



Structural studies of organic titanium compounds
by Keith Donald Watenpaugh

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
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Abstract:

Using the "Symbolic Addition Procedure" the structures of three organic compounds of titanium are solved by x-ray diffraction.

Dichlorodiphenoxytitanium(IV) crystallizes in space group $P2_1/n$ with $a = 9.82 \text{ \AA}$, $b = 14.01 \text{ \AA}$, $c = 9.84 \text{ \AA}$, $\beta = 94^\circ 50'$. The compound is dimerically located around the center of symmetry, the two titaniums being joined with oxygen bridges, each titanium being penta coordinated in the form of a trigonal bipyramid.

The first hydrolysis product of tetraethoxytitanium (IV) crystallizes in space group $P2_1/a$ with $a = 27.99 \text{ \AA}$, $b = 22.42 \text{ \AA}$, $c = 23.21 \text{ \AA}$, $\beta = 117^\circ 15'$. Chemical analysis and density measurements indicate the compound to have the empirical formula $\text{Ti}_{70} \text{O}_{24} (\text{C}_2\text{H}_5)_{19}$ with 8 molecules per unit cell. The compound, is made up of TiO_6 octahedra sharing edges. Bonds from oxygen atoms to neighboring titanium atoms varies from one to four. Due to the complexity of the compound, all the carbon atoms could not be located.

μ -oxo-bis [chlorobis(2, 4-pentandionato)titanium(IV)] . chloroform crystallizes in space group $P2_1/n$, with $a = 15.744 \text{ \AA}$, $b = 22.63 \text{ \AA}$, $c = 8.89 \text{ \AA}$, $\beta = 100^\circ$. The two titanium atoms are six-coordinated in an octahedral arrangement to oxygen and chlorine atoms with an oxygen bridge between the two titaniums. The acetylacetonate groups are in the cis arrangement in the octahedra and are distorted, out of the planar rings due to steric effects. A chloroform molecule appears to be hydrogen bonded to the molecule.

Large oxygen containing bond angles are found in the compounds due to sp hybridization of the orbitals.

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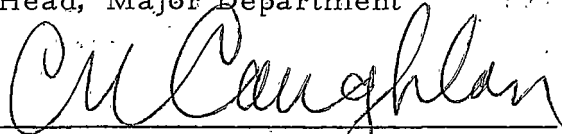
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ABSTRACT

Using the "Symbolic Addition Procedure" the structures of three organic compounds of titanium are solved by x-ray diffraction.

Dichlorodiphenoxytitanium(IV) crystallizes in space group $P2_1/n$ with $a = 9.82\text{\AA}$, $b = 14.01\text{\AA}$, $c = 9.84$, $\beta = 94^\circ 50'$. The compound is dimerically located around the center of symmetry, the two titaniums being joined with oxygen bridges, each titanium being penta coordinated in the form of a trigonal bipyramid.

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μ -oxo-bis [chlorobis(2, 4-pentandionate)titanium(IV)] · chloroform crystallizes in space group $P2_1/n$ with $a = 15.744$, $b = 22.63$, $c = 8.89$, \AA , $\beta = 100^\circ 18'$. The two titanium atoms are six-coordinated in an octahedral arrangement to oxygen and chlorine atoms with an oxygen bridge between the two titaniums. The acetylacetonate groups are in the cis arrangement in the octahedra and are distorted out of the planar rings due to steric effects. A chloroform molecule appears to be hydrogen bonded to the molecule.

Large oxygen containing bond angles are found in the compounds due to sp hybridization of the orbitals.

INTRODUCTION.

Work on the chemistry of organic compounds of titanium began in the middle of the nineteenth century. However, during the last several decades, with increased interest in metal organic compounds in general, the organic compounds of titanium have also been the subject of considerable study. These compounds have found a number of industrial applications because of their interesting chemical and physical properties. Since accurate knowledge of their structures has been lacking, probably because of certain inherent difficulties in studying their structures, many wrong conclusions have been made concerning reaction mechanisms.

One important and intensively studied class of organic compounds of titanium is the alkyl and aryl titanates, with the general formula $Ti(OR)_4$. Extensive studies of the chemical properties of these compounds have been carried out by many different groups using molecular weight determinations, analytical data and dipole moment values. As a result of these studies, structures were postulated for the associated compounds and these proposed structures were used extensively to explain the chemistry of the organic titanates (1, 2, 3), although no actual structure determinations were made until 1963. The structure of tetraethyl titanate was determined in 1963 by Ibers (4),

and the structure of monomethyltriethyl titanate by Witters (5) in 1964. Neither of these determinations agreed with the proposed structures in solution and thus suggested that the interpretation of the chemistry of this class of compounds based on postulated structures was probably incorrect. For this reason, it was of interest to continue the structural studies of this class of compounds. Particular interest exists in the structure of the hydrolysis products of tetraethyl titanate. Molecular weight evidence (1) indicates that the tetraethyl titanate exists as a trimer in solution, yet crystal structures studies have shown the organic titanates to be tetramers. Since the hydrolysis product forms by adding small amounts of water to solutions of the tetraethyl titanate, determination of the structure should indicate what molecular species exist in solution and something about the polymerization process upon hydrolysis.

A class of compounds closely related to the alkyl and aryl titanates is the alkoxy and aryloxytitanium halides, $TiX_n(OR)_{4-n}$, where X is a halogen. Certain chemical and physical characteristics, such as the intense color of the phenoxy titanium halides, suggested that there were significant differences in structures. No x-ray crystal structures of these halide compounds had been previously reported and thus it appeared significant to determine the structures.

A third general class of the organic titanium compounds are the chelated compounds. The most widely studied compound of this class is dichlorobis (acetylacetonato) titanium (IV), which exhibits interesting spectroscopic features. As a result of spectral studies (6, 7), it was concluded that the acetylacetonate groups were arranged in a cis configuration around the titanium. This is an interesting conclusion since the cis configuration seems less sterically favorable than the trans configuration. Thus, verification of this as well as study of the bonding in relation to the color of the compound is significant. Also of interest are the hydrolysis products of the acetylacetonate complex. These have been mentioned in the literature, but no detailed studies have been reported.

Recognizing this lack of structural information, a study was undertaken of three of the compounds from the above classes with the expectation of being able to answer some of the questions proposed through the structural knowledge obtained.

This dissertation contains the study and discussion of the crystal and molecular structures of dichlorodiphenoxytitanium(IV), the first hydrolysis product of tetraethyl titanate, and a hydrolysis product of dichlorobis (acetylacetonato) titanium(IV). Each of the structures was solved by the "symbolic addition procedure," the theory of which is presented in some detail.

PART I

GENERAL THEORY

Introduction and the Phase Problem

When x-ray beam impinges on a single crystal, the crystal acts as a three-dimensional grating diffracting the beam. The position of a diffracted wave from a plane of atoms in the crystal is given by the Bragg equation, $n\lambda = 2d \sin \theta$. The wave will have a certain amplitude and phase angle relative to the incident beam. The amplitude and phase are dependent on the relative positions of atoms in the unit cell and may be defined as

$$F(hkl) = \sum_{j=1}^N f_j e^{2\pi i(hx_j + ky_j + lz_j)} = |F(hkl)| e^{i\phi(hkl)}$$

where f_j = scattering factor of the j th atom for the particular diffraction angle,

(h, k, l) = Miller indices describing a particular set of planes,

(x_j, y_j, z_j) = position of the j th atom in the unit cell,

$\phi(hkl)$ = phase angle of the diffracted beam relative to the incident beam.

The intensity of a diffracted wave is proportional to the square of the amplitude of the wave, i. e.

$$I(hkl) \propto |F(hkl)|^2.$$

It is this term which is experimentally measured but the phase angle cannot be measured. If the phase could be measured directly, the electron density of the unit cell of a crystal could be calculated with the Fourier series, i. e.

$$\rho(xyz) = \frac{1}{V} \sum_h \sum_k \sum_l |F(hkl)| e^{-\phi(hkl)} e^{-2\pi i(hx+ky+lz)}$$

where V = volume of the unit cell,

(h, k, l) = indices of all reflecting planes which range over all possible integers,

$\phi(hkl)$ = phase angle associated with $F(hkl)$,

$|F(hkl)|$ = absolute value of the structure factor.

If sufficiently small intervals of x, y, z were taken over the unit cell, a contour map of the electron density would indicate regions where atoms were located. Atoms with a large number of electrons would give regions of higher densities and their locations could easily be determined. However, since the phase angle cannot be directly measured, other methods must be devised for obtaining it.

Indirect Methods of Solving Crystal Structures

In the early days of x-ray crystallography, structures were solved by trial and error. From a trial structure, the structure factors were calculated and compared with the experimentally measured

structure factors. The correctness of the proposed structure could be indicated by the agreement (or disagreement) between calculated and observed structure factors. A function used to measure the agreement between calculated and observed structure factors is the reliability index or R-factor defined as

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

where F_o = observed structure factor,

F_c = calculated structure factor,

The summations are over all the structure factors.

Most structures that have been solved have used the "heavy atom" method. If a compound contains a heavy atom, this atom will dominate the phases of the structure factors. Thus, if the correct position of the heavy atom can be found in the unit cell, one can use the calculated phases from the heavy atom and observed structure factors to produce a Fourier map which frequently shows the positions of the lighter atoms.

In 1934, Patterson (8) published a paper describing a new method using what has become known as the "Patterson function."

This function is

$$\begin{aligned}
 P(uvw) &= \int_V \rho(\mathbf{xyz}) \rho(\mathbf{x} + u, \mathbf{y} + v, \mathbf{z} + w) dV \\
 &= \frac{1}{V} \sum_h \sum_k \sum_l |F(hkl)|^2 e^{-2\pi i(hu + kv + lw)}
 \end{aligned}$$

Note that the phase does not appear in this function. The value of the function at (u, v, w) is simply the average value of the product of the electron densities at the ends of a vector of functional length (u, v, w) all originating at the origin. If there are n atoms in the unit cell, there will be $n(n-1)$ non-origin peaks in the Patterson map. Therefore, even with a simple structure, a rather complex Patterson map results. This is complicated further by the fact that the atoms are not point particles and different atoms with similar interatomic vectors may be superimposed in the Patterson map.

The use of the Patterson map and the heavy atom methods or a combination of the two methods is by far the most common method of solving crystal structures at the present time. Complete discussion of these methods appears in standard texts on x-ray crystallography methods. A detailed consideration of the use of these two methods in solving a specific structure is given by Li (9).

Direct Methods of Solving Crystal Structures

Recently, at least for the centrosymmetric crystals, a new method has been used with increasing success. This method is facilitated in the centrosymmetric case by the fact that the phase angle of a structure factor must be a multiple of π and the cosine of the phase angle, therefore, is ± 1 . The method, thus far, has not proved as useful in solving non-centric structures in which an infinite number of phase angles are possible.

The "symbolic addition procedure" used in solving structures involves a relationship between structure factors. This relationship is usually referred to as the \sum_2 relationship. A brief discussion of its history and theory follows.

In 1947, Harker and Kasper (10) reported that, although the phase of the structure factors could not be determined, there were some explicit relationships between amplitudes of structure factors and phases. Using certain algebraic inequality relationships such as the Cauchy inequality, restrictions exist on the choice of phases which are possible. Since the specific relationships will depend on the symmetry of the crystal, many relationships between structure factors may be developed. Thus, additional relationships have been developed by Okaya and Nitta (11), Karle and Hauptman (12), and Hauptman and Karle (13).

These inequalities have been used with a certain amount of success in solving some structures. In 1952, a series of papers (14, 15, 16) was published in which was given a relationship of particular value for phase determinations. Basically, the relationship was the same in each paper but derived in different ways. In 1953, Hauptman and Karle (17) and Hughes (16) obtained the same relationship by two additional derivations.

Sayre's (14) derivation of the relationship is based upon an examination of the electron density when the atoms were replaced by the "squared atoms." The electron density at location x in a unit cell is given by the Fourier series

$$\rho(x) = \frac{1}{V} \sum_H F_H e^{-2\pi i Hx}$$

F_H = structure factor with indices H ,

H = set of indices (h, k, l) ,

Hx = $(hx + ky + lz)$,

V = volume of the unit cell.

The squared density at x may be represented by the Fourier series

$$\rho^2(x) = \frac{1}{V} \sum_H {}^{sq}F_H e^{-2\pi i Hx}$$

where ${}^{sq}F_H = g_H F_H$.

The g_H takes into account the change in shape of the new density. The squared density may also be written

$$\rho^2(\mathbf{x}) = \rho(\mathbf{x}) \rho(\mathbf{x}) = \left[\frac{1}{V} \sum_H F_H e^{-2\pi i H \mathbf{x}} \right] \left[\frac{1}{V} \sum_H F_H e^{-2\pi i H \mathbf{x}} \right]$$

According to convolution theory of Fourier series, this becomes

$$\rho^2(\mathbf{x}) = \frac{1}{V} \sum_{H_1} \left[\frac{1}{V} \sum_{H_2} F_{H_1} F_{H_2} \right] e^{-2\pi i (H_1 + H_2) \mathbf{x}}$$

If we let $H_1 + H_2 = H$ and since the summations run over all integers

$${}^{sq}F_H = g_H F_H = \frac{1}{V} \sum_{H_2} F_{H_1} F_{H_2}$$

giving the Sayre relation

$$F_H = \frac{1}{g_H V} \sum_{H_2} F_{H_2} F_{H-H_2} \quad (1)$$

Zachariasen (16) and Hughes (18) developed a similar relation using normalized unitary structure factors rather than the usual structure factors. Normalized unitary structure factors take into account the fact that the x-ray scattering power of atoms decreases

as the scattering angle increases. The normalized unitary structure factor is defined by

$$U_H = \sum_{j=1}^N \frac{Z_j}{Z} e^{2\pi i H x_j}$$

where Z_j = number of electrons on the j th atom,

Z = total number of electrons in the unit cell.

For the centrosymmetric case, this may be given by

$$U_H = 2 \sum_{j=1}^{N/2} g_j \cos 2\pi H x_j$$

where $g_j = \frac{Z_j}{Z}$.

The Hughes derivation of the sign relationship is as follows:

$$U_{H_1} = 2 \sum_i g_i \cos 2\pi H_1 x_i$$

$$U_{H_2} = 2 \sum_j g_j \cos 2\pi H_2 x_j$$

$$U_{H_1} U_{H_2} = 4 \sum_i \sum_j g_i g_j \cos 2\pi H_1 x_i \cos 2\pi H_2 x_j$$

$$\begin{aligned}
&= 2 \sum_i \sum_j g_i g_j [\cos 2\pi(H_1 x_i + H_2 x_j) + \cos 2\pi(H_1 x_i - H_2 x_j)] \\
&= 2 \sum_i g_i^2 [\cos 2\pi(H_1 + H_2)x_i + \cos 2\pi(H_1 - H_2)x_i] \\
&+ 2 \sum_i \sum_{\substack{j \\ i \neq j}} g_i g_j [\cos 2\pi(H_1 x_i + H_2 x_j) + \cos 2\pi(H_1 x_i - H_2 x_j)]
\end{aligned}$$

If the average is taken over all possible values of H_1 keeping $H_1 + H_2 = H$ constant, then

$$\sum_i \cos 2\pi(H_1 - H_2)x_i = \sum_i \cos 2\pi(H - 2H_2)x_i = 0$$

since H_2 will have all possible integral values both positive and negative. Also

$$\sum_i \sum_{\substack{j \\ i \neq j}} g_i g_j [\cos 2\pi(H_1 x_i + H_2 x_j) + \cos 2\pi(H_1 x_i - H_2 x_j)] = 0$$

where $i \neq j$

Now, if all the atoms are the same, $g_i = \frac{1}{N}$, where N equals the number

of atoms in the unit cell and the mean value

$$\begin{aligned} \overline{U_{H_1} U_{H_2}} &= \frac{2}{N} \sum_i g_i \cos 2\pi(H_1 + H_2)x_i \\ &= \frac{1}{N} U_{H_1 + H_2} \end{aligned}$$

Thus, the Hughes relationship is

$$U_H = N \overline{(U_{H_1} U_{H_2})} \quad (2)$$

Hauptman and Karle (17) using a statistical approach to the phase problem, independently derived several expressions which can be used to determine the sign of a reflection, the most important being the \sum_2 relationship given by

$$sE_H \sim s \sum_{H_1} E_{H_1} E_{H-H_1} \quad (3)$$

E_H is the normalized structure factor which is similar to the unitary structure factor except that it reduces the atoms to point atoms by canceling the vibrational contribution in the structure factor. $s(E_H)$ means the "sign of E_H ."

The three relations (1, 2, 3) are essentially the same since the signs of the structure factors, unitary structure factors and the

normalized structure factors must be the same. However, they all have the common limitation that without knowing the signs of the E_{H_1} and E_{H_2} , the sign of E_H cannot be determined.

Karle and Hauptman (17) have also showed that certain phases are determined only by the choice of the origin and not by the structure. For example, the structure factors of a centrosymmetric crystal are

$$F(hkl) = \sum_{j=1} f_j \cos 2\pi(hx_j + ky_j + lz_j)$$

If the origin were moved to $(1/2, 1/2, 1/2)$, then

$$\begin{aligned} F'(hkl) &= \sum_j f_j \cos 2\pi[h(x_j + \frac{1}{2}) + k(y_j + \frac{1}{2}) + l(z_j + \frac{1}{2})] \\ &= \sum_j f_j [\cos 2\pi(hx_j + ky_j + lz_j) \cos \pi(h + k + l) \\ &\quad + \sin 2\pi(hx_j + ky_j + lz_j) \sin \pi(h + k + l)] \\ &= \sum_j f_j [\cos 2\pi(hx_j + ky_j + lz_j) \cos \pi(h + k + l) \\ &= (-1)^{h+k+l} F(hkl) \end{aligned}$$

Therefore, when $(h + k + l) =$ an even integer, the $F(hkl)$ is called a "structure invariant." Hauptman and Karle discussed these structure invariants and showed that the structure factors of three linearly independent vectors (h, k, l) , modulo 2, could be assigned arbitrary phases.

Sayre (14), Zachariasen (16), Karle and Hauptman (17) and others have shown that if the values of the structure factors with known phases are large, then usually the relationship $S_H = S_{H_1} \times S_{H-H_1}$ holds for each set of $(H_1, H-H_1)$. Therefore, by knowing the phases of only two large structure factors or normalized structure factors, the sign of a third structure factor may be determined. If the new one is large, it, in turn, may be used to determine the signs of additional structure factors.

Generally, three known signs are not enough to determine the signs of sufficient structure factors to solve a structure. Additional signs can be found using inequalities and other less general sign relationships, but these may not help much in giving useful phases to generate additional phases by the \sum_2 relationship. Also, all too frequently, wrong phases are inserted into this chain process early in the determination with disastrous results. Zachariasen (16) suggested that after three origin determining signs or phases are picked, a set of symbolic signs may be assigned where necessary. The signs of

many additional structure factors may be determined as combinations of these symbolic signs along with the origin determining signs.

This method was hardly used until 1963 when Karle and Karle (19) began using it in their "symbolic addition procedure." Their main contribution to the procedure was the use of the Hauptman and Karle probability relationships. For the \sum_2 relationship

$$sE_H \sim s \sum_{H_1} E_{H_1} E_{H-H_1}$$

they had derived the probability of the sign being positive as the function

$$P_+(E_H) = \frac{1}{2} + \frac{1}{2} \tanh \frac{1}{2N^{1/2}} E_H \sum_{H_1} E_{H_1} E_{H-H_1} \quad (4)$$

assuming that all atoms in the unit cell were identical. By requiring the sign of a normalized structure factor to have a high probability of being correct before it is used to determine signs of other normalized structure factors, the assignment of wrong signs may be nearly eliminated. Using this probability equation (4), it is seen that one \sum_2 relationship may be enough to determine with high probability the sign of a particular structure factor, while in other cases many relationships would be necessary.

As the number of signs being determined in terms of symbolic signs increases, relations between the symbolic signs appear. For example, some E_H may have relations which assign it signs (ab), (c), (ab), (ab), (c), etc. This would indicate that sign (ab) and sign (c) are the same. If this same relation between symbolic signs appears for other structure factors, then one of the symbolic signs may be eliminated. The importance of eliminating symbolic signs is readily understood when one considers the number of possible sign combinations. If there are n symbolic signs left at the end of a sign determination, then there are 2^n possible combinations, from which the correct set must be chosen. Usually, fewer final symbolic signs remain after a determination of a set of signs than were initially assigned. In some cases all of the symbolic signs can be eliminated.

To determine which combination of signs is correct, an E-map is usually calculated. An E-map is similar to an electron density map except that normalized structure factors are used in calculating the Fourier series. The difference between the E-map and the electron density map is that the E-map assumes point atoms without vibration and the electron density map contains more diffuse peaks due to the vibration of the atoms and their form factors. Once an E-map has been calculated over the unit cell, it must be examined for a reasonable chemical structure. The validity of many E-maps can be ascertained

on chemical grounds. If several possible structures remain which are chemically reasonable, incorrect structures may be ruled out on the basis of the agreement between the observed and calculated structure factors or the failure of a structure to refine by the least-squares technique. The correct E-map does not always indicate the positions of all the atoms in a structure. If, however, a majority of the atoms are found or if the heavy atoms are found, then by the use of partial structure factor calculations and Fourier maps, the remaining atoms may be located.

This method of symbolic sign determination has proven to be extremely powerful in the structure studies reported here, since in each case a major portion of the structure could be ascertained from the E-map.

PART II

THE CRYSTAL STRUCTURE OF DICHLORODIPHENOXYTITANIUM(IV)

Preparation of the Crystals

Crystals of $\text{TiCl}_2(\text{OC}_6\text{H}_5)_2$ were prepared by heating $\text{TiCl}_3(\text{OC}_6\text{H}_5)$ in a closed container at 120 to 150 degrees and one mm. Hg. pressure. The $\text{TiCl}_3(\text{OC}_6\text{H}_5)$ disproportionates, liberating TiCl_4 and crystals of $\text{TiCl}_2(\text{OC}_6\text{H}_5)_2$ collect on the walls of the container.

The $\text{TiCl}_3(\text{OC}_6\text{H}_5)$ was prepared by a method first described by Luchinski and Altmann (20), which was used by Crowe and Caughlan (21) 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 and cooling crystals of $\text{TiCl}_3(\text{OC}_6\text{H}_5)$ are obtained.

Crystals of $\text{TiCl}_2(\text{OC}_6\text{H}_5)_2$ have a deep red color and are unstable in moist air although they hydrolyze much less readily than either TiCl_4 or the simple titanium alkoxides. Crystals were sealed in Pyrex capillaries and one was selected for the x-ray study. Its approximate dimensions were 0.2 x 0.2 x 1 mm.

Density Determination of $\text{TiCl}_2(\text{OC}_6\text{H}_5)_2$

The density of the crystals was determined by measuring the density of a solution of carbon tetrachloride in benzene in which the

crystals remained suspended. The density of $\text{TiCl}_2(\text{OC}_6\text{H}_5)_2$ was determined to be 1.493 g/cm^3 .

Collection of the Data

The linear absorption coefficient for $\text{CuK}\alpha$ radiation is 91.04 cm^{-1} and for $\text{MoK}\alpha$ 10.34 cm^{-1} . For the size of crystal used, the absorption of $\text{CuK}\alpha$ radiation would affect the intensity measurements enough that absorption corrections would have to be applied. With $\text{MoK}\alpha$ radiation, however, the absorption is negligible.

Intensity data was originally taken on the crystal using a Buerger precession camera using $\text{MoK}\alpha$ radiation. From these pictures, $\text{P2}_1/n$ symmetry was indicated by lattice parameters and systematic extinctions, i. e., $k \neq 2n$ for the $0k0$ zone and $h+l \neq 2n$ for the $h0l$ zone. Using the cell dimensions and assuming four molecules per unit cell, the calculated density is 1.50 g/cm^3 . Table I gives a summary of the cell data.

The intensity data used in the structure determination was collected on a General Electric XRD-5 diffractometer with a General Electric single crystal orienter and scintillation counter for detector. Independent reflections were collected by the 2θ -scan technique (moving crystal-moving counter method) using 100 second scans and reading the background for 50 seconds on each side of the peak. The scan rate in 2θ was two degrees per minute, the take-off angle four

TABLE I

Summary of Crystal Data for $\text{TiCl}_2(\text{OC}_6\text{H}_5)_2$

$$a = 9.821(3) \text{ \AA}$$

$$b = 14.006(4) \text{ \AA}$$

$$c = 9.836(3) \text{ \AA}$$

$$\beta = 94^\circ 50'(10')$$

Space Group $P2_1/n$

Molecules per unit cell 4

Calculated density = 1.50 g/cm^3 Measured density = 1.49 g/cm^3

degrees. Zirconium filtered molybdenum radiation was used. The diffractometer setting for the individual reflections were calculated using a computer program by Witters (22). 2600 reflections were collected of which 1175 were treated as observed, that is, at least 300 counts above background.

The intensity data was corrected for the Lorentz-polarization factor using a computer program from the crystallographic library (23). Form factors for individual reflections were also calculated by this program. The form factor tables were taken from the International Tables for Crystallography (24).

Structure Determination

Initial attempts to solve this structure were made with the standard method of interpreting of a three-dimensional Patterson map. For the crystal symmetry $P2_1/n$, there are equivalent atoms at coordinates

$$x, y, z;$$

$$-x, -y, -z;$$

$$1/2 + x, 1/2 - y, 1/2 + z;$$

$$1/2 - x, 1/2 + y, 1/2 - z.$$

Considering the vector between an atom at x, y, z and at $1/2 - x, 1/2 + y, 1/2 - z$, we obtain $u = 1/2 - 2x, v = 1/2, w = 1/2 - 2z$.

This means that for every atom in the unit cell, a peak is obtained on

the $v = 1/2$ section of the Patterson map due to the screw symmetry up the y axis. The other vectors which one can work with, due to symmetry transformations of the equivalent atoms, are the center of symmetry $(2x, 2y, 2z)$ and the one due to the diagonal glide $(1/2, 1/2 - 2y, 1/2)$. The section at $v = 1/2$, and the line at $u = 1/2, w = 1/2$ are called the Harker section and line respectively.

The major peak on the Harker section was at $(1/2, 1/2, 0)$. This indicated a titanium atom with coordinates $(0, y, 1/4)$. The major peak on the Harker line was at $v = .45$ indicating the y coordinates of titanium was $.025$. This peak was also present with approximately the expected peak height. Around each of the peaks were "satellite" peaks which one would expect to get from titanium to chlorine vectors, also with the correct peak heights. Some remaining "satellite" peaks could be attributed to titanium to oxygen vectors; thus, explaining every major peak in the Patterson map. Table II gives the atomic positions found from the Patterson map. Table III shows the calculated and actual peak heights due to the vectors between atoms given in Table II.

Using these titanium and chlorine positions the structure factor calculation gave an R -index of 52% which was not unreasonable for this number of atoms considering the pseudo-special position of the titanium. A Fourier map showed the positions of the oxygens and some rather distorted phenyl rings. With these new positions calculated from the

TABLE II
Coordinates Obtained for Incorrect Structure of



Atom	x	y	z
Ti	.000	.025	.250
Cl(1)	-.175	.025	.650
Cl(2)	.200	.025	.675
O(1)	.000	.025	.075

TABLE III

Assignments of Vectors Due to Incorrect Structure

of $\text{TiCl}_2(\text{OC}_6\text{H}_5)_2$

Peak No.	Assignment	Positions			Peak Height	Calc. Height
		x	y	z		
1	Ti-Ti	.500	.500	.00	162	122
2	Ti-Cl(1)	.700	.450	.100	35	47
3	Ti-Cl(2)	.325	.450	.075	42	47
4	Ti-O(1)	.500	.450	.350	36	22
5	Ti-Cl(1)	.675	.500	.600	95	94
6	Ti-Cl(2)	.300	.500	.575	108	94
7	Ti-O(1)	.500	.500	.175	98	72
8	Ti-Cl(1)	.800	.000	.400	110	94
9	Ti-Cl(2)	.175	.000	.425	106	94
10	Ti-Ti	.000	.050	.500	67	61
11	Ti-(1)	.000	.050	.325	47	44
12	Ti-Cl(1)	.175	.050	.100	35	47
13	Ti-Cl(2)	.800	.050	.075	35	47
14	Ti-Ti Cl(1)-Cl(1) Cl(2)-Cl(2)	.500	.450	.500	162	194

Fourier map, the R-index dropped to 42%. This cannot be considered good when all the atoms are included, but least-squares refinement of the structure factors was used anyway to see if the structure would refine. The R-index dropped to about 35% in three cycles of full matrix refinement indicating that the structure was probably incorrect. Additional attempts to interpret the Patterson map always lead to the same structure.

Although this structure explained all the major peaks, two peaks were missing from the $v = 1/2$ section which should have been present. These were the double weight Cl-Cl vector peaks arising from the screw symmetry. Thus, although the structure was ruled out, no other structure could be postulated at that time which was more satisfactory.

At this point, it was decided to try the symbolic sign determination which has been briefly described. Computer programs were written to calculate the normalized structure factors and find the \sum_2 relations, and to search through them for symbolically assigned phases. The largest 242 normalized structure factors (>1.4) were used. The initial choice of signs are shown in Table IV. More than 5000 sign relations were calculated, some reflections having as many as 100 relations contributing to their signs. Subsequently, 230 signs were assigned with only one arbitrary choice remaining. Using these two

TABLE IV

Initial Choice of Signs for $\text{TiCl}_2(\text{OC}_6\text{H}_5)_2$

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

possible sets of signs, two three-dimensional E-maps were computed. The correct structure was immediately apparent in one of the E-maps. Upon checking the signs after refinement, all 230 signs proved to be correct. Table V shows the new values of the principal measured and calculated vectors as compared to those in Table III.

The structure factor calculation with new titanium, chlorine and oxygen positions gave an R-index of 42%. Using these structure factors, a Fourier map was calculated which gave the positions of the carbons in the phenyl rings. With these positions, the R-index dropped to 29%. The only difference between the incorrect and the correct structure was that the two molecules were moved 1 Å closer together along the z axis. This, in effect, changed the z coordinate of titanium to that of the chlorines and those of the chlorines to the z coordinate of the titanium. The peak on the Harker section which had been interpreted as a 4 weighted Ti-Ti peak, was now interpreted as 8 Cl(1)-Cl(2) vectors which fell in approximately the same place. The Ti-Cl vectors could be explained by either the correct or incorrect structure.

Refinement of the Structure

Refinement started with the atom positions which gave an R-index of 29%. The full matrix least-squares refinement program of Busing, Levy and Martin was used (25). Three cycles varying

TABLE V

Assignment of Vectors Due to the Correct Structure

of $\text{TiCl}_2(\text{OC}_6\text{H}_5)_2$

Peak No.	Assignment	Peak Height	Calc. Height
1	Ti-Ti	162	144
2	Ti-Cl(1)	35	47
3	Ti-Cl(2)	42	47
4	Ti-O(1)	36	22
5	Ti-Cl(1)	95	94
6	Ti-Cl(2)	108	94
7	Ti-Ti	98	81
8	Ti-Cl(1)	106	94
9	Ti-Cl(2)	110	94
10	Cl(1)-Cl(2)	67	72
11	Ti-Ti	47	31
12	Ti-Cl(1)	35	47
13	Ti-Cl(2)	35	47
14	Ti-Ti Cl(1)-Cl(1) Cl(2)-Cl(2)	162	194

positional parameters decreased the R-index to 19%; three cycles varying positional parameters and individual isotropic temperature factors reduced the R-index to 11%; and three cycles varying positional parameters and anisotropic temperature factors brought the R-index to 6.1%. During this refinement, all reflections were weighted equally.

Final positional parameters are listed in Table VI. Table VII lists the anisotropic temperature factors, and Table VIII 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 IX and X. Table XI contains the observed and calculated structure factors.

Discussion of the Structure

Figure 1 shows the arrangement of the molecule 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 oxygen bridges. The titanium-oxygen distances vary considerably, the shortest being 1.744(10) Å, the next 1.910(9) Å, and the longest 2.122(9) Å. The ionic Ti-O distance in rutile is 1.944 Å, whereas in Ti_3O_5 the distances range from 1.83 to 2.7 (26).

