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The Crystal and Molecular Structure of μ -Oxo-bis[chlorobis(2,4-pentanedionato)titanium(IV)]-Chloroform, $[\text{TiCl}(\text{C}_5\text{H}_7\text{O}_2)_2]_2 \text{O} \cdot \text{CHCl}_3$

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μ -Oxo-bis[chlorobis(2,4-pentanedionato)titanium(IV)]-chloroform crystallized in space group $P2_1/n$ with $a = 15.744$, $b = 22.628$, $c = 8.888$ Å, $\beta = 100.30^\circ$, and $z = 4$. The structure was solved by a combination of the symbolic sign determination method and an interpretation of the Patterson map. The final R value for 1091 observed reflections is 7.4%. The structure is made up of essentially two octahedrally coordinated $\text{TiCl}(\text{C}_5\text{H}_7\text{O}_2)_2$ units joined by an oxygen atom, the titanium octahedron being somewhat distorted. The acetylacetonate groups are *cis* to each other and the oxygen atom joining the two parts of the molecule together is an approximate center of symmetry for the molecule. The acetylacetonate groups are planar but the coordinating titanium atom is considerably out of this plane on two of the groups. The bond angle at the oxygen atom joining the two titanium atoms is 167.5° and the two titanium-oxygen distances from this oxygen atom are the shortest in the molecule (1.79 and 1.81 Å) indicating double-bond character to these Ti-O bonds. Thus, sp hybridization is postulated for this oxygen atom, with a certain amount of double-bond character to these Ti-O bonds arising from donation of the electrons from oxygen to the unfilled d titanium orbitals. It is suggested that the color of the compound is due to these electrons. The chloroform molecule is apparently hydrogen bonded to two oxygens of acetylacetonate groups on one titanium, the chloroform carbon-oxygen distances being 3.21 and 3.35 Å. The remaining distances and angles in the structure appear to be normal.

Introduction

Rosenheim and co-workers¹ and later Dilthey² studied the reaction between titanium tetrachloride and 2,4-pentanedione and isolated a compound with the empirical formula $\text{TiCl}_2(\text{C}_5\text{H}_7\text{O}_2)_2$. (The 2,4-pentanedionate group, $\text{C}_5\text{H}_7\text{O}_2^-$, is represented throughout this paper as the acetylacetonate group, *i.e.*, *acac*.) More recently the bis acetylacetonates of titanium(IV) have been studied by Mehrotra, *et al.*,³⁻⁵ Yamamoto and Kambara,⁶ Fay, Pinnavaia, Serpone, and Lowry,⁷ and Bradley and Holloway.⁸ As a result of the last two studies based upon nmr and infrared spectra, the conclusions were reached that the acetylacetonate groups were *cis* and that this structure was stabilized relative to the *trans* by π -electron donation from the *acac* groups to vacant d orbitals in the titanium. It was our intention to study the crystal structure of $\text{TiCl}_2(\text{acac})_2$, but in the process of crystallizing and transferring these crystals into capillaries for X-ray diffraction work, the partially hydrolyzed and solvated crystal $[\text{TiCl}(\text{acac})_2]_2 \cdot \text{O} \cdot \text{CHCl}_3$ was produced. Although the analysis indicated small variations from the theoretical values expected for $\text{TiCl}_2(\text{acac})_2$, it was not certain until near the completion of the structural analysis that the compound was in fact $[\text{TiCl}(\text{acac})_2]_2 \cdot \text{O} \cdot \text{CHCl}_3$. If we had determined the molecular weight of the compound, the correct molecular formula would have been apparent.

Experimental Section

Crystals of this compound were made by the method suggested by Dilthey² for $\text{TiCl}_2(\text{acac})_2$. Chloroform solutions of acetylacetonate and titanium tetrachloride were mixed so that the ratio of acetylacetonate to titanium tetrachloride was 2:1. The chloroform used was previously dried and the reaction was carried out in a closed flask from which atmospheric moisture was eliminated, but no special drying precautions were taken. The deep red solution was warmed for several hours and part of the chloroform was distilled. Upon cooling, crystals formed and these were recrystallized from chloroform.

The crystals are orange-yellow and hydrolyze in moist air, although they are much more stable than either TiCl_4 or titanium alkoxides. The crystals were analyzed for carbon, hydrogen, chlorine, and TiO_2 . Table I summarizes the analytical data.

TABLE I

	Obsd		Calculated			
	%	Atoms	$\text{TiCl}_2(\text{acac})_2$		$[\text{TiCl}(\text{acac})_2]_2 \cdot \text{O} \cdot \text{CHCl}_3$	
Titanium	14.4	2	15.11	2	13.72	2
Chlorine	23.4	4.4	22.37	4	25.38	5
Oxygen	20.4	8.6	20.19	8	20.62	9
Carbon	37.3	20.8	37.89	20	36.11	21
Hydrogen	4.5	30	4.45	28	4.18	29

It is apparent from Table I that the observed results lie between those for the two compounds listed. It is possible that the crystals that were analyzed were actually a mixture of the two compounds and that the one used for X-ray examination turned out to be the partially hydrolyzed compound.

The crystal selected for X-ray work was enclosed in a capillary and had dimensions of $0.1 \times 0.2 \times 1.0$ mm. X-Ray data showed this to have $P2_1/n$ symmetry as indicated by the systematic extinctions, *i.e.*, $k \neq 2n$ for $0k0$ reflections, $h + l \neq 2n$ for the $h0l$ zone, and the lattice parameters $a = 15.744$, $b = 22.628$, $c = 8.888$ Å, and $\beta = 100.30^\circ$, as determined on the diffractometer (standard deviation about ± 0.002 Å). On the basis of the measured density, 1.47 g/cc, there are four molecules

- (1) A. Rosenheim, W. Loewenstamm, and L. Singer, *Ber.*, **36**, 1833 (1903).
- (2) W. Dilthey, *ibid.*, **37**, 588 (1904).
- (3) K. C. Pande and R. C. Mehrotra, *Chem. Ind.* (London), 1198 (1958).
- (4) R. C. Mehrotra, *J. Indian Chem. Soc.*, **30**, 585 (1953).
- (5) D. C. Bradley, R. C. Mehrotra, and W. J. Wardlaw, *J. Chem. Soc.*, 2027 (1952).
- (6) A. Yamamoto and S. Kambara, *J. Am. Chem. Soc.*, **79**, 43 (1957).
- (7) R. C. Fay, T. J. Pinnavaia, N. Serpone, and R. N. Lowry, Proceedings of the 9th International Conference on Coordination Chemistry, St. Moritz-Bad, Switzerland, Sept 5-9, 1966, p 486.
- (8) D. C. Bradley and C. E. Holloway, *ref 7*, p 483.

per unit cell. The linear absorption coefficient for Mo K α radiation is 9.89 cm⁻¹.

The intensity 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 θ - 2θ scan technique (moving crystal-moving counter method) using 40-sec scans and reading the background for the 40 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. A total of 2000 reflections were collected of which 1091 were treated as observed. The data were corrected for the Lorentz-polarization factor using an IBM 1620 computer.⁹ No absorption corrections were applied. For structure factor calculations, form factors from the literature were used.¹⁰ Anomalous terms of the form factors were not used.

Structure Determination and Refinement

The structure was deduced by a combination of the symbolic sign determination method of Karle and Karle¹¹ and an interpretation of the Patterson map. The normalized structure factors were calculated and the sign relations built up. From the E map, calculated from these signs, the positions of the titanium atoms, the oxygen atoms, and the chlorine atoms around the titanium were evident. These positions were checked with the Patterson synthesis and with a minimum function calculated from the Ti-Ti vector. Thus, the correct positions of the titanium atoms and the chlorine atoms around them, and the acetylacetonate groups around the titanium atoms, were deduced. Refinement of these positions was then carried out, and a Fourier map calculated. From this it became evident that there was a molecule of chloroform of solvation in the crystal. Inclusion of this in the next structure factor calculation and refinement indicated that this was in fact correct. Three more cycles of refinement, the last one including anisotropic temperature factors, reduced the R value to 7.4%.¹² The values for shift divided by error were the following: positional parameters: mean, 0.2917; maximum, 0.9; all parameters: mean, 0.3610; maximum, 2.5.

Final positional and thermal parameters with standard deviations are listed in Tables II and III. Table III shows the anisotropic temperature factors and mean-square amplitudes of vibration along the principal axis of the thermal ellipsoid. For calculations of these, an orthogonal coordinate system was used in which the x and y axes coincide with the a and b crystallographic axes. The bond lengths and bond angles with standard deviations are listed in Tables IV and V. Table VI contains the observed and calculated structure factors. Table VII shows the equations for the best least-squares planes for Ti(acac) groups and the coordination around the titanium atoms.

(9) 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. Coughlan, C. T. Li, G. W. Svetich, D. Swank, K. W. Watenpaugh, and R. W. Witters.

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

(11) I. L. Karle and J. Karle, *Acta Cryst.*, **16**, 969 (1963).

(12) Refinement was carried out using the University of Washington System Tape for Crystallographic Calculations. The full-matrix least-squares refinement is that of W. R. Busing, K. O. Martin, and H. A. Levy, ORFLS, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962, modified for the University of Washington Tape.

TABLE II
ATOMIC COORDINATES

	x	y	z
Ti(1)	0.2302 (4)	0.1296 (2)	0.0174 (6)
Ti(2)	0.7507 (4)	0.0267 (2)	0.0224 (5)
Cl(1)	0.3112 (6)	0.1413 (4)	0.2610 (7)
Cl(2)	0.8281 (5)	0.0283 (4)	0.2680 (7)
Cl(3)	0.8668 (7)	0.1675 (5)	0.4884 (9)
Cl(4)	0.8492 (7)	0.1865 (5)	0.7999 (9)
Cl(5)	0.9954 (8)	0.2329 (6)	0.6930 (14)
O(1)	0.2522 (12)	0.0526 (8)	0.0001 (16)
O(2)	0.1653 (13)	0.1336 (9)	0.7985 (19)
O(3)	0.1204 (13)	0.1207 (9)	0.0875 (19)
O(4)	0.3296 (13)	0.1556 (9)	0.9337 (19)
O(5)	0.2007 (12)	0.2187 (8)	0.0218 (19)
O(6)	0.6873 (11)	0.0352 (9)	0.8037 (17)
O(7)	0.6381 (12)	0.0304 (10)	0.0850 (19)
O(8)	0.8524 (10)	0.0395 (8)	0.9369 (17)
O(9)	0.7458 (14)	0.1169 (9)	0.0369 (20)
C(1)	0.8863 (23)	0.2226 (15)	0.6419 (39)
C(2)	0.4387 (21)	0.1556 (18)	0.7808 (33)
C(3)	0.3501 (24)	0.1478 (14)	0.7948 (40)
C(4)	0.2889 (27)	0.1303 (16)	0.6741 (37)
C(5)	0.2031 (29)	0.1251 (16)	0.6753 (37)
C(6)	0.1263 (20)	0.1153 (14)	0.5370 (28)
C(7)	0.9882 (19)	0.1268 (15)	0.1710 (35)
C(8)	0.0641 (19)	0.1588 (17)	0.1255 (29)
C(9)	0.0705 (20)	0.2178 (16)	0.1209 (30)
C(10)	0.1379 (18)	0.2476 (14)	0.0666 (27)
C(11)	0.6344 (26)	0.1865 (13)	0.5539 (38)
C(12)	0.9651 (18)	0.0396 (15)	0.7818 (30)
C(13)	0.8744 (25)	0.0327 (13)	0.7953 (34)
C(14)	0.8051 (22)	0.0259 (15)	0.6765 (36)
C(15)	0.7198 (22)	0.0248 (13)	0.6759 (26)
C(16)	0.6458 (20)	0.0199 (15)	0.5413 (29)
C(17)	0.5058 (18)	0.0542 (14)	0.1676 (32)
C(18)	0.5926 (20)	0.0735 (16)	0.1280 (26)
C(19)	0.6134 (22)	0.1297 (16)	0.1346 (30)
C(20)	0.6916 (23)	0.1508 (16)	0.0867 (30)
C(21)	0.7130 (24)	0.2185 (14)	0.0898 (42)

TABLE III
THERMAL PARAMETERS AND MEAN-SQUARE DISPLACEMENT^{a,b}
(These are given as B_{1j} 's rather than B_{ij} 's) Mean Square Displacement A^2

	B(11)	B(22)	B(33)	B(12)	B(23)	B(31)	MAX	MEAN	MIN
Ti(1)	5.1	4.3	1.6	-0.3	1.9	-0.1	0.07	0.05	0.01
Ti(2)	4.5	3.5	1.5	-0.3	1.7	-0.5	0.06	0.04	0.01
Cl(1)	8.4	6.5	0.8	-0.8	1.5	-0.4	0.11	0.02	0.01
Cl(2)	6.0	5.7	1.5	-0.7	1.7	-0.3	0.09	0.06	0.01
Cl(3)	10.4	10.5	2.9	1.5	2.3	-0.6	0.15	0.11	0.03
Cl(4)	13.0	8.3	3.4	0.0	3.3	1.2	0.17	0.11	0.03
Cl(5)	9.1	11.1	12.4	-1.4	9.4	-0.7	0.17	0.14	0.10
O(1)	7.9	4.4	-0.5	1.6	1.1	1.4	0.11	0.05	0.00
O(2)	6.1	6.2	2.3	0.3	1.1	-0.2	0.08	0.07	0.03
O(3)	4.2	3.4	1.9	-0.5	0.5	0.6	0.06	0.04	0.02
O(4)	5.6	7.3	1.6	-2.3	2.5	-1.0	0.11	0.06	0.00
O(5)	6.7	6.0	2.2	1.4	2.2	0.2	0.10	0.06	0.02
O(6)	5.5	6.9	1.2	0.7	-0.1	-0.2	0.09	0.07	0.01
O(7)	4.5	5.4	3.0	0.6	1.4	-0.6	0.07	0.05	0.03
O(8)	3.0	6.5	0.8	-0.5	1.1	0.5	0.06	0.04	0.00
O(9)	7.0	6.3	1.4	1.3	1.3	0.6	0.10	0.07	0.01
C(1)	9.1	7.0	6.9	-3.4	5.5	-0.7	0.17	0.08	0.03
C(2)	4.2	16.3	2.7	-2.2	2.5	-0.7	0.21	0.06	0.01
C(3)	3.1	6.3	6.1	1.7	-0.3	1.9	0.10	0.07	0.02
C(4)	3.7	6.8	3.9	1.5	-0.3	1.5	0.10	0.06	0.03
C(5)	6.5	6.0	3.9	1.4	-0.6	0.5	0.10	0.07	0.04
C(6)	7.0	6.7	1.5	0.5	-2.1	0.2	0.11	0.08	0.01
C(7)	2.5	7.6	6.9	-1.4	3.0	-1.5	0.12	0.07	0.01
C(8)	1.3	6.7	2.4	1.6	-1.1	-0.9	0.09	0.03	0.01
C(9)	3.6	4.6	5.9	-1.8	1.4	-2.3	0.11	0.05	0.02
C(10)	1.7	4.8	2.6	0.6	-0.4	-0.1	0.06	0.04	0.02
C(11)	15.0	1.4	7.5	-3.4	4.0	-0.5	0.20	0.08	0.01
C(12)	2.7	10.8	3.2	0.1	2.0	1.1	0.14	0.05	0.01
C(13)	7.8	4.1	2.4	0.7	-0.1	0.8	0.11	0.06	0.02
C(14)	2.5	8.6	4.7	-0.4	3.2	-0.3	0.11	0.08	0.03
C(15)	8.6	4.5	-0.9	-2.3	-0.1	0.4	0.13	0.04	0.01
C(16)	6.0	8.3	2.7	-0.1	-1.2	-0.4	0.11	0.09	0.03
C(17)	3.3	7.7	4.0	0.5	2.5	-1.5	0.10	0.06	0.01
C(18)	4.3	3.7	1.1	0.6	0.7	-0.3	0.06	0.04	0.02
C(19)	6.3	3.1	3.2	-1.7	0.7	-1.3	0.09	0.05	0.02
C(20)	5.6	7.8	1.0	1.2	-1.2	-1.3	0.11	0.07	0.03
C(21)	12.4	2.6	8.5	1.4	2.8	-1.3	0.16	0.11	0.02

^a The anisotropic temperature factors for O(1) and C(15) are nonpositive definite. For mean-square displacement, the B_{33} 's were given values of 0.0001, which was less than the standard deviation. ^b Standard deviations of B_{ij} 's are approximately 0.1 for titanium and chlorine atoms, 0.5 for oxygen atoms, and 1.0 for carbon atoms.

TABLE IV

BOND DISTANCES (Å) FOR $[\text{TiCl}(\text{acac})_2]_2 \cdot \text{O} \cdot \text{CHCl}_3$			
Ti(1)-O(1)	1.79 (2)	Acetylacetonate Group (3)	
Ti(1)-O(2)	2.03 (3)	O(6)-C(15)	1.35 (4)
Ti(1)-O(3)	1.95 (3)	O(8)-C(13)	1.37 (5)
Ti(1)-O(4)	1.94 (3)	C(12)-C(13)	1.46 (6)
Ti(1)-O(5)	2.07 (3)	C(13)-C(14)	1.38 (8)
Ti(1)-Cl(1)	2.32 (2)	C(14)-C(15)	1.34 (5)
Ti(2)-O(1)	1.81 (2)	C(15)-C(16)	1.52 (6)
Ti(2)-O(6)	2.03 (3)	Acetylacetonate Group (4)	
Ti(2)-O(7)	1.95 (2)	O(7)-C(18)	1.31 (6)
Ti(2)-O(8)	1.91 (2)	O(9)-C(20)	1.28 (6)
Ti(2)-O(9)	2.05 (2)	C(18)-C(17)	1.53 (6)
Ti(2)-Cl(2)	2.30 (1)	C(18)-C(19)	1.31 (6)
Acetylacetonate Group (1)		C(19)-C(20)	1.45 (7)
O(2)-C(5)	1.35 (6)	C(20)-C(21)	1.57 (6)
O(4)-C(3)	1.34 (5)	Chloroform Group	
C(2)-C(3)	1.43 (6)	C(1)-Cl(3)	1.83 (6)
C(3)-C(4)	1.37 (9)	C(1)-Cl(4)	1.81 (6)
C(4)-C(5)	1.36 (7)	C(1)-Cl(5)	1.71 (5)
C(5)-C(6)	1.58 (8)	C(1)-O(5)	3.21 (6)
Acetylacetonate Group (2)		C(1)-O(4)	3.35 (6)
O(3)-C(8)	1.32 (6)		
O(5)-C(10)	1.31 (5)		
C(7)-C(8)	1.51 (8)		
C(8)-C(9)	1.34 (6)		
C(9)-C(10)	1.41 (7)		
C(10)-C(11)	1.49 (5)		

TABLE V

BOND ANGLES (DEG) FOR $[\text{TiCl}(\text{acac})_2]_2 \cdot \text{O} \cdot \text{CHCl}_3$			
O(1)-Ti(1)-Cl(1)	96.3 (3)	Acetylacetonate Group (2)	
O(1)-Ti(1)-O(2)	91.9 (4)	Ti(1)-O(3)-C(8)	133.5 (13)
O(1)-Ti(1)-O(3)	97.0 (4)	Ti(1)-O(5)-C(10)	132.8 (13)
O(1)-Ti(1)-O(4)	94.6 (4)	O(3)-C(8)-C(7)	110.8 (21)
O(1)-Ti(1)-O(5)	176.0 (5)	O(3)-C(8)-C(9)	125.7 (24)
O(5)-Ti(1)-Cl(1)	87.6 (4)	C(7)-C(8)-C(9)	123.5 (22)
O(5)-Ti(1)-O(2)	84.1 (4)	C(9)-C(10)-C(11)	118.8 (19)
O(5)-Ti(1)-O(3)	83.0 (4)	O(5)-C(10)-C(9)	121.4 (21)
O(5)-Ti(1)-O(4)	84.9 (5)	O(5)-C(10)-C(11)	119.7 (20)
O(2)-Ti(1)-O(4)	85.5 (4)	Acetylacetonate Group (3)	
O(2)-Ti(1)-O(3)	89.2 (4)	Ti(2)-O(6)-C(15)	126.5 (12)
O(2)-Ti(1)-Cl(1)	170.3 (4)	Ti(2)-O(8)-C(13)	135.6 (12)
O(3)-Ti(1)-O(4)	167.3 (5)	O(8)-C(13)-C(12)	118.3 (23)
O(1)-O(1)-Ti(2)	167.5 (11)	O(8)-C(13)-C(14)	114.7 (23)
O(1)-Ti(2)-Cl(2)	96.9 (3)	C(12)-C(13)-C(14)	126.7 (24)
O(1)-Ti(2)-O(6)	89.4 (4)	C(13)-C(14)-C(15)	131.0 (26)
O(1)-Ti(2)-O(7)	93.8 (4)	C(14)-C(15)-C(16)	129.1 (21)
O(1)-Ti(2)-O(8)	96.5 (4)	O(6)-C(15)-C(14)	121.6 (22)
O(1)-Ti(2)-O(9)	175.8 (4)	O(6)-C(15)-C(16)	108.9 (19)
O(9)-Ti(2)-Cl(2)	86.8 (4)	Acetylacetonate Group (4)	
O(9)-Ti(2)-O(6)	87.0 (4)	Ti(2)-O(7)-C(18)	133.5 (14)
O(9)-Ti(2)-O(7)	83.9 (4)	Ti(2)-O(9)-C(10)	130.7 (14)
O(9)-Ti(2)-O(8)	85.3 (4)	O(7)-C(18)-C(17)	114.3 (21)
O(6)-Ti(2)-O(7)	87.3 (4)	O(7)-C(18)-C(19)	126.3 (24)
O(6)-Ti(2)-O(8)	84.8 (4)	C(17)-C(18)-C(19)	119.4 (22)
O(6)-Ti(2)-Cl(2)	173.3 (4)	C(18)-C(19)-C(20)	121.4 (24)
O(7)-Ti(2)-O(8)	166.9 (5)	O(9)-C(20)-C(21)	115.9 (23)
Acetylacetonate Group (1)		O(9)-C(20)-C(19)	123.8 (25)
Ti(1)-O(2)-C(5)	123.3 (13)	Chloroform	
Ti(1)-O(4)-C(3)	131.0 (13)	Cl(3)-C(1)-Cl(4)	103.7 (18)
O(4)-C(3)-C(2)	117.5 (24)	Cl(3)-C(1)-Cl(5)	108.5 (19)
O(4)-C(3)-C(4)	120.6 (26)	Cl(4)-C(1)-Cl(5)	107.7 (19)
C(2)-C(3)-C(4)	121.8 (25)		
C(3)-C(4)-C(5)	123.5 (27)		
C(4)-C(5)-C(6)	129.1 (28)		
O(2)-C(5)-C(6)	105.3 (24)		
O(2)-C(5)-C(4)	125.3 (30)		

Discussion of the Structure

Figure 1 shows the projection of the structure down the c axis. Since this is the short axis, most of the structure is evident. Figure 2 shows the bond dis-

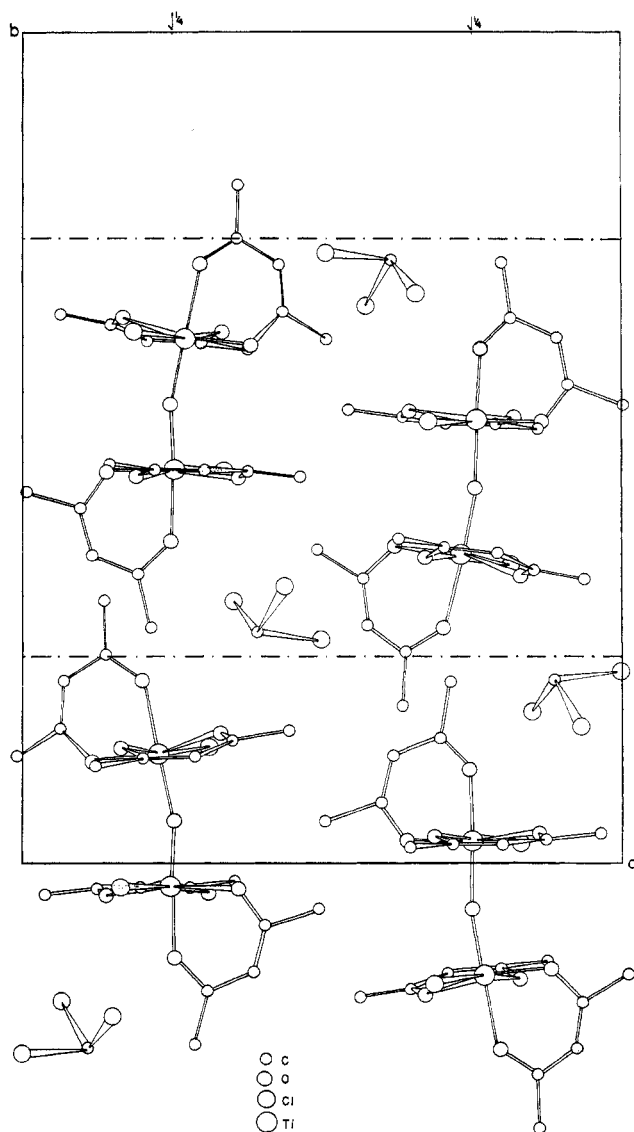


Figure 1.—The structure of $[\text{TiCl}(\text{acac})_2]_2 \cdot \text{O} \cdot \text{CHCl}_3$ in the unit cell viewed down the c axis.

tances around the titanium atoms and the numbering of atoms for the tables. From these figures it is evident that the titanium atoms are octahedrally coordinated, the coordination octahedron being somewhat distorted. The acetylacetonate groups are *cis* to each other which agrees with the solution studies of the dichlorodiacetylacetonate of titanium(IV).^{7,8} The two portions of the molecule are approximately related to each other by a center of symmetry at the joining oxygen, although one part is not actually symmetrically related to the other. The chloroform appears to be bonded by a weak hydrogen bond to each molecule. There is no intermolecular bonding. Several features of the structure warrant further discussion.

The titanium-chlorine distances (2.32 and 2.30 Å) are slightly longer than the 2.219- and 2.209-Å distances in $\text{TiCl}_2(\text{OC}_6\text{H}_5)_2$ ¹³ and the 2.185-Å distance for TiCl_4 .¹⁴

(13) K. Watenpaugh and C. N. Caughlan, *Inorg. Chem.*, **5**, 1782 (1966).

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

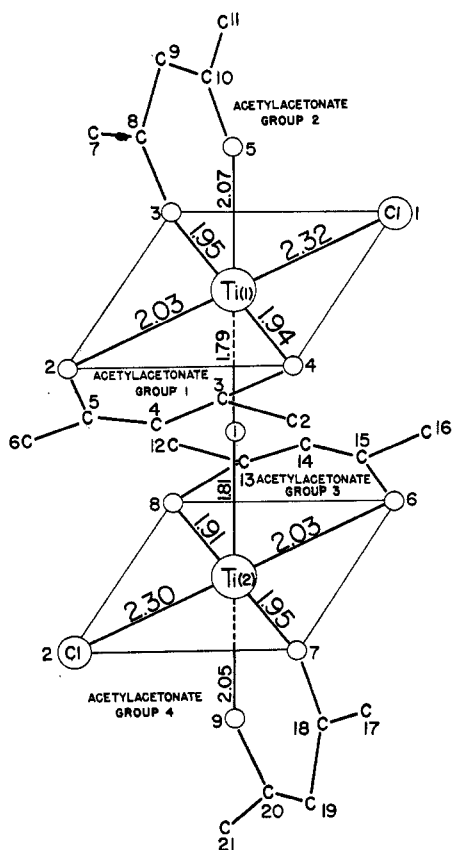


Figure 2.—The structure of $[\text{TiCl}(\text{acac})_2]_2\text{O} \cdot \text{CHCl}_3$ showing coordination and distance around titanium.

i.e., in $[\text{TiCl}_2(\text{C}_5\text{H}_5)_2]\text{O}$ ¹⁷ where the angle was 180° and in $\text{TiCl}_2(\text{OC}_6\text{H}_5)_2$ ¹³ where the angle was 165.9° . It should be noted that the distances from O(1) to Ti(1) and Ti(2) are the two shortest titanium–oxygen distances, *i.e.*, 1.79 and 1.81 Å, which are only slightly longer than the short Ti–O distance in $\text{TiCl}_2(\text{OC}_6\text{H}_5)_2$ ¹³ and approximately equal to the short distance in $[\text{TiCl}_2(\text{C}_5\text{H}_5)_2]\text{O}$.¹⁷ The same arguments as proposed for these two compounds suggest partial double-bond character for these Ti–O bonds in $[\text{TiCl}(\text{acac})_2]_2\text{O} \cdot \text{CHCl}_3$ arising from donation of the electrons from p_y and p_z filled oxygen orbitals to the unfilled titanium orbitals.

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

Thus sp hybridization is postulated for this oxygen, O(1).

It appears that the chloroform molecule is hydrogen bonded to the oxygens of the acetylacetonate groups. The titanium–carbon–chlorine bond angles to the chloroform molecule are 109.5 , 108.1 , and 118.4° indicating that the hydrogen of the chloroform is pointing directly toward the titanium atom. The actual distances from the chloroform carbon to the oxygen atoms and the titanium atom are the following: O(4)–C(1) = 3.35 Å; O(5)–C(1) = 3.21 Å; Ti(1)–C(1) = 4.18 Å. Thus it appears that there is a bifurcated hydrogen bond from the chloroform carbon to O(5) and O(4), although this may be merely a dipolar attraction of CHCl_3 to the oxygens.

It has been suggested by Fay, *et al.*,⁷ that the color in $\text{TiCl}_2(\text{acac})_2$ is due to charge transfer from the chlorine atom to the titanium atom. There is no indication in $[\text{TiCl}(\text{acac})_2]_2\text{O} \cdot \text{CHCl}_3$ as evidenced by the Ti–Cl bond lengths of such charge transfer. There is certainly involvement of the p electrons of O(1) in the d orbitals of titanium and probably also from oxygens on the acetylacetonate groups. It is, thus, suggested that in this compound the color is probably due to these electrons. The spectral characteristics of this compound have not yet been investigated.

It is evident, from examination of the bond distances and angles, and the least-squares planes around the titanium atoms, that the coordination octahedra are somewhat distorted, although the bond angle distortions are not more than about 10° from a regular octahedron. The titanium atoms are about 0.2 Å from the planes formed by Cl(1), O(2), O(3), O(4) and Cl(2), O(6), O(7), O(8).

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