45. Studies of Organometallic Compounds XVI[1])
The Crystal Structure of Di-μ-ethoxy-bis(dibenzylethoxy-titanium(IV))

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Summary. The crystal structure of di-μ-ethoxy-bis(dibenzylethoxy-titanium(IV)), [(EtO)$_2$Ti-(CH$_2$Ph)$_2$]$_2$, has been determined from analysis of photographic X-ray data. The crystal system is monoclinic, $a = 7.93(2)$, $b = 15.99(2)$, $c = 13.40(2)$ Å, $\beta = 92.7(3)°$, space group P2$_1$/c. The molecule is a dimer situated about a crystallographic center of symmetry. The two Ti atoms are joined by oxygen bridges. Each Ti atom is penta-coordinated in the form of a distorted trigonal bipyramid.

1. Introduction. – The present work is part of our study on organometallic compounds having Ti(IV)–C σ-bonds. We wish to report on the X-ray crystallographic analysis of diethoxy titanium dibenzyl, originally prepared by *Zucchini et al.* [1] [2]. This compound was found to be a dimer on the basis of molecular weight determination and from the NMR. spectrum at room temperature [2]. Two quartets found at τ = 5.58 and 5.91 were assigned to the CH$_2$ protons of the ethoxy groups, one pair of which probably bridges the two Ti atoms.

The present analysis establishes the structure to be di-μ-ethoxy-bis(dibenzyl-ethoxy-titanium(IV)).

2. Experimental Part. – Diethoxy titanium dibenzyl was prepared by the reaction of tetrabenzyl titanium with a stoichiometric amount of ethyl alcohol in pentane [2]. The product obtained was recrystallized from ether giving large rectangular red crystals. No density determination could be made owing to the sensitivity to oxygen and moisture. For X-ray analysis the crystals were sealed in *Lindemann* glass tubes under nitrogen.

Preliminary oscillation, *Weissenberg* and precession photographs indicated a monoclinic cell: $a = 7.93(2)$, $b = 15.99(2)$, $c = 13.40(2)$ Å, $\beta = 92.7(3)°$, V = 1697 Å^3, space group P2$_1$/c, Z = 4 (TiC$_{18}$H$_{24}$O$_2$, M.W. = 320.3), D$_x$ = 1.25.

The layers 0kl – 7kl were recorded by the equi-inclination *Weissenberg* method, using Ni-filtered CuKα radiation (λ = 1.5418 Å) on multiple-film packs. Intensities were estimated visually by comparison with a standard calibration strip. A total of 2439 reflections were measured and corrected for *Lorentz*-polarization effects. A spot shape correction [3] was also applied. 1485 reflections were considered 'observed' and used in all subsequent calculations.

3. Structure Analysis and Refinement. – The *Patterson* synthesis revealed a dominant peak in a general position at 3.2 Å from the origin. Assuming that this is a Ti–Ti vector, it follows that the molecule is binuclear with a center of symmetry at the origin. The position of the Ti atom is confirmed by a strong vector in the (u, $^1/_2$, w) *Harker* section, and also on the (0, v, $^1/_2$) *Harker* line.

A 'heavy-atom' F$_0$-synthesis (R = 44%) revealed all but 10 of the light atoms in the dimer. These were found in a second F$_0$-synthesis. Two rounds of isotropic

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full-matrix least-squares refinement lowered R to 16%. After refinement of the inter-layer scaling two cycles of anisotropic block-diagonal least-squares analysis, with an overall scale factor, reduced R to 10.3%. All hydrogen atoms were then located in a $(F_0 - F_c)$-synthesis and included in structure factor calculations at calculated positions but not refined $(B = 4\ \text{Å}^2)$. Refinement was terminated at $R = 8.9\%$ when the majority of parameter shifts were less than 0.4 e.s.d. Unit weights were used throughout (justified by the uniform distribution of the quantity $\langle w(F_0 - F_c)^2 \rangle$). Tables of observed and calculated structure factors and anisotropic thermal parameters are available from the author.

The final positional parameters and interatomic distances and angles are given in Tables 1 to 3.

Table 1. *Final positional parameters* (estimated standard deviations X 10^4 in parentheses)

Atom	x/a	y/b	z/c
Ti	0.0271(3)	0.0209(1)	0.1163(1)
O(1)	− 0.1149(7)	0.0467(4)	0.0056(5)
C(1)	− 0.2640(15)	0.1011(8)	0.0131(9)
C(2)	− 0.2167(19)	0.1920(9)	0.0197(10)
O(2)	− 0.0762(10)	0.0883(5)	0.2062(6)
C(3)	− 0.1500(20)	0.1426(10)	0.2845(11)
C(4)	− 0.3215(21)	0.1216(13)	0.3030(13)
C(5)	− 0.0083(15)	− 0.0885(8)	0.2058(9)
C(6)	0.1285(15)	− 0.0857(7)	0.2757(8)
C(7)	0.1134(17)	− 0.0374(8)	0.3637(9)
C(8)	0.2449(18)	− 0.0344(9)	0.4290(9)
C(9)	0.3860(19)	− 0.0784(9)	0.4118(10)
C(10)	0.4069(18)	− 0.1264(9)	0.3250(10)
C(11)	0.2779(17)	− 0.1295(8)	0.2590(9)
C(12)	0.2647(15)	0.0779(8)	0.1288(9)
C(13)	0.2714(14)	0.1528(8)	0.0669(9)
C(14)	0.3211(15)	0.1487(8)	− 0.0371(9)
C(15)	0.3145(16)	0.2208(9)	− 0.0952(9)
C(16)	0.2559(18)	0.2967(9)	− 0.0571(10)
C(17)	0.2088(19)	0.2994(8)	0.0465(11)
C(18)	0.2145(17)	0.2299(8)	0.1049(9)

Table 2. *Bond lengths* $(Å)$ (estimated standard deviations X 10^3 in parentheses)

Ti.....Ti'	3.197(3)	C(7) – C(8)	1 330(18)
Ti – C(6)	2.820(11)	C(8) – C(9)	1.350(21)
Ti – C(13)	2.958(12)	C(9) – C(10)	1.410(21)
Ti' – O(1)	2.104(7)	C(10) – C(11)	1.320(19)
Ti – O(1)	1.865(7)	C(11) – C(6)	1.403(18)
O(1) – C(1)	1.475(14)	Ti – C(12)	2.091(12)
C(1) – C(2)	1.502(19)	C(12) – C(13)	1.459(17)
Ti – O(2)	1.837(8)	C(13) – C(14)	1.467(17)
O(2) – C(3)	1.501(18)	C(14) – C(15)	1.390(17)
C(3) – C(4)	1.433(23)	C(15) – C(16)	1.404(20)
Ti – C(5)	2.147(13)	C(16) – C(17)	1.454(21)
C(5) – C(6)	1.400(16)	C(17) – C(18)	1.359(19)
C(6) – C(7)	1.419(17)	C(18) – C(13)	1.415(17)

Table 3. *Bond angles* (degrees) (estimated standard deviations X 10 in parentheses)

Ti – O(1) – Ti'	107.1(1)	Ti – C(5) – C(6)	103.3(3)
Ti – O(1) – C(1)	122.1(0)	C(5) – C(6) – C(7)	118.7(3)
Ti' – O(1) – C(1)	130.6(1)	C(5) – C(6) – C(11)	120.7(4)
O(1) – C(1) – C(2)	112.1(4)	C(6) – C(7) – C(8)	118.1(4)
O(1) – Ti – O(2)	96.9(1)	C(7) – C(8) – C(9)	119.9(6)
Ti – O(2) – C(3)	176.0(13)	C(8) – C(9) – C(10)	123.7(8)
O(2) – C(3) – C(4)	112.9(5)	C(9) – C(10) – C(11)	117.1(7)
O(1) – Ti – C(12)	118.4(1)	C(10) – C(11) – C(6)	120.5(5)
O(1) – Ti – C(5)	122.3(0)	Ti – C(12) – C(13)	111.6(4)
O(1) – Ti – O(1')	72.9(0)	C(12) – C(13) – C(14)	121.5(4)
O(2) – Ti – C(12)	96.9(1)	C(12) – C(13) – C(18)	119.3(4)
O(2) – Ti – C(5)	92.1(1)	C(13) – C(14) – C(15)	119.0(4)
O(2) – Ti – O(1')	169.8(2)	C(14) – C(15) – C(16)	121.2(1)
O(1') – Ti – C(12)	87.5(1)	C(15) – C(16) – C(17)	118.4(5)
O(1') – Ti – C(5)	94.1(1)	C(16) – C(17) – C(18)	121.5(6)
C(5) – Ti – C(12)	116.8(1)	C(17) – C(18) – C(13)	120.5(4)

4. Results and Discussion. – Fig. 1, a projection of the molecule on the (100) plane, also shows the atom-labelling scheme used.
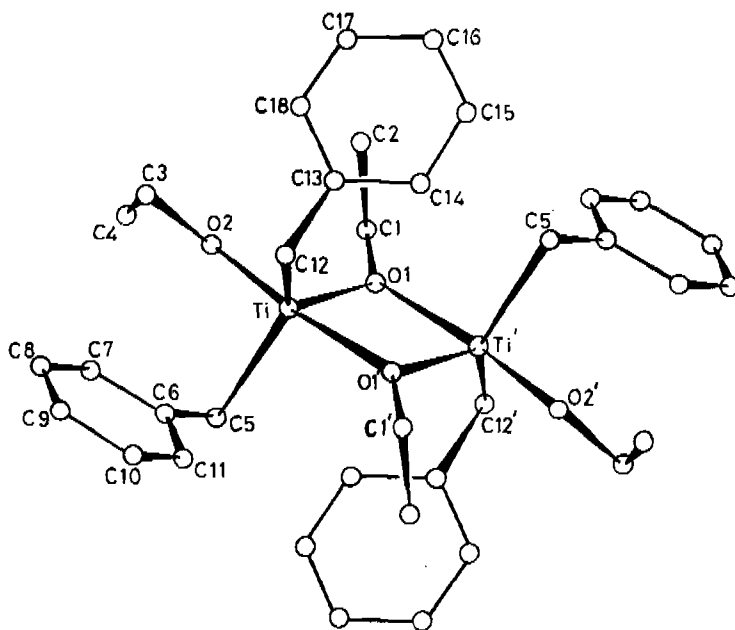

Fig. 1. *Projection of the molecule on the (100) plane*

Diethoxy titanium dibenzyl is a centrosymmetric dimer with penta-coordinated Ti atoms connected by oxygen bridges. The Ti coordination, shown in Fig. 2, corresponds to a distorted trigonal bipyramid (TBP). The equatorial plane of the TBP is formed by atoms O(1), C(5) and C(12), with the Ti atom 0.19 Å above it. One of the apical atoms, O(1'), is 0.27 Å more distant from the Ti atom than the other, O(2). The atoms Ti, Ti', O(1), O(1'), O(2) and O(2') are nearly in a plane (Table 4).
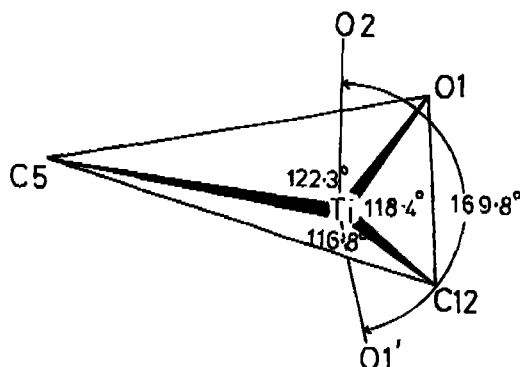
Fig. 2. *Coordination around the titanium atom in* $(EtO)_2Ti(CH_2Ph)_2$ *dimer*

Table 4. *Various least-squares planes in the molecule*

Equation of plane for atoms Ti, Ti', O(1), O(1'), O(2) & O(2'); 0.6087x + 0.7607y − 0.2251z = 0. Deviation in Å: Ti, − 0.009; Ti', 0.009; O(1), − 0.006; O(1'), 0.006; O(2), 0.005; O(2'), − 0.005

Equation of plane for benzyl group C(5) − C(11); 0.3830x + 0.7969y − 0.4669z + 2.4892 = 0. Deviation in Å: C(5), 0.001; C(6), − 0.002; C(7), − 0.004, C(8), 0.010; C(9), − 0.010; C(10), 0.005; C(11), 0.001.

Equation of plane for benzyl group C(12) − C(18); − 0.9661x − 0.2117y − 0.3120z + 2.7127 = 0. Deviation in Å: C(12), 0.042; C(13), − 0.038; C(14), − 0.018; C(15), 0.033; C(16), − 0.001; C(17), − 0.003; C(18), − 0.016.

In the dimers of $Cl_2Ti(OPh)_2$ [4] and $Cl_2Ti(OEt)_2$ [9], the Ti(IV) atoms are also penta-coordinated and their molecular geometries are remarkably similar to that of the title compound.

For the bridging Ti–O distances, Ti–O(1) is 1.87 Å while Ti–O(1') is 2.10 Å (compared with 1.91 and 2.12 Å in dimer $Cl_2Ti(OPh)_2$ [4], and 1.96 and 2.03 Å in dimer $Cl_2Ti(OEt)_2$ [9]). The non-bridging Ti–O(2) distance is long (1.84 Å) compared with 1.77 Å in dimer $Cl_2Ti(OPh)_2$, and 1.74 Å in dimer $Cl_2Ti(OEt)_2$, but shorter than the Ti–O distances (1.95 and 1.99 Å) in rutile [7].

For the bridging ethoxy groups the angle Ti–O(1)–C(1) is 122.1° compared with 176.0° for the Ti–O(2)–C(3) angle. Such a large angle has been observed (175°) in the dimer of $(PhO)_4Ti \cdot HOPh$ [5], where the Ti(IV) atom is octahedrally coordinated.

The Ti–Ti' distance is 3.197 Å and the Ti–O(1)–Ti' angle is 107.1°, compared with 3.309 Å and 109° in the dimer of $(PhO)_4Ti \cdot HOPh$ [5], and 3.274 Å and 108.5° in the dimer of $Cl_2Ti(OPh)_2$ [4]. The distances Ti–C(12) and Ti–C(5) are 2.091 and 2.147 Å respectively, compared with 2.08 Å in $[(PhCH_2)_3Ti]_2O$ [8], and 2.13 Å (mean) in $(PhCH_2)_4Ti$ [6]. As for the Ti...C_β distances, Ti–C(13) is 2.958 Å with an angle at C(12) of 111.6° (compared with 2.979 Å and 113.4° in $[(PhCH_2)_3Ti]_2O$ [8]), while Ti–C(6) is shorter (2.820 Å) and the angle at C(5) smaller (103.3°). The shorter distance and smaller angle may be compared with those observed in $(PhCH_2)_4Ti$ [6].

The benzyl groups are planar (Table 4), their least-squares planes being at an angle of 112.2° to one another.

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46. Zur Frage der Existenz isomerer, äquatorial koordinierter 1:2-Co(III)-Komplexe aus symmetrischen o,o'-Dihydroxyazofarbstoffen

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Summary. 2,2'-Dihydroxy-3,3'-dimethyl-5,5'-di-*t*-butyl-1,1'-azobenzene has been metallized to the 1:2-Co-(III)-complex. In addition to the main product a further complex was isolated by chromatography in a yield of about 2% and proved to be an isomer of the main complex. The cause of the isomerism could not be elucidated.

In [1] wurden erstmals isomere, äquatorial koordinierte Cr(III)- und Co(III)-1:2-Komplexe aus symmetrischen o,o'-Dihydroxydiarylazofarbstoffen beschrieben. Nachdem für eine grosse Zahl isomerer 1:2-Co(III)-Komplexe aus unsymmetrischen o,o'-Dihydroxydiarylazofarbstoffen die «N_α/N_β-Isomerie» bewiesen werden konnte [2], besteht noch Unklarheit über die Struktur der aus symmetrischen Liganden entstehenden Isomeren.

Im Gegensatz zu den «N_α/N_β-Isomeren», welche im Falle von unsymmetrischen o,o'-Dihydroxyazobenzolen oder von 2-Hydroxy-1,2'-azonaphtholen(1') als Liganden meistens in günstigen Mengenverhältnissen entstehen [1] [2], daher auch leicht erkannt und in präparativem Maßstabe isoliert werden können, treten die Isomeren aus den symmetrischen o,o'-Dihydroxydiarylazoliganden nur in sehr untergeordneter Menge (~1%) auf, weshalb sie leicht der Beobachtung (z.B. bei dünnschichtchromatographischen Untersuchungen) entgehen und daher als nicht existierend oder allenfalls als Nebenprodukte (z.B. durch Oxydation zustande gekommene «Dimere») betrachtet und sogar angezweifelt werden können[1].

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[1]   Private Korrespondenzen mit Fachkollegen.