

## The Crystal and Molecular Structure of Cyclotetra[ $\mu$ -oxo-chloro- $\pi$ -cyclopentadienyltitanium(IV)]

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The crystal and molecular structure of cyclotetra[ $\mu$ -oxo-chloro- $\pi$ -cyclopentadienyltitanium(IV)],  $[(\pi\text{-C}_5\text{H}_5)\text{TiClO}]_4$ , has been determined from three-dimensional X-ray diffractometer data. The compound crystallizes in the orthorhombic space group  $Cmc2_1$  with four tetramers in a unit cell of dimensions  $a = 15.320$ ,  $b = 11.715$ ,  $c = 14.515$  Å. The structure was refined by least-squares methods using 1347 independent reflexions to give  $R = 0.042$ . The molecules consist of tetrameric rings with the titanium atoms tetrahedrally coordinated. The eight-membered  $\text{-Ti-O-Ti-}$  ring is far from planar, and the arrangement of the chlorine atoms and the cyclopentadienyl rings is such that they are alternately above and below the ring. Of the four cyclopentadienyl rings, two are ordered and two are systematically disordered; thus the tetramers have only approximate  $C_s$  symmetry. The Ti-Cl distances vary from 2.263–2.270 Å, the Ti-O distances from 1.776–1.799 Å, and the Ti-( $\pi\text{-C}_5\text{H}_5$ ) distances (taken to the centres of the rings) from 2.02–2.04 Å.

### Introduction

There has been much interest in polymers formed with Ti-O-Ti chains (Spirer, 1962). Polymers of quite low molecular weight ( $\approx 1700$ ) which have good heat resistant properties can be obtained by hydrolysis of titanium alkoxides. Here the titanium has sixfold coordination and the organic groups are bonded to titanium through oxygen. However in compounds in which titanium is directly bonded to organic carbon, the coordination is fourfold and it has been suggested (Saunders & Spirer, 1965) that such compounds might more readily form polymers of a linear structure and higher molecular weight.

During investigations into polymer formation by organo-titanium compounds, a compound of formula  $[(\pi\text{-C}_5\text{H}_5)\text{TiClO}]_n$  was first prepared by Gorsich (1960) who reported  $n \geq 3$ . He was unable to determine the value of  $n$  by cryoscopic or ebullioscopic molecular-weight determinations because of the compound's limited solubility in organic solvents. Subsequently Saunders & Spirer (1965) examined its molecular weight by light scattering. They determined the molecular weight as 630; 658 is required for a value of  $n = 4$ . They also reported some preliminary X-ray work on the crystals which were found to be orthorhombic of space group  $Cmcm$  with unit-cell dimensions  $a = 15.28$ ,  $b = 11.69$ ,  $c = 14.50$  Å: the density indicated that there were 16 of the structural units  $(\pi\text{-C}_5\text{H}_5)\text{TiClO}$  in the cell. On the basis of this evidence Saunders & Spirer postulated a tetrameric ring structure (*i.e.*  $n = 4$ ) with a tetrahedral arrangement at the titanium atom together with the symmetry required for the  $Cmcm$  space group.

An X-ray structural study of this compound was undertaken to characterize it unequivocally and to determine its detailed conformation. It has been found that the compound is a tetrameric ring with  $n = 4$  and

the titanium tetrahedrally coordinated, but the space group is  $Cmc2_1$  and not  $Cmcm$  so that the conformation of the molecule differs from that envisaged by Saunders & Spirer. A preliminary account of this work has already been published (Skapski, Troughton & Sutherland, 1968).

### Experimental

Cyclotetra[ $\mu$ -oxo-chloro- $\pi$ -cyclopentadienyltitanium(IV)] is obtained when  $(\pi\text{-C}_5\text{H}_5)\text{TiCl}_3$  in methanol solution is hydrolysed by water; it crystallizes from xylene as yellow plates. Suitable crystals were kindly provided by Dr L. Spirer. Preliminary oscillation and Weissenberg photographs confirmed the earlier report that the crystals were orthorhombic with systematic absences given by  $hkl$ :  $h + k = 2n + 1$  and  $h0l$ :  $l = 2n + 1$ . These absences are consistent with the space groups  $Cmc2_1$  (No. 36),  $C2cm$  (No. 40), or  $Cmcm$  (No. 63).

The initial intensity data, on which the structure was solved, were collected using the equi-inclination Weissenberg technique and measured visually by Dr H. H. Sutherland of the University of Hull. Layers  $h$ , 0–8,  $l$  and correlating layers  $h$ ,  $k$ , 0–2, taken with Cu  $K\alpha$  radiation, gave a total of 1279 independent reflexions, of which 348 were unobserved.

The intensity data, on which the final structure and its atomic parameters are based, were measured on a Siemens off-line automatic four-circle diffractometer. A crystal of approximate dimensions 0.65 mm  $\times$  0.39 mm  $\times$  0.09 mm was mounted with the  $c$  axis parallel to the  $\phi$  axis of the diffractometer. Cu  $K\alpha$  radiation at a take-off angle of  $4.5^\circ$ , a Ni  $\beta$  filter and a Na(Tl)I scintillation counter were used. The  $\theta$ - $2\theta$  scan technique was employed, with a 'five-point' measuring procedure (one side of the peak, background, full peak, background on the other side of the peak, other side of the peak). The diffractometer automatically selects

measuring times up to a preset maximum or attenuators (nickel) if appropriate so as to achieve similar counting statistics for all but the weakest reflexions. 1347 independent reflexions to  $\theta=70^\circ$  were measured, of which 17 were judged insignificant as the net count was below 2.58 times the standard deviation (*i.e.* below the 99% confidence limit) and were assigned a count equal to this value. The 800 reflexion was used as a reference every 20 reflexions: the net count of this reflexion did not alter noticeably over the period of data collection (approximately 2 days). The data were scaled using the reference reflexion and Lorentz-polarization and absorption corrections were applied. As the crystal was quite large and anisotropic in shape and the linear absorption coefficient was also large [ $\mu(\text{Cu } K\alpha)=144.6 \text{ cm}^{-1}$ ], it was considered necessary to apply an absorption correction. This was done by means of the Gaussian integration method, with an  $8 \times 8 \times 8$  grid, described by Busing & Levy (1957) with crystal path-lengths determined by the vector analysis procedure of Coppens, Leiserowitz & Rabinovich (1965).

The unit-cell dimensions and their estimated probable errors, measured on the Siemens diffractometer (Cu  $K\alpha_1=1.54051 \text{ \AA}$ ) are  $a=15.320 \pm 0.005$ ,  $b=11.715 \pm 0.005$  and  $c=14.515 \pm 0.005 \text{ \AA}$  at  $20^\circ\text{C}$ :  $U=2605.1 \text{ \AA}^3$ ;  $D_{\text{obs}}=1.66 (\pm 0.02) \text{ g.cm}^{-3}$  (Saunders & Spirer, 1965);  $D_{\text{calc}}=1.676 \text{ g.cm}^{-3}$  for 16 of the structural units ( $\pi\text{-C}_5\text{H}_5$ )TiClO,  $F(000)=1312$ , M.W.=657.6.

#### Solution and refinement of the structure

The initial solution of this structure presented some problems. The titanium and chlorine atoms have comparable scattering power for X-rays and, as there were sixteen of each in the unit cell, a quite complicated Patterson map was expected and indeed found. The Patterson synthesis showed that the molecules lie mainly in the  $xy$  plane and that they must be based on the  $z=0$  or  $z=\frac{1}{2}$  levels if the structure belonged either to the *Cmcm* or *C2cm* space groups; the origin in  $z$  is arbitrary for the *Cmc2<sub>1</sub>* space group. Only one independent vector of approximately  $2.3 \text{ \AA}$  could be found, to correspond with an expected Ti-Cl distance, although this appeared to be a multiple peak. All the other strongest peaks were greater than  $3.5 \text{ \AA}$  from the origin and were attributed to Ti-Ti and non-bonded Ti-Cl vectors, but no immediate solution for the arrangement of the titanium and chlorine atoms was apparent. A sharpened Patterson synthesis, although changing the relative intensities of the peaks, did not produce any significant new peaks.

Also at this stage it was not possible to eliminate any of the three possible space groups with certainty. The evidence indicating whether the structure was centrosymmetric or non-centrosymmetric was conflicting: Saunders & Spirer (1965) had found that the crystals showed neither piezoelectric properties nor optical activity, which led them to state that the space group

was *Cmcm*; reflexion statistics gave  $\langle|E|\rangle=0.921$  while a perfect centrosymmetric structure requires  $\langle|E|\rangle=0.798$  and a perfect non-centrosymmetric structure requires  $\langle|E|\rangle=0.886$ . This latter evidence implied that the structure was non-centrosymmetric with some inherent disorder, which later proved to be the case. Additionally, attempts to fit the postulated ring structure into the known unit cell suggested that the space group *Cmcm* imposed too many symmetry requirements to allow such a molecule to be accommodated. It was therefore decided to pursue a solution in the non-centrosymmetric space groups.

A number of trial solutions were tested, often with only some of the titanium and chlorine atoms included. Finally a 'solution' was found in *C2cm*, based on two out of the three possible independent titanium atoms and one of the two possible independent oxygen atoms (bonded by the two titanium atoms), which reached a conventional  $R$  value ( $=\sum||F_o|-|F_c||/|F_o|$ ) of 0.378, after refinement. Hitherto no solution had given an  $R$  value better than 0.45. The titanium atoms were in positions  $(xy\frac{1}{2})$ , lying on a mirror plane. The Fourier synthesis showed two peaks approximately  $1 \text{ \AA}$  above and below this mirror, both of which were in a reasonable position for a titanium atom to complete a -Ti-O-Ti- eight-membered ring. This suggested that either the ring was disordered across this mirror or, more likely, the true space group was *Cmc2<sub>1</sub>*, which does not require such a mirror. Refinement of all the titanium and oxygen atoms in *Cmc2<sub>1</sub>* reduced  $R$  to 0.33. The chlorine atoms were easily found from the resultant Fourier synthesis, and further refinement including the chlorine atoms took  $R$  to 0.25. (This arrangement of titanium and chlorine atoms fully explained the Patterson map, and it was apparent that the overlap and coincidences of many independent vectors had obscured its solution.) One of the cyclopentadienyl rings was located from the next Fourier synthesis, and further refinement including this gave  $R=0.20$ . It was obvious from a difference Fourier synthesis at  $R=0.20$  that the other two cyclopentadienyl rings were disordered. Describing these rings with half-atoms in the best positions obtainable from the difference Fourier synthesis gave  $R=0.136$  after further refinement. Another difference synthesis omitting the disordered rings did not suggest any more satisfactory way of describing them. More refinement, with the titanium and chlorine atoms anisotropic, reduced  $R$  to 0.133.

The final structure obtained from the visual data was unsatisfactory on two counts: (1) the standard deviations of the Ti-O-Ti angles were too large for it to be certain that the Ti-O-Ti bonds were non-linear; (2) the final difference Fourier synthesis without the disordered rings was of insufficient resolution for the disorder to be properly described. As the crystals were large and of excellent quantity and a diffractometer had become available since the structure determination was originally undertaken, it was decided to recollect the data on the diffractometer.

Refinement of the titanium and chlorine atoms anisotropically and the oxygen atoms and the carbon atoms of the ordered cyclopentadienyl ring isotropi-

cally on the diffractometer data gave an R value of 0.122. It was apparent from a difference Fourier synthesis that the remaining two cyclopentadienyl rings

Table 1. Observed and calculated structure factors (in electrons × 10) for [(π-C5H5)TiClO]4

\*Indicates an unobserved reflexion. E indicates an extinction reflexion.

Table with multiple columns listing observed and calculated structure factors for various reflections. The table includes reflection indices (h, k, l) and corresponding observed (Fo) and calculated (Fc) values. Some entries are marked with asterisks or letters to denote specific types of reflexions.

Table 1 (cont.)

12	18,00L	114	1	84	20	18	361	204	0	18,00L	222
1	18,00L		2	180	123	1	60	604	0	18,00L	202
4	18,00L	458	4	282	279	0	83	87	0	18,00L	182
1	18,00L	356	0			0	642	904	4	18,00L	202
5	18,00L	376	2	1,358	1,748	0	450	450	6	18,00L	217
3	18,00L	237	2	1,358	1,304	0	409	409	6	18,00L	209
4	18,00L	96	4	519	562	0	130	133	7	18,00L	182
3	18,00L	168	4	443	462	0	124	125	6	18,00L	202
6	18,00L	136	8	620	637	7	125	104	7	18,00L	176
9	18,00L	181	15	781	790	0	167	153	3	18,00L	196
0	18,00L	359	12	716	247	0	65	91	0	18,00L	202
9	18,00L	272				10	322	201	1	18,00L	202
10	18,00L	291				11	58	96	1	18,00L	202
11	18,00L	243							2	18,00L	209
			1	104	162				3	18,00L	209
			1	321	237	8	11,75L	93	4	18,00L	209
7	10,25L	76	3	192	327	1	131	145	5	18,00L	182
1	10,25L	235	4	48	84	0	120	96	6	18,00L	182
2	10,25L	235	5	979	565	3	151	161	7	18,00L	182
1	10,25L	194	6	297	285	4	131	135	8	18,00L	172
4	10,25L	405	7	642	662	5	124	129	9	18,00L	202
4	10,25L	148	8	247	102	6	249	271	1	18,00L	222
2	10,25L	337	9	346	367	7	216	191	2	18,00L	222
7	10,25L	187	10	142	98	8	147	152	3	18,00L	222
4	10,25L	102	11	169	169	9	146	122	4	18,00L	222
0	10,25L	102	12	103	72	0			5	18,00L	222
			13	60	94	0			6	18,00L	222
						10	205	248	7	18,00L	222
						11	98	96	8	18,00L	222
						12	510	313	9	18,00L	222
						13	361	240	10	18,00L	222
						14	362	329	11	18,00L	222
						15	182	184	12	18,00L	222
						16	341	350	13	18,00L	222
									14	18,00L	222
									15	18,00L	222
									16	18,00L	222
									17	18,00L	222
									18	18,00L	222
									19	18,00L	222
									20	18,00L	222
									21	18,00L	222
									22	18,00L	222
									23	18,00L	222
									24	18,00L	222
									25	18,00L	222

R value decreased after refinement to 0.046. Further refinement with the dispersion correction the right way, and the 220 reflexion removed because of extinction, gave a final R value of 0.042. The final average ratio of shift to standard deviation was 0.06, and the maximum ratio was 0.36.

In the refinement, the usual least-squares function,  $\sum \omega(F_0 - F_c)^2$ , was minimized. The atomic scattering factors used were those tabulated by Cromer & Waber (1965), and the values for the real and imaginary parts of the dispersion correction were those given by Cromer (1965). The anomalous dispersion was treated as follows: for each reflexion a structure factor was calculated without and with the dispersion correction, and the observed structure factor was multiplied by the ratio of these two; refinement was then carried out using the 'corrected' structure factor. The unobserved reflexions were included throughout the refinement of the structure on the diffractometer data but were omitted from all estimates of the agreement factor R. Because of the approximately constant counting statistics in the measurement of the data, unit weight was given to each reflexion in the refinement: an analysis of the final distribution of  $\omega\Delta^2$  did not suggest any more appropriate weighting scheme. A final difference Fourier synthesis showed no peak greater than 0.35 e.Å<sup>-3</sup>, and the highest peaks were in the neighbourhood of the disordered cyclopentadienyl rings.

Table 1 gives a list of the final observed and calculated structure factors. Tables 2 and 3 give the final atomic parameters and their standard deviations: these standard deviations have been estimated from block-diagonal matrix refinement and are, therefore, a slight underestimate of the true deviations. Tables 4 and 5 give the most significant bond lengths and angles respectively, with their standard deviations: these standard deviations are estimated using the diagonal approximation, but no further significant error is introduced by this as there are no strong parameter correlations.

were disordered systematically to give two separate orientations of each ring rather than being completely disordered. Further refinement including the disordered rings reduced R to 0.064. Refinement with the ordered cyclopentadienyl ring, also anisotropic, took R to 0.055. The hydrogen atoms for this ring were then included, fixed in their calculated positions, and further refinement with the oxygen atoms anisotropic gave R=0.050. All atoms were now allowed to refine anisotropically, with fixed hydrogen atoms for all cyclopentadienyl rings added, to give R=0.047; for this and all subsequent work, it was necessary to transfer from full-matrix to block-diagonal refinement because of the number of parameters. This refinement was followed by the application of a dispersion correction: with the sign of Δf'' one way, the R value increased after refinement to 0.056; with the sign of Δf'' reversed, the

Table 2. Position parameters

Numbers in parentheses here and in subsequent Tables are estimated standard deviations.

	x	y	z
Ti(1)	0	-0.00767 (28)	0
Ti(2)	0	0.39775 (17)	0.06632 (15)
Ti(3)	0.16052 (9)	0.20633 (11)	-0.01755 (13)
Cl(1)	0	-0.12298 (31)	-0.12506 (24)
Cl(2)	0	0.54153 (27)	-0.03853 (23)
Cl(3)	0.25088 (21)	0.16560 (32)	0.10141 (13)
O(1)	0.09205 (40)	0.08240 (51)	-0.02012 (54)
O(2)	0.09185 (53)	0.31310 (60)	0.03034 (54)
C(11)*	0.0299 (10)	0.5405 (11)	0.1804 (9)
C(12)	0.0857 (14)	0.4420 (14)	0.1970 (10)
C(13)	0.0285 (9)	0.3551 (13)	0.2216 (10)
C(14)	-0.0604 (12)	0.3809 (12)	0.2131 (12)
C(15)	-0.0632 (16)	0.4925 (16)	0.1903 (12)
C(21)	0.0380 (13)	-0.0072 (18)	0.1571 (12)
C(22)	0.0928 (18)	-0.0906 (16)	0.1190 (14)
C(23)	0.0329 (10)	-0.1740 (13)	0.0855 (10)

Table 2 (cont.)

	x	y	z
C(24)	-0.0620 (16)	-0.1410 (22)	0.1085 (13)
C(25)	-0.0565 (20)	-0.0358 (20)	0.1497 (16)
C(31)	0.2621 (7)	0.3199 (11)	-0.1015 (10)
C(32)	0.1801 (9)	0.3349 (9)	-0.1407 (8)
C(33)	0.1487 (8)	0.2316 (10)	-0.1763 (6)
C(34)	0.2152 (9)	0.1513 (11)	-0.1633 (7)
C(35)	0.2860 (7)	0.2064 (13)	-0.1167 (8)
H(11)†	0.0479	0.6254	0.1641
H(12)	0.1563	0.4381	0.1935
H(13)	0.0500	0.2706	0.2410
H(14)	-0.1126	0.3233	0.2260
H(15)	-0.1219	0.5389	0.1801
H(21)	0.0599	0.0678	0.1905
H(22)	0.1627	-0.0927	0.1136
H(23)	0.0505	-0.2535	0.0491
H(24)	-0.1159	-0.1942	0.0898
H(25)	-0.1145	-0.0120	0.1697
H(31)	0.3007	0.3835	-0.0679
H(32)	0.1450	0.4146	-0.1430
H(33)	0.0857	0.2166	-0.2082
H(34)	0.2123	0.0637	-0.1851
H(35)	0.3461	0.1654	-0.0980

\* Carbon atoms are numbered  $C(mn)$  where  $m$  is the ring number and  $n$  is the atom number in the ring. Atoms are numbered successively around the ring.

† Hydrogen atoms bear the same numbers as the carbon atoms to which they are bonded. These are calculated positions, and therefore no standard deviations are given.

There is of course the possibility that the structure is entirely ordered, *i.e.* monoclinic with  $\beta=90^\circ$ , space group  $Cc$ , and that the apparent disorder of the cyclopentadienyl rings arises by imposing a mirror plane in orthorhombic symmetry. To test this possibility the data were assumed to be either of type  $hkl$  or  $\bar{h}kl$ , and the different possible models obtained by reducing the symmetry were refined. No model gave an  $R$  value bet-

ter than 0.060, and even then the 'temperature factors' were quite unacceptable.

The solution and refinement of the structure were carried out using the *Crystal Structure Calculations*

Table 4. Selected bond lengths

Ti(1)-Cl(1)	2.263 (4) Å
Ti(1)-O(1)	1.785 (6)
Ti(1)-C(21)	2.35 (2)
Ti(1)-C(22)	2.44 (2)
Ti(1)-C(23)	2.37 (2)
Ti(1)-C(24)	2.41 (2)
Ti(1)-C(25)	2.36 (2)
Ti(1)-C(p2)*	2.04
Ti(2)-Cl(2)	2.270 (4)
Ti(2)-O(2)	1.799 (8)
Ti(2)-C(11)	2.40 (1)
Ti(2)-C(12)	2.36 (2)
Ti(2)-C(13)	2.35 (1)
Ti(2)-C(14)	2.33 (2)
Ti(2)-C(15)	2.33 (2)
Ti(2)-C(p1)*	2.02
Ti(3)-Cl(3)	2.264 (4)
Ti(3)-O(1)	1.792 (6)
Ti(3)-O(2)	1.776 (8)
Ti(3)-C(31)	2.382 (13)
Ti(3)-C(32)	2.357 (11)
Ti(3)-C(33)	2.330 (9)
Ti(3)-C(34)	2.365 (11)
Ti(3)-C(35)	2.402 (11)
Ti(3)-C(p3)*	2.044
C—C <sub>mean</sub> (ring 1)	1.43 (3)
C—C <sub>mean</sub> (ring 2)	1.44 (3)
C(31)-C(32)	1.391 (17)
C(32)-C(33)	1.401 (16)
C(33)-C(34)	1.399 (18)
C(34)-C(35)	1.433 (18)
C(35)-C(31)	1.396 (20)

\* Cp(1), Cp(2), Cp(3) are the respective centres of the three cyclopentadienyl rings 1, 2, 3.

Table 3. Anisotropic thermal parameters

The anisotropic thermal ellipsoid is of the form  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ .

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Ti(1)	0.00333 (48)	0.00352 (41)	0.00177 (52)	0	0	0.00008 (28)
Ti(2)	0.00398 (16)	0.00333 (20)	0.00239 (14)	0	0	-0.00022 (15)
Ti(3)	0.00256 (9)	0.00426 (14)	0.00305 (9)	-0.00005 (10)	-0.00006 (8)	0.00012 (12)
Cl(1)	0.00708 (34)	0.00651 (42)	0.00330 (24)	0	0	-0.00160 (26)
Cl(2)	0.00679 (32)	0.00522 (36)	0.00338 (24)	0	0	0.00132 (23)
Cl(3)	0.00459 (21)	0.01593 (56)	0.00686 (24)	-0.00143 (29)	-0.00265 (23)	0.00421 (32)
O(1)	0.0044 (5)	0.0077 (8)	0.0052 (5)	-0.0020 (5)	-0.0005 (5)	-0.0005 (6)
O(2)	0.0074 (7)	0.0064 (8)	0.0062 (6)	0.0032 (6)	0.0011 (6)	-0.0000 (5)
C(11)	0.0057 (17)	0.0027 (14)	0.0012 (9)	0.0003 (10)	-0.0012 (8)	-0.0015 (9)
C(12)	0.0074 (20)	0.0044 (19)	0.0019 (10)	-0.0020 (16)	-0.0015 (12)	0.00013 (12)
C(13)	0.0024 (12)	0.0062 (21)	0.0020 (10)	-0.0005 (10)	0.0007 (10)	0.0030 (16)
C(14)	0.0033 (13)	0.0138 (35)	0.0020 (15)	0.0002 (18)	-0.0007 (10)	0.0006 (16)
C(15)	0.0111 (27)	0.0041 (21)	0.0024 (12)	0.0042 (18)	0.0003 (15)	-0.0016 (12)
C(21)	0.0069 (20)	0.0087 (27)	0.0021 (11)	0.0012 (16)	0.0005 (12)	-0.0010 (14)
C(22)	0.0104 (26)	0.0051 (22)	0.0037 (14)	-0.0004 (20)	-0.0011 (17)	0.0006 (15)
C(23)	0.0050 (13)	0.0054 (18)	0.0017 (9)	0.0000 (11)	-0.0010 (9)	0.0023 (11)
C(24)	0.0085 (23)	0.0141 (39)	0.0028 (14)	-0.0028 (25)	0.0016 (16)	0.0040 (20)
C(25)	0.0127 (33)	0.0097 (31)	0.0043 (17)	0.0018 (30)	0.0007 (20)	0.0029 (20)
C(31)	0.0037 (8)	0.0129 (22)	0.0128 (16)	-0.0014 (11)	0.0006 (10)	0.0073 (16)
C(32)	0.0087 (13)	0.0077 (13)	0.0043 (8)	0.0009 (11)	0.0012 (9)	0.0030 (9)
C(33)	0.0073 (11)	0.0122 (17)	0.0020 (6)	-0.0003 (11)	0.0005 (7)	0.0008 (9)
C(34)	0.0088 (13)	0.0109 (17)	0.0040 (8)	0.0019 (12)	0.0027 (9)	0.0004 (10)
C(35)	0.0044 (8)	0.0194 (26)	0.0046 (9)	0.0004 (12)	0.0016 (7)	0.0008 (14)

Table 5. Selected bond angles

Cl(1)—Ti(1)—O(1)	102.8 (2)°
Cl(1)—Ti(1)—C(p2)*	115.2
O(1)—Ti(1)—O(1')	104.4 (6)
O(1)—Ti(1)—C(p2)	115.0
Cl(2)—Ti(2)—O(2)	102.4 (3)
Cl(2)—Ti(2)—C(p1)	117.1
O(2)—Ti(2)—O(2')	102.9 (6)
O(2)—Ti(2)—C(p1)	115.0
Cl(3)—Ti(3)—O(1)	101.7 (3)
Cl(3)—Ti(3)—O(2)	102.3 (3)
Cl(3)—Ti(3)—C(p3)	116.6
O(1)—Ti(3)—O(2)	103.4 (3)
O(1)—Ti(3)—C(p3)	115.7
O(2)—Ti(3)—C(p3)	115.2
Ti(1)—O(1)—Ti(3)	159.7 (4)
Ti(2)—O(2)—Ti(3)	164.8 (5)
C(p1')—Ti(2)—C(p1'')	3.6
C(p2')—Ti(1)—C(p2'')	7.8
C(35)—C(31)—C(32)	107.0 (1.1)
C(31)—C(32)—C(33)	110.6 (1.1)
C(32)—C(33)—C(34)	106.3 (1.1)
C(33)—C(34)—C(35)	108.2 (1.1)
C(34)—C(35)—C(31)	107.7 (1.1)

\* C(p1) and C(p2) are the mean centres of the disordered cyclopentadienyl rings. C(p1'), C(p1''), C(p2'), C(p2'') are the centres of each orientation of the disordered rings and C(p3) is the centre of the ordered ring.

System X-ray-63 (Stewart, 1965). The calculations were carried out either on the Imperial College IBM 7090 or on the London University Atlas machines.

### Description and discussion of the structure

Fig. 1 (a) and (b) shows the conformation of the eight-membered —Ti—O—Ti— ring, which is far from planar. The arrangement of the four titanium atoms is such that the Ti(1)—Ti(2) and Ti(3)—Ti(4) distances are nearly equal (4.846 and 4.918 Å), and the angle between the planes containing Ti(1), Ti(2), Ti(3) and Ti(1), Ti(2), Ti(4) is 146.2°, and similarly that between the planes Ti(3), Ti(4), Ti(1) and Ti(3), Ti(4), Ti(2) is 145.7°. The Ti—O—Ti bonds are distorted from linearity such that the angle Ti(1)—O(1)—Ti(3) is 159.7 ( $\sigma=0.4$ )° and the angle Ti(2)—O(2)—Ti(3) is 164.8 ( $\sigma=0.5$ )°. In the dimer  $[(\pi\text{-C}_5\text{H}_5)\text{TiCl}_2]_2\text{O}$  (Allegra & Ganis, 1962) the Ti—O—Ti bond is linear.

The arrangement of the chlorine atoms and the cyclopentadienyl rings is such that they are alternately above and below the 'plane' of the ring [Fig. 1(a)]. Of the four cyclopentadienyl rings two are ordered and two are disordered [Fig. 1(b)]. Thus, although the tetramers lie astride mirror planes in space group  $Cmc2_1$  the individual molecules do not have strict  $C_s$  symmetry. The tetramers also possess approximate  $\bar{4}$  ( $S_4$ ) symmetry. The disordered cyclopentadienyl rings are not, in fact, completely disordered and each ring lies in two distinct orientations as indicated in Fig. 1(b). Although the description of these rings in the least-squares refinement must be something of an approximation, it appears that the centre of each disordered ring lies distinctly to one side of the mirror plane,

implying that some of the other coordinating atoms are fractionally disordered as well, a fact which is supported by the distribution of the anisotropic temperature factors of all the chlorine atoms. Least-squares planes have been calculated through the ordered cyclopentadienyl ring, and through one orientation of each of the disordered rings. The maximum deviation of an atom from each ring is 0.019, 0.020, 0.036 Å respectively: thus the disordered rings have not become unduly distorted compared with the ordered ring in the least-squares refinement.

The titanium atoms are tetrahedrally coordinated, assuming that the cyclopentadienyl rings are monodentate ligands. It can be seen from the tetrahedral angles given in Table 5 that there are distortions from the

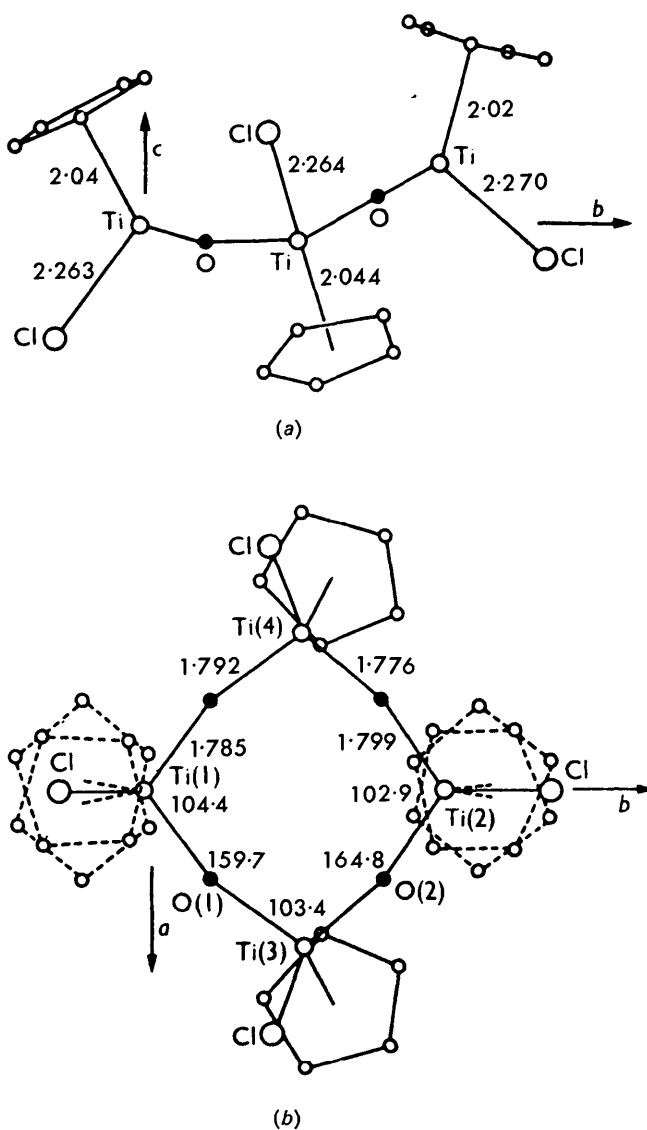


Fig. 1. (a) [100] projection and (b) [001] projection of the structure of  $[(\pi\text{-C}_5\text{H}_5)\text{TiClO}]_4$ .

ideal  $109^\circ$  in order to minimize the angular strain in the eight-membered ring and to accommodate the relatively bulky cyclopentadienyl ligands. The Ti-Cl distances vary from 2.263–2.270 ( $\sigma=0.004$ ) Å, the Ti-O distances from 1.776–1.799 ( $\sigma=0.007$ ) Å, and the Ti-( $\pi$ -C<sub>5</sub>H<sub>5</sub>) distances (taken to the centres of the rings) from 2.02–2.04 Å. These can best be compared with the distances found in the two structures [( $\pi$ -C<sub>5</sub>H<sub>5</sub>)TiCl<sub>2</sub>]<sub>2</sub>O (Allegra & Ganis, 1962) and ( $\pi$ -C<sub>5</sub>H<sub>5</sub>)TiCl<sub>3</sub> (Ganis & Allegra, 1962) which were determined from two-dimensional projections. They found Ti-Cl distances varying from 2.27–2.30 Å, and Ti-O and Ti-( $\pi$ -C<sub>5</sub>H<sub>5</sub>) distances of 1.74 and 2.04 Å respectively. Thus all the bond lengths in the different structures are similar. There are no unusual intermolecular contacts and therefore the crystal structure is determined only by the efficient packing of the molecules.

The tetrameric ring structure of [( $\pi$ -C<sub>5</sub>H<sub>5</sub>)TiClO]<sub>4</sub> is the first of its type containing a transition metal; the nearest equivalent is the cyclic P<sub>4</sub>O<sub>11</sub><sup>4-</sup> ion found in the metaphosphates Al<sub>4</sub>(P<sub>4</sub>O<sub>12</sub>)<sub>3</sub> (Pauling & Sherman, 1957) and (NH<sub>4</sub>)<sub>4</sub>P<sub>4</sub>O<sub>12</sub> (Romers, Ketelaar & MacGillavry, 1951). Tetrameric alkoxides of titanium are known (Ibers, 1963; Witters & Caughlan, 1965; Wright & Williams, 1966), but in these the titanium atoms are octahedrally coordinated and the tetramer consists of four such octahedra joined by edges.

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## The Crystal Structure of DL-4 $\beta$ ,10 $\beta$ -Dimethyl-6-ethylamino-4-hydroxycarbonyl-2, 3, 5 $\beta$ , 10-tetrahydrophenanthr-1-one lactam, C<sub>19</sub>H<sub>21</sub>O<sub>2</sub>N\*

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The title compound crystallizes in the monoclinic space group  $P2_1/c$  with four molecules in a unit cell of dimensions  $a=10.901$ ,  $b=9.738$ ,  $c=16.389$  Å;  $\beta=117.17^\circ$ . The structure was determined by the symbolic-addition procedure using low-temperature diffractometer data and refined by the least-squares method to  $R=3.9\%$  for 3101 observed reflexions.

### Introduction

Wiesner and Ho recently attempted to prepare the lactam (I) and intended to use it as an intermediate for a

synthesis of hexacyclic diterpene alkaloids. Although the material which they obtained gave the correct elemental analysis, its ultraviolet and nuclear magnetic-resonance spectra did not agree with the proposed structure. This crystal structure determination, which was undertaken in order to establish unambiguously the structure of the synthetic intermediate, revealed the

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