the approximate positions determined from the E map and R = 0.29, where $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. The structure was refined using the full-matrix least-squares refinement program of Busing, Levy, and Martin.[11] Three cycles varying positional parameters decreased the R index to 0.19, three cycles varying positional parameters and individual temperature factors reduced the R index to 0.11, and three cycles varying positional parameters and anisotropic temperature factors brought the R index to 0.061. In the refinement all observed reflections were equally weighted.

Final positional and thermal parameters with standard deviations are listed in Tables II and III. Table III lists the thermal parameters, and Table IV lists the anisotropic thermal parameters in terms of the mean-square amplitudes of vibration along the principal axes of the thermal ellipsoids. The bond lengths and bond angles with standard deviations are listed in Tables V and VI. Table VII contains the observed and calculated structure factors.

TABLE II

ATOMIC COORDINATES

	x	y	z
Ti(1)	0.5031 (2)[a]	0.4714 (1)	0.3389 (2)
Cl(2)	0.3207 (3)	0.5353 (3)	0.2275 (3)
Cl(3)	0.6958 (3)	0.5269 (3)	0.2663 (3)
O(4)	0.4927 (7)	0.4166 (5)	0.5156 (6)
O(5)	0.4972 (9)	0.3628 (5)	0.2518 (7)
C(6)	0.4807 (10)	0.3167 (7)	0.5381 (9)
C(7)	0.5958 (13)	0.2656 (8)	0.5736 (11)
C(8)	0.5827 (15)	0.1675 (8)	0.5929 (12)
C(9)	0.4563 (16)	0.1256 (8)	0.5801 (12)
C(10)	0.3388 (15)	0.1779 (9)	0.5510 (12)
C(11)	0.3510 (12)	0.2769 (9)	0.5272 (11)
C(12)	0.4816 (11)	0.2919 (7)	0.1575 (11)
C(13)	0.4564 (12)	0.3191 (8)	0.0218 (11)
C(14)	0.4349 (15)	0.2486 (10)	−0.0768 (11)
C(15)	0.4444 (13)	0.1504 (10)	−0.0392 (14)
C(16)	0.4707 (13)	0.1282 (8)	0.0974 (13)
C(17)	0.4908 (13)	0.1983 (8)	0.1991 (11)

[a] The number in parentheses is the standard deviation and refers to the least significant digits.

Discussion of the Structure

Figure 1 shows the arrangement of the molecules in the unit cell. Dichlorodiphenoxytitanium(IV) is a dimer located around the center of symmetry. The titanium atoms are each pentacoordinated and are connected by two oxygen bridges. The titanium–oxygen distances vary considerably, the shortest being 1.744 (10) A, the next 1.910 (9) A, and the longest 2.122 (9) A. The ionic Ti–O distance in rutile is 1.944 A, whereas in Ti_3O_5 the Ti–O distances range from 1.83 to 2.7 A.[12]

The two titanium–chlorine distances are nearly the same (2.219 (6) and 2.209 (6) A) and are slightly longer than those reported for $TiCl_4$, *i.e.*, 2.185 A.[13]

There are several noteworthy features about the structure that warrant further discussion. The plane formed by the two titaniums, the bridging oxygens O(4) and O(4′), and the carbons C(6) and C(6′) is planar to within the standard error of the determination.[14] The equation of the plane is 0.99709X −

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[9] I. L. Karle and J. Karle, *Acta Cryst.*, **16**, 969 (1963).

[10] A. J. C. Wilson, *Nature*, **150**, 152 (1942).

[11] W. R. Busing, K. O. Martin, and H. A. Levy, ORFLS, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

[12] S. Asbrink and A. Magneli, *Acta Cryst.*, **12**, 575 (1959).

[13] "Tables of Interatomic Distance and Configuration in Molecules and Ions," Supplement Special Publication No. 18, The Chemical Society, London, 1965, p M20S.

[14] The Least Squares Plane Program is one of the programs written at Montana State University and is part of our Crystallographic Library. It follows the method described by V. Schomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Cryst.*, **12**, 600 (1959). Each point was given unit weighting for these calculations.

TABLE III

THERMAL PARAMETERS AND STANDARD DEVIATIONS

	$\beta(1,1)$[a]	$\beta(2,2)$	$\beta(3,3)$	$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$
Ti(1)	0.0134 (3)[b]	0.0035 (1)	0.0058 (1)	0.0005 (2)	−0.0003 (2)	−0.0006 (2)
Cl(2)	0.0164 (5)	0.0068 (2)	0.0130 (4)	0.0016 (3)	−0.0049 (3)	−0.0009 (3)
Cl(3)	0.0142 (5)	0.0068 (2)	0.0136 (4)	0.0003 (3)	0.0039 (3)	−0.0015 (3)
O(4)	0.0113 (10)	0.0041 (4)	0.0063 (7)	0.0002 (5)	0.0012 (6)	−0.0004 (4)
O(5)	0.0203 (14)	0.0043 (4)	0.0082 (9)	0.0007 (7)	0.0000 (9)	−0.0016 (6)
C(6)	0.0087 (15)	0.0038 (5)	0.0059 (10)	0.0006 (8)	0.0022 (9)	−0.0005 (6)
C(7)	0.0144 (18)	0.0045 (6)	0.0113 (14)	0.0021 (10)	0.0015 (12)	0.0010 (8)
C(8)	0.0183 (21)	0.0036 (6)	0.0137 (16)	0.0007 (10)	0.0020 (15)	−0.0001 (8)
C(9)	0.0212 (23)	0.0033 (6)	0.0111 (15)	−0.0006 (11)	0.0039 (15)	−0.0007 (8)
C(10)	0.0174 (22)	0.0053 (8)	0.0124 (15)	−0.0023 (11)	0.0047 (15)	−0.0030 (9)
C(11)	0.0115 (18)	0.0060 (8)	0.0129 (14)	0.0003 (10)	0.0020 (12)	−0.0026 (8)
C(12)	0.0105 (15)	0.0046 (6)	0.0090 (12)	−0.0001 (8)	0.0030 (11)	−0.0016 (8)
C(13)	0.0145 (19)	0.0062 (7)	0.0075 (13)	−0.0012 (10)	0.0017 (12)	−0.0013 (8)
C(14)	0.0205 (23)	0.0084 (10)	0.0092 (13)	−0.0012 (13)	0.0002 (13)	−0.0031 (10)
C(15)	0.0146 (20)	0.0069 (9)	0.0159 (18)	−0.0014 (11)	0.0036 (14)	−0.0051 (11)
C(16)	0.0144 (19)	0.0041 (7)	0.0170 (18)	0.0007 (9)	0.0009 (15)	−0.0028 (10)
C(17)	0.0158 (19)	0.0042 (6)	0.0096 (13)	0.0021 (9)	0.0015 (13)	−0.0010 (7)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] The number in parentheses is the standard deviation and refers to the least significant digits.

TABLE IV

THERMAL PARAMETERS

	Mean-square amplitude of vibration, A^2		
Atom	Max	Med	Min
Ti(1)	0.0667	0.0362	0.0262
Cl(2)	0.1088	0.0637	0.0427
Cl(3)	0.0823	0.0702	0.0484
O(4)	0.0551	0.0416	0.0293
O(5)	0.1005	0.0514	0.0299
C(6)	0.0459	0.0383	0.0224
C(7)	0.0772	0.0553	0.0363
C(8)	0.0894	0.0660	0.0349
C(9)	0.1050	0.0506	0.0318
C(10)	0.1027	0.0568	0.0347
C(11)	0.0792	0.0571	0.0403
C(12)	0.0611	0.0478	0.0300
C(13)	0.0762	0.0582	0.0333
C(14)	0.1031	0.0905	0.0344
C(15)	0.1123	0.0654	0.0370
C(16)	0.0917	0.0697	0.0323
C(17)	0.0816	0.0510	0.0319

TABLE V

Bond distance,[a] A		Bond distance,[a] A	
Ti(1)-Ti(1′)	3.274 (3)	C(8)–C(9)	1.369 (28)
Ti(1)–Cl(2)	2.209 (6)	C(9)–C(10)	1.376 (30)
Ti(1)–Cl(3)	2.219 (6)	C(10)–C(11)	1.413 (21)
Ti(1)–O(4)	1.910 (9)	C(11)–C(6)	1.386 (22)
Ti(1)–O(4′)	2.122 (9)	C(12)–C(13)	1.390 (21)
Ti(1)–O(5)	1.744 (10)	C(13)–C(14)	1.388 (27)
O(4)–C(6)	1.422 (14)	C(14)–C(15)	1.424 (25)
O(5)–C(12)	1.359 (19)	C(15)–C(16)	1.382 (25)
C(6)–C(7)	1.359 (24)	C(16)–C(17)	1.404 (26)
C(7)–C(8)	1.395 (19)	C(17)–C(12)	1.374 (20)

[a] The number in parentheses is the standard deviation and refers to the least significant digits.

TABLE VI

Bond angles, deg	
Cl(2)–Ti(1)–Cl(3)	112.1 (1)
Cl(2)–Ti(1)–O(4)	120.7 (1)
Cl(2)–Ti(1)–O(4′)	90.2 (2)
Cl(2)–Ti(1)–O(5)	96.7 (3)
Cl(3)–Ti(1)–O(4)	123.1 (2)
Cl(3)–Ti(1)–O(4′)	89.4 (2)
Cl(3)–Ti(1)–O(5)	98.1 (3)
O(4)–Ti(1)–O(4′)	71.5 (2)
O(4)–Ti(1)–O(5)	95.4 (3)
O(4′)–Ti(1)–O(5)	167.0 (3)
Ti(1)–O(4)–Ti(1′)	108.5 (3)
Ti(1)–O(4)–C(6)	123.2 (4)
Ti(1′)–O(4)–C(6)	128.3 (4)
Ti(1)–O(5)–C(12)	165.9 (6)
O(4)–C(6)–C(7)	118.7 (7)
O(4)–C(6)–C(11)	118.1 (7)
C(11)–C(6)–C(7)	123.2 (7)
C(6)–C(7)–C(8)	118.0 (8)
C(7)–C(8)–C(9)	120.2 (9)
C(8)–C(9)–C(10)	121.9 (9)
C(9)–C(10)–C(11)	118.4 (9)
C(10)–C(11)–C(6)	118.2 (8)
O(5)–C(12)–C(13)	117.1 (8)
O(5)–C(12)–C(17)	119.6 (8)
C(13)–C(12)–C(17)	123.3 (8)
C(12)–C(13)–C(14)	118.7 (8)
C(13)–C(14)–C(15)	120.2 (9)
C(14)–C(15)–C(16)	118.2 (10)
C(15)–C(16)–C(17)	122.6 (9)
C(16)–C(17)–C(12)	117.0 (8)

$0.05708Y - 0.0541Z = 4.6626$, where $X = x + z \cos\beta$; $Y = y$; $Z = z \sin\beta$ (x, y, and z are coordinates in terms of the nonorthogonal monoclinic cell; X, Y, and Z are orthogonal coordinates; 4.6626 is the origin to plane distance in A). The sum of the square deviations of the atoms from this plane is 3×10^{-8} A^2. The two titaniums, the two bridging oxygens, and the other two nonbridging oxygens also lie nearly in a plane. The best least-square plane formed by these has the equation $0.99683X - 0.06548Y - 0.04500Z = 4.6289$, with the sum of the square deviation from the plane 3×10^{-4} A^2 and X, Y, and Z defined as above.

Titanium is pentacoordinated, the coordination being in the form of a distorted trigonal bipyramid. Figure 2 shows the coordination with some of the bond angles, the others being listed in Table V. The equatorial plane of the trigonal bipyramid is formed by Ti, Cl(2), Cl(3), and O(4) and has the equation $-0.02709X + 0.85075Y + 0.52487Z = 7.4018$ with the sum of the

TABLE VII

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $TiCl_2(OC_6H_5)_2$[a]

0 0 L		
2	291	-348
4	760	722
10	257	-233
12	195	168
0 1 L		
1	633	648
2	828	-764
3	415	-390
4	455	-404
5	330	321
6	191	-224
7	351	341
9	214	-202
0 2 L		
0	429	430
1	160	145
2	1763	-1681
3	422	370
4	230	249
5	155	-156
6	139	171
8	212	202
10	135	-137
11	139	-140
12	127	127
0 3 L		
1	374	371
2	337	396
3	472	-564
4	418	-422
6	84	89
7	269	258
8	191	187
9	198	-201
13	118	114
0 4 L		
0	790	803
1	416	-438
2	863	-825
3	334	326
5	632	-632
6	196	183
7	283	265
8	111	-84
9	96	-93
10	149	-135
0 5 L		
2	653	682
3	394	-430
4	174	-189
5	96	95
9	148	-147
0 6 L		
0	764	744
1	482	-431
2	429	-426
3	636	629
4	103	90
5	857	-852
7	363	353
10	132	-119
11	114	-106
0 7 L		
1	153	-122
2	291	344
3	359	-346
4	361	-356
8	136	127
0 8 L		
2	175	-162
3	529	539
4	107	-117
5	321	-322
6	191	-201
7	341	315
0 9 L		
1	141	154
2	418	414
4	260	-261
6	95	112
8	292	288
0 10 L		
0	196	-201
2	153	138
3	122	113
5	408	-381
6	185	175
7	235	250
0 11 L		
1	100	-117
2	104	116
4	132	-117
5	95	94
8	141	143
0 12 L		
0	324	-293
2	377	358
3	248	248
5	270	-255
7	156	150
0 13 L		
2	150	144
3	221	204
4	143	-140
10	118	-110
0 14 L		
0	313	-267
2	115	107
5	136	-142
0 16 L		
0	195	-156
2	145	147
6	115	-97
0 18 L		
0	234	-178
2	118	96
0 20 L		
0	159	-128
1 0 L		
1	809	742
3	51	-5
5	245	238
7	334	327
9	150	-173
1 1 L		
0	1307	1383
1	246	248
2	496	-492
3	662	-655
5	270	-263
6	693	682
1 2 L		
0	155	-144
1	520	525
2	445	428
3	761	-792
4	228	-229
5	213	205
6	142	-126
7	242	235
8	107	-107
9	228	-212
10	128	-122
13	129	116
1 3 L		
0	1048	1015
1	231	237
2	250	-212
3	54	82
4	611	-614
5	78	-92
6	347	334
7	148	[illegible]
8	316	-316
11	184	-166
1 4 L		
0	82	-64
1	267	255
2	402	482
3	352	-381
4	191	-205
5	108	117
7	178	171
8	249	243
9	127	-129
1 5 L		
0	669	664
3	220	229
4	406	-373
5	316	-295
6	274	276
7	198	193
8	121	-120
9	157	143
11	166	-162
1 6 L		
1	65	67
2	234	247
3	496	-464
4	497	-497
8	182	176
9	121	-121
1 7 L		
0	213	-201
1	323	296
2	547	-550
3	120	110
5	271	-250
7	91	82
9	108	92
11	175	-178
1 8 L		
2	452	453
3	262	-264
4	248	-245
5	88	92
6	89	-75
8	199	202
1 9 L		
1	120	128
3	78	-86
5	120	-116
9	196	208
11	156	-140
1 10 L		
1	81	84
2	273	274
3	146	157
8	193	183
1 11 L		
0	120	-126
1	319	329
2	313	304
3	135	135
4	110	101
5	162	-154
7	108	87
11	120	-107
1 12 L		
2	134	147
8	110	94
1 13 L		
0	150	-120
4	118	112
5	139	-132
6	127	-113
1 14 L		
3	148	128
9	118	116
1 15 L		
0	221	-197
6	139	-126
1 16 L		
3	127	132
1 17 L		
0	188	-163
1 19 L		
0	148	-114
-1 0 L		
1	761	674
3	178	-167
5	111	-105
7	182	192
9	284	-290
-1 1 L		
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2	935	-956
3	939	-862
4	712	633
5	638	-623
6	179	162
8	274	290
10	323	-334
12	192	194
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2	511	486
3	625	-605
4	252	-246
5	342	335
6	249	-224
7	401	395
8	221	-236
9	233	-202
10	128	-147
11	104	96
-1 3 L		
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2	619	-597
3	519	519
4	182	-171
5	199	-208
6	95	-100
7	207	183
10	120	-116
11	106	-106
12	146	168
-1 4 L		
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2	420	394
3	223	-253
4	160	-188
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6	79	48
7	220	216
8	297	306
9	177	-182
-1 5 L		
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2	196	-221
3	508	502
4	174	-129
5	783	-776
7	415	400
9	124	-139
10	188	-203
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3	387	-369
4	574	-557
5	186	-177
8	107	100
9	138	-132
-1 7 L		
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2	622	-614
3	331	347
4	91	102
5	580	-551
7	452	446
-1 8 L		
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2	591	573
3	127	-132
4	178	-183
8	157	162
-1 9 L		
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2	81	70
3	191	194
5	368	-368
7	246	251
-1 10 L		
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3	256	256
4	216	-206
8	167	170
-1 11 L		
1	166	190
2	341	322
3	199	199
5	283	-285
6	106	110
7	271	257
10	117	101
-1 12 L		
2	219	230
3	106	102
4	189	-165
9	117	94
-1 13 L		
2	124	113
5	220	-216
7	134	130
10	132	120
-1 14 L		
1	106	-119
3	174	161
4	157	-140
9	127	122
-1 17 L		
2	122	103
2 0 L		
0	1926	1859
2	800	859
4	803	-758
6	856	827
8	178	-163
12	129	116
2 1 L		
0	603	537
1	589	607
2	104	58
3	380	-378
4	143	113
5	195	208
6	252	-33
7	228	213
9	172	-162
2 2 L		
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1	724	767
2	732	658
3	392	-378
4	709	-714
5	122	113
6	700	697
7	164	-154
8	285	-300
9	159	148
11	163	-156
2 3 L		
0	125	-141
1	188	201
2	228	236
3	420	-431
4	511	-496
5	139	128
6	150	-120
7	328	331
8	186	175
9	114	-123
2 4 L		
0	511	-467
1	692	716
3	433	-413
4	916	-907
5	82	70
6	600	596
8	245	-233
2 5 L		
0	205	-225
2	441	488
3	399	-411
4	206	-197
6	92	-87
8	184	180
9	179	-173
10	106	-99
2 6 L		
0	96	151
1	551	619
3	175	-213
4	172	-173
5	99	115
6	235	249
8	100	-103
9	205	196
11	192	-175
2 7 L		
1	95	87
2	398	427
3	196	-221
4	177	-160
8	170	156
9	127	-125
10	150	-150
2 8 L		
1	719	766
2	134	-118
3	362	-372
4	95	-136
6	214	-225
9	186	187
11	141	-129
2 9 L		
2	348	363
4	271	-282
8	269	253
2 10 L		
1	472	541
3	159	-157
4	174	173
5	114	139
9	174	169
11	159	-160
2 11 L		
2	107	103
4	150	-156
8	146	148
2 12 L		
1	178	170
3	110	-112
4	217	200
5	152	-144
6	125	-119
2 13 L		
2	160	156
3	170	159
4	95	-97
2 14 L		
1	156	155
4	196	188
6	191	-185
2 15 L		
3	117	109
2 16 L		
4	149	154
6	162	-162
2 18 L		
0	131	-115
-2 0 L		
2	576	588
4	260	-225
6	271	267
8	115	-124
10	255	-261
12	186	172
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1	699	725
2	752	-774
3	327	-354
4	262	-254
5	338	361
6	189	-170
7	314	328
9	209	-216
-2 2 L		
1	537	583
2	125	99
3	213	-242
4	459	-474
6	470	498
8	148	161
11	113	-121
12	152	168
-2 3 L		
1	138	155
2	120	179
3	558	-593
4	301	-333
7	242	244
8	156	157
9	219	-216
-2 4 L		
1	601	637
2	107	115
3	239	-237
4	423	-420
5	213	-211
6	380	370
7	138	136
8	228	-223
10	170	-181
-2 5 L		
1	57	-19
2	484	523
3	255	-294
6	108	-106
9	189	-188
10	99	-100
-2 6 L		
1	572	598
2	164	-133
4	196	-197
5	427	-448
7	212	201
-2 7 L		
1	99	-104
2	214	254
3	150	-147
4	324	-319
6	115	-137
7	156	152
8	146	143
-2 8 L		
1	642	668
3	108	-86
6	86	-86
7	185	185
-2 9 L		
1	118	-113
2	365	373
3	95	108
4	196	-233
5	114	-111
6	143	153
8	226	242
-2 10 L		
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2	85	-101
3	184	-196
5	134	-133
7	135	142
-2 11 L		
2	121	113
3	188	184
4	156	-146
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2	185	198
4	212	221
5	128	-136
-2 13 L		
2	200	216
3	205	207
4	198	-197
-2 14 L		
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4	125	128
-2 15 L		
2	100	120
3	111	127
-2 16 L		
6	134	-146
3 0 L		
1	182	-122
3	253	-293
5	267	257
7	259	262
3 1 L		
1	238	245
2	508	498
3	209	-210
4	355	-379
5	163	100
6	596	585
10	156	-149
12	149	148
3 2 L		
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1	743	749
2	174	172
3	320	-380
4	143	-161
5	212	224
6	142	-123
7	166	168
9	146	-142
10	115	-105
3 3 L		
0	309	-312
1	738	762
2	199	228
3	320	-352
4	692	-744
5	124	-132
6	320	334
7	172	-183
8	185	-190
3 4 L		
0	248	-207
2	330	336
3	351	-368
6	124	-138
8	210	236
9	115	-116
10	104	-102
3 5 L		
1	635	652
2	321	357
3	91	-121
4	373	-391
5	79	-86
6	206	229
7	179	203
3 6 L		
1	121	-127
2	297	323
3	250	-265
4	248	-282
8	202	203
3 7 L		
1	703	705
2	206	-218
3	209	-205
5	136	-131
3 8 L		
0	77	-61
2	306	310
4	252	-286
6	175	-169
8	179	207
3 9 L		
0	86	-119
1	468	466
2	266	-309
3	230	-235
3 10 L		
0	227	-214
2	274	275
3	188	196
8	167	189
3 11 L		
0	219	195
1	487	484
2	263	269
4	227	244
5	146	-161
3 12 L		
2	206	212
3	118	104
4	195	-201
3 13 L		
2	99	-88
4	136	143
3 14 L		
3	145	155
4	107	-109
3 15 L		
4	118	123
6	124	-116
3 16 L		
3	121	121
-3 0 L		
1	177	275
3	500	-503
5	181	164
7	118	129
9	131	-137
-3 1 L		
1	1175	1126
2	593	584
3	252	-263
4	561	-578
5	75	-78
6	715	716
7	78	-79
8	233	-232
10	113	-105
-3 2 L		
1	779	800
2	113	114
3	530	-572
4	259	-257
5	406	418
6	309	-287
7	179	173
8	103	-135
9	177	-173
10	118	-127
-3 3 L		
1	370	391
2	459	451
3	437	-457
4	671	-727
5	106	102
6	583	613
7	115	-119
8	179	-186
10	98	129
11	155	-171
-3 4 L		
1	77	87
2	340	351
3	422	-446
5	85	104
6	99	-78
7	135	149
8	305	324
9	113	-125
-3 5 L		
1	610	657
2	129	144
3	324	-325
4	647	-663
5	114	-119
6	287	301
8	195	-226
11	118	-120
-3 6 L		
3	262	-280
4	238	-260
6	85	-87
8	174	166
9	132	-145
-3 7 L		
1	796	820
2	206	-199
3	301	-312
9	118	135
11	131	-130
-3 8 L		
2	228	223
3	134	-149
4	174	-180
8	191	199
10	108	-109
-3 9 L		
1	651	661
2	96	-84
3	252	-246
4	124	120
9	148	161
11	128	-128
-3 10 L		
2	394	409
3	212	218
5	91	-100
8	171	179
-3 11 L		
1	381	355
2	106	121
3	193	-208
4	104	99
7	115	106
-3 12 L		
3	163	159
4	224	-229
-3 13 L		
1	156	160
2	124	-129
4	156	155
6	157	-152
-3 14 L		
1	100	-97
3	170	154
-3 15 L		
4	179	175
6	129	-139
-3 16 L		
3	124	110
-3 17 L		
4	134	121
4 0 L		
0	1134	1087
2	454	-486
6	111	107
8	235	251
10	223	-215
12	270	192
4 1 L		
0	305	263
1	532	548
3	384	-370
4	118	106
5	228	214
7	134	127
9	136	-122
4 2 L		
0	530	495
1	302	331
2	82	71
3	72	-67
4	155	160
5	213	-216
8	99	97
10	228	-232
12	143	147
4 3 L		
0	202	150
1	104	123
2	189	198
3	402	-402
4	210	-215
5	162	142
6	143	-137
7	209	228
8	145	137
4 4 L		
1	121	151
2	423	-455
3	142	160
4	287	-295
5	223	-257
6	111	123
7	277	292
10	122	-124
4 5 L		
0	122	-128
2	138	160
3	249	-285
4	100	-116
5	86	50
6	103	-121
8	153	166
9	125	-129
4 6 L		
0	307	253
1	92	94
2	152	-182
3	284	303
5	434	-472
7	220	233
10	106	-113
4 7 L		
2	220	230
5	103	-107
6	134	157
4 8 L		
1	295	307
2	120	-122
5	305	-352
6	106	-132
7	172	193
4 9 L		
1	242	-242
2	299	310
4	152	-168
8	191	198
4 10 L		
1	138	142
2	143	149
3	262	155
5	127	-129
7	224	253
4 11 L		
2	91	87
3	246	246
4	162	-158
4 12 L		
0	186	-169
5	230	-237
4 13 L		
1	104	-115
2	209	180
3	134	139
4 15 L		
3	107	109
-4 0 L		
2	92	-131
6	646	644
8	171	-176
-4 1 L		
1	511	506
2	136	-139
3	425	-435
4	68	48
5	369	373
6	224	-107
7	92	96
-4 2 L		
1	108	94
3	314	-322
4	527	-533
6	362	359
8	129	-124
9	93	89
11	135	-114
-4 3 L		
1	193	163
3	451	-454
4	341	-358
5	207	206
6	104	-102
8	136	138
9	122	-128
10	115	-124
-4 4 L		
1	361	366
2	68	-77
3	78	-87
4	257	-271
5	79	-111
6	430	435
8	238	-262
11	121	-133
-4 5 L		
2	387	397
3	399	-413
5	95	75
8	192	201
10	125	-120
-4 6 L		
1	301	338
2	179	-165
4	110	-112
5	159	-174
6	85	82
8	114	-130
9	120	136
-4 7 L		
1	120	117
2	217	240
3	235	-237
4	213	-223
6	214	-248
8	157	153
-4 8 L		
1	189	174
2	129	-153
3	199	-205
9	132	150
-4 9 L		
2	219	214
4	110	-114
8	245	261
-4 10 L		
1	418	415
-4 11 L		
8	145	158
-4 12 L		
2	205	204
4	238	240
5	143	-140
-4 13 L		
2	99	112
3	136	132
4	115	-116
-4 15 L		
3	127	116
5 0 L		
1	356	335
3	189	-179
5	243	227
7	212	206
9	184	-185
5 1 L		
0	1158	1100
1	88	-81
2	544	-541
4	326	327
5	135	-124
8	230	227
10	193	-176
5 2 L		
1	509	509
2	75	74
3	419	-437
5	155	138
7	199	204
9	113	-112
5 3 L		
0	619	575
2	527	-536
3	189	203
5	271	-294
7	104	106
5 4 L		
1	132	146
2	117	110
3	320	-315
8	96	111
9	125	-129
5 5 L		
0	415	378
1	155	-133
2	128	-148
3	409	437
5	397	-414
7	291	311
5 6 L		
0	234	221
2	171	195
3	188	-194
4	160	-178
5 7 L		
0	191	172
1	132	-134
2	221	-243
3	256	266
5	439	-481
7	214	232
5 8 L		
2	178	183
4	125	-118
8	127	158
5 9 L		
0	132	-125
2	86	-96
3	248	259
4	132	-122
5	162	-195
7	181	202
5 10 L		
0	195	-163
2	92	74
3	132	130
5 11 L		
2	314	301
3	134	145
5	285	-288
5 12 L		
2	179	174
5 13 L		
0	175	-146
2	136	133
5 14 L		
1	103	-96
3	115	121
5 15 L		
0	198	-161
-5 0 L		
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5	206	201
7	192	192
-5 1 L		
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2	522	-530
3	146	143
4	203	196
5	110	-65
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-5 2 L		
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2	129	130
3	391	-380
4	257	-246
5	174	152
6	96	-96
9	142	-130
-5 3 L		
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2	402	-413
4	110	115
5	233	-243
6	213	199
-5 4 L		
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3	257	-259
4	212	-204
5	96	73
7	96	107
8	145	148
-5 5 L		
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2	418	-430
3	277	265
4	192	-182
5	335	-350
7	192	211
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3	143	-152
4	188	-202
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8	114	116
-5 7 L		
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3	175	188
5	327	-344
6	104	-117
7	178	175
-5 8 L		
2	205	207
3	239	-229
4	231	-242
8	185	188
-5 9 L		
3	223	255
4	149	157
5	145	-151
7	129	147
-5 10 L		
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2	377	389
-5 11 L		
2	145	149
5	178	-184
7	199	214
-5 12 L		
4	179	-181
-5 13 L		
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5	167	-159
6 0 L		
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6	263	271
6 1 L		
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1	365	369
3	207	-202
7	223	206
9	160	-148
6 2 L		
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2	213	-226
5	115	-129
6	98	89
6 3 L		
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2	212	205
3	219	-219
4	143	-136
7	188	195
9	141	-137
6 4 L		
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2	202	-226
3	152	162
4	159	-163
5	135	-133
6	192	198
7	135	135
6 5 L		
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3	199	-200
4	174	-171
6 6 L		
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2	114	-108
3	214	229
5	263	-278
6 7 L		
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3	142	-166
4	106	-102
6 8 L		
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5	150	-145
6 9 L		
2	174	196
4	148	-150
6 10 L		
2	171	173
5	125	-130
6 12 L		
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6 13 L		
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-6 0 L		
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10	210	-202
-6 1 L		
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2	149	-171
3	78	-63
4	136	-101
7	213	214
9	134	-117
-6 2 L		
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5	192	-196
8	100	122
10	128	-96
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3	132	-138
4	256	-265
5	103	-24
7	134	137
9	193	-200
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4	108	109
5	281	-286
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7	104	102
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3	127	-104
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3	135	-137
4	307	-318
5	100	-12
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5	239	-245
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8	111	113
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4	166	-162
6	156	163
-6 10 L		
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3	129	124
5	170	-169
7	150	146
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5	157	-166
-6 13 L		
4	148	-147
7 0 L		
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3	164	168
5	118	118
7	231	212
7 1 L		
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1	219	208
2	115	128
4	257	-246
6	345	338
7	96	-99
7 2 L		
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2	113	104
3	250	-257
5	96	-72
6	103	65
7	166	162
7 3 L		
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3	104	-110
4	290	-294
6	227	231
8	174	-173
7 4 L		
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2	192	176
3	99	-96
4	146	-150
7 5 L		
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2	117	134
4	189	-179
6	155	157
7 6 L		
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4	188	-202
7 7 L		
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2	96	-119
3	95	-102
7 8 L		
0	106	-110
2	182	173
3	103	-115
4	125	-109
7 9 L		
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7 11 L		
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3	172	-162
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7	166	173
9	155	-149
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3	124	-121
4	134	-123
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-7 5 L		
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2	92	-90
4	160	-170
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7	113	103
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8 0 L		
2	266	271
4	139	-126
6	328	320
8 1 L		
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1	114	88
2	108	102
8 2 L		
1	156	145
2	93	111
3	96	-113
4	298	-286
6	157	154
8 3 L		
0	136	-114
2	135	139
3	99	-92
4	91	-87
8 4 L		
1	248	242
2	115	103
4	207	-205
6	192	181
8 5 L		
0	129	-131
2	141	124
4	96	-97
8 6 L		
1	231	226
4	95	-102
8 7 L		
2	185	177
3	98	-94
8 8 L		
1	200	181
3	125	-140
8 9 L		
0	117	-90
2	143	141
4	122	-122
8 10 L		
1	226	219
-8 0 L		
2	88	-116
4	288	-292
6	223	218
-8 1 L		
1	231	230
2	163	-192
3	200	-178
4	98	-46
5	135	128
6	136	-70
-8 2 L		
1	114	99
2	235	258
3	172	-188
4	149	-140
6	256	261
-8 3 L		
3	224	-219
-8 4 L		
1	223	224
2	121	88
4	178	-178
6	163	165
8	122	-135
-8 5 L		
3	93	-93
-8 6 L		
1	239	224
3	121	-134
4	110	-134
-8 8 L		
1	295	289
3	104	-97
-8 10 L		
1	171	168
3	107	-108
-8 11 L		
3	134	132
-8 12 L		
1	149	132
10 0 L		
0	209	187

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

square deviation of the atoms from the plane being 4×10^{-2} A^2. The apex oxygen O(4′) forms the longest Ti–O bond, while the other apex oxygen O(5) forms the shortest, the difference being almost 0.4 A.

An especially noteworthy feature is the unusually large bond angle for C(12)–O(5)–Ti. This angle is 165.9°. The other oxygen bond angles are Ti–O(4)–Ti = 108.5°, Ti–O(4)–C(6) = 123.2°, and Ti(1′)–O(4)–C(6) = 128.3°. The angle at O(5) is most unusual. An oxygen bond angle of 180° has been observed in pyrophosphate anion by Levi and Peyronel,[15] in $Cl_5Ru–O–RuCl_5$ by Mathieson, Mellor, and Stephenson,[16] and in $[TiCl_2(C_5H_5)]_2O$ by Corradini and Allegra.[17] An oxygen bond angle of about 150° has been observed in $H_3Si–O–SiH_3$ by several authors.[18] The case in $TiCl_2(OC_6H_5)_2$ is somewhat different in that the two atoms attached to oxygen are different, whereas the others involve the same kind of atom

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(15) G. R. Levi and B. Peyronel, *Z. Krist.*, **92**, 190 (1935).

(16) A. McL. Mathieson, D. P. Mellor, and N. C. Stephenson, *Acta Cryst.*, **5**, 185 (1952).

(17) P. Corradini and G. Allegra, *J. Am. Chem. Soc.*, **81**, 5511 (1959).

(18) Reference 13, p M19S.

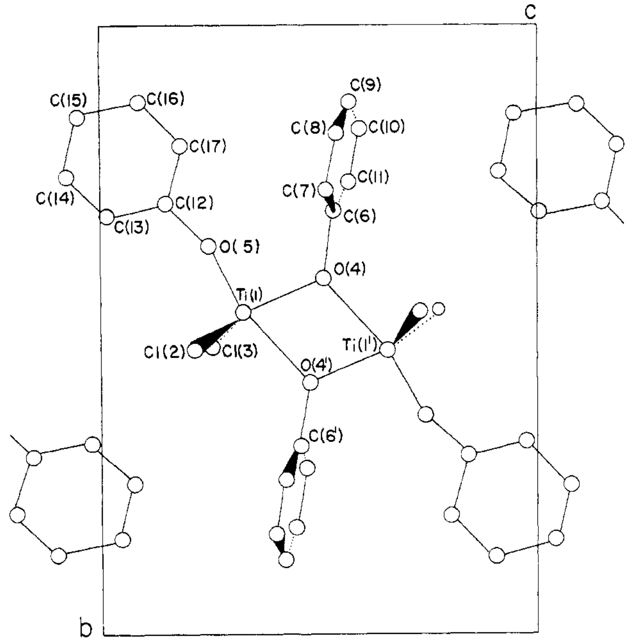

Figure 1.—Arrangement of one dimer unit of $TiCl_2(OC_6H_5)_2$ projected in the unit cell.

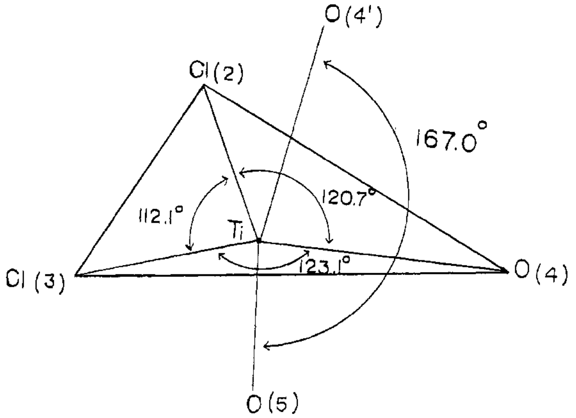

Figure 2.—Coordination around the titanium atom in $TiCl_2(OC_6H_5)_2$ dimer.

on each side of the oxygen. It should also be noted that the bond distance between C(12) and O(5) is short, *i.e.*, 1.36 (2) A, suggesting a partial double-bond character, and also the O(5)–Ti distance is short, *i.e.*, 1.744 A.

Consider now the nature of the bonding around the titanium atom and the oxygen atoms. In $TiCl_4$, which is tetrahedral and one would assume contains sp^3 hybridization and σ bonds, the Ti–Cl bond distance is 2.185 A. The Ti–O distance in rutile is 1.988 A, and this is assumed to be ionic. In $[TiCl_2C_5H_5]_2O$ the Ti–O distance is 1.78 A, and in this Corradini and Allegra[17] postulate a partial double-bond character for this bond arising from donation of electrons from p_y and p_z filled oxygen orbitals to the d unfilled titanium orbitals. An sp hybridization is postulated for the oxygen.

Because of the planar nature of the O(4) bonds and the fact that these are directed at nearly 120°, we postulate this oxygen is sp^2 hybridized and has three σ bonds. The lone pair of electrons is apparently involved in a π bond with d orbitals of titanium. Because of the short bond distance of 1.36 A between C(12) and O(5), this is assumed to possess double-bond character, and the large bond angle on O(5) indicates probable sp hybridization. One pair of electrons is involved in a π bond with the carbon C(12); the other pair of electrons must be involved in bonding with titanium in a π bond formed by hybridization of the p orbital on oxygen and the d orbitals of titanium.

The color is due either to delocalized electrons in the C_6H_5OTi group or to splitting of the d energy levels by the five ligands surrounding the titanium. The long Ti–O bond is to be expected from repulsion of the atoms in the equatorial plane, since the two chlorines are large and the O′(4)–Ti–O(4) bond angle is only 71.5°.

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