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STRUCTURE OF CYCLOPENTADIENYLCYCLOHEPTATRIENYLTITANIUM

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SUMMARY

An X-ray diffraction study of cyclopentadienylcycloheptatrienyltitanium shows the compound to be a sandwich compound with both rings π-bonded to the metal. The ring planes include an angle of 2.2°. The distance of Ti to the carbon atoms of the C_5H_5 ring (2.32 Å) is normal, but the distance to the carbons of the C_7H_7 ring (2.19 Å) is anomalously short.

INTRODUCTION

In 1970 Van Oven and De Liefde Meyer[1] reported the synthesis and some properties of cyclopentadienylcycloheptatrienyltitanium $C_5H_5TiC_7H_7$. From its IR spectrum, which is very similar to the spectrum of $C_5H_5VC_7H_7$[2], it was concluded that the five-membered ring is π-bonded to the metal. The NMR spectrum indicates that the compound has a sandwich structure, analogous to that of $C_5H_5VC_7H_7$[3]. Since little is known about the geometry of sandwich compounds of this type, we were asked to determine the structure of $C_5H_5TiC_7H_7$ by means of X-ray diffraction.

RESULTS AND DISCUSSION

The structure of the molecule as found by the X-ray study is schematically shown in Fig. 1. The bond lengths and angles are listed in Table 1.

Fig. 1 and Table 1 show that both the C_5H_5 and the C_7H_7 rings are π-bonded to the metal. The titanium is sandwiched between the rings, which are both planar within the experimental error. The angle between the planes of the rings is 2.2±0.3°.

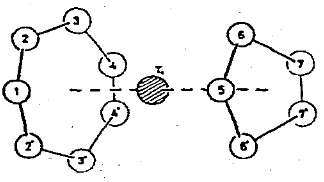

Fig. 1. The cyclopentadienylcycloheptatrienyltitanium molecule. The molecule possesses mirror symmetry.

TABLE 1

MOLECULAR GEOMETRY (for numbering of atoms see Fig. 1)
Ti-RING DISTANCES: Ti–C_7H_7 1.490 Å AND Ti–C_5H_5 1.994 Å

Bond lengths (*Å*)^{a,b}				*Bond angles* (°)	
C(1)–C(2)	1.426(5)	Ti–C(1)	2.165(4)	C(2′)–C(1)–C(2)	127.7(4)
C(2)–C(3)	1.403(6)	Ti–C(2)	2.184(3)	C(1)–C(2)–C(3)	127.8(3)
C(3)–C(4)	1.370(6)	Ti–C(3)	2.203(3)	C(2)–C(3)–C(4)	128.8(3)
C(4)–C(4′)	1.383(10)	Ti–C(4)	2.210(3)	C(3)–C(4)–C(4′)	129.5(2)
C(5)–C(6)	1.402(4)	Ti–C(5)	2.315(4)	C(6′)–C(5)–C(6)	108.3(4)
C(6)–C(7)	1.386(5)	Ti–C(6)	2.319(3)	C(5)–C(6)–C(7)	107.6(3)
C(7)–C(7′)	1.404(8)	Ti–C(7)	2.326(3)	C(6)–C(7)–C(7′)	108.3(2)

[a] Estimated standard deviations are given in parentheses, in terms of the last decimal place. [b] Bond lengths not corrected for libration.

TABLE 2

AVERAGE VALUES (IN Å) OF M–C AND C–C BOND LENGTHS AND M-RING DISTANCES IN $C_5H_5TiC_7H_7$ AND SOME RELATED SANDWICH COMPOUNDS

	$C_5H_5TiC_7H_7$	$C_5H_5VC_7H_7$[a]	$C_5H_5TiC_8H_8$[b]
M–C C_5H_5	2.321	2.23	2.353
M–C C_nH_n	2.194	2.25	2.323
C–C C_5H_5	1.396	1.42	1.396
C–C C_nH_n	1.397	1.40	1.395
M–C_5H_5	1.994	1.90	2.030
M–C_nH_n	1.490	1.50	1.439

[a] See ref. 3. [b] See ref. 5.

No significant differences have been observed between the C–C bond lengths, which average 1.396 Å for the five-membered ring and 1.397 Å for the seven-membered ring. These values (not corrected for libration) agree with the C–C distances in related sandwich compounds (Table 2). The average distance from Ti to the carbon atoms of the five-membered ring is 2.321 Å. This is a normal value (Table 2), the difference between it and the corresponding distance for $C_5H_5VC_7H_7$ reflecting the difference of the atomic radii of Ti (1.32 Å) and V (1.22 Å). The average distance from Ti to the carbon atoms of the seven-membered ring is only 2.194 Å, which is much shorter than the "normal" distance from Ti to carbons in π-bonded rings, and is even shorter than the corresponding distance in $C_5H_5VC_7H_7$. No explanation can yet be offered for this anomalously short Ti–C distance.

De Liefde Meyer and Jellinek[4] have suggested that the difference in behaviour of titanium and vanadium in compounds of type $(C_5H_5)_2MR_n$, where R is an alkyl, aryl or allyl group, is mainly attributable to steric factors. It was assumed that the distance of Ti to cyclopentadienyl carbons is fairly constant and larger than the corresponding V–C distances. Our results show that one should be extremely careful about such assumptions.

Both between and in the layers, the intermolecular distances exceed the sum of the Van der Waals radii (C 1.7 Å and H 1.1 Å), indicating that the interaction between the molecules in the crystal is small.

An analysis of the thermal motions of the atoms by Cruickshank's procedure[6] has shown that the thermal motions can be described in terms of rigid-body translations and librations. A large libration is observed around the axis approximately perpendicular to the C_5H_5- and C_7H_7-rings. The r.m.s. amplitude of libration is 0.19 rad, and about three times larger than the librations around the remaining axes. The libration corrections in the bond lengths are estimated at 0.015 Å for C–C and 0.01 Å for Ti–C. An alternative interpretation of the large thermal parameters observed lies in the assumption of disorder in the crystal. Whether such a disorder would be static or dynamic cannot be concluded from the present experiment.

EXPERIMENTAL

Crystals of $C_5H_5TiC_7H_7$ were obtained from H. O. van Oven. As the compound is readily affected by oxygen and moisture, the crystals used for the X-ray experiments were covered with a thin layer of Tixo glue. For the intensity measurements a crystal with dimensions of 0.28 × 0.25 × 0.13 mm was used. The crystallographic data and details of the experimental work are summarized in Table 3.

In the adopted centrosymmetric space group *Pnma*, having an eightfold general position, the molecule must occupy a special position in the unit cell, as $Z = 4$. The possible mirror plane of the molecule (containing the Ti atom) was assumed to coincide with the crystallographic mirror plane.

The position of the Ti atom was found from a Patterson synthesis. After anisotropic refinement of the Ti parameters, the positions of the carbon atoms could be read from a Fourier synthesis of reflections with reliable sign. The hydrogen atoms

TABLE 3

CRYSTALLOGRAPHIC DATA AND DETAILS OF EXPERIMENTAL METHODS

Data	*Method*
Orthorhombic, space group *Pnma* or $Pna2_1$	Weissenberg photographs of zero and higher layer lines
$a = 11.040$ e.s.d. 0.002 Å	Weissenberg photographs of zero layer lines
$b = 10.805$ e.s.d. 0.002 Å	λ(Cu-$K\alpha$) 1.5418, λ(Cu-$K\alpha_1$) 1.5405, λ(Cu-$K\alpha_2$)
$c = 8.040$ e.s.d. 0.004 Å	1.5443 Å. Calibration with NaCl spots, a(NaCl) = 5.64006 Å. Least squares adjustment of $\sin^2\theta/\lambda^2$ values of 48 $0kl$ and 41 $h0l$ reflections
$D_M = 1.40 \pm 0.05$ g/cm^3	Specific gravity by flotation method
$Z = 4$, $D_x = 1.41$ g/cm^3	
2370 independent intensities	Automatic nonius diffractometer, Zr filtered Mo-radiation, $\theta - 2\theta$ scan, $\sin\theta/\lambda < 0.837$ Å^{-1}. Reflections with I (net) < 0 were hereafter disregarded
1956 F(hkl) values	Corrections for L.P. and absorption (according to Busing and Levy[6], crystal bounded by seven planes, μ 8.61 cm^{-1})

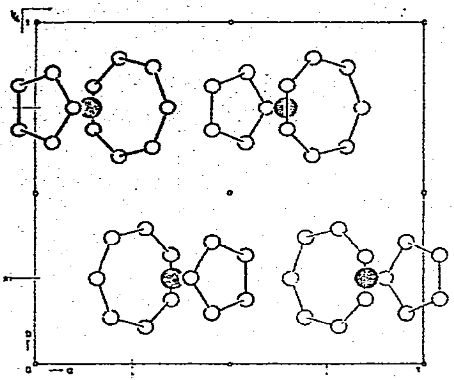

Fig. 2. Projection of the structure along the *c* axis. The molecules in the crystal are arranged in layers. Their mirror planes coincide with the mirror planes in space group *Pnma*. The distance between the mirror planes is 5.403 Å.

were revealed by a difference map $[F_o - F_c(\mathrm{Ti,C})]$, calculated after anisotropic refinement of C and Ti. In the final stages of the refinement the H-atoms were placed at positions calculated from the known geometry of the rings, at a distance of 1.08 Å from the C-atoms. During the last few refinement cycles the H-atoms were taken into account with fixed isotropic temperature factors; for the H-atoms of the five- and seven-membered ring the values for B(iso) were taken as 4.5 Å^2 and 3.9 Å^2, resp., larger than the value $< 8\pi^2 \cdot U_{jj} >$ of the corresponding C-atom. The weighing scheme $W = [W_c^{-1} + 0.0003|F|^2]^{-1}$ was applied, W_c being the weight of the individual reflections based on counting statistics. The 190 reflections having $F_c < 1$ were given zero weight in the final stage of refinement.

TABLE 4

FINAL COORDINATES FOR THE INDEPENDENT PART OF ONE OF THE MOLECULES[a] (for numbering see Fig. 1)

Atom	*x/a*	*y/b*	*z/c*
Ti	0.35536(6)	0.2500	0.45861(8)
C(1)	0.1595(4)	0.2500	0.4714(6)
C(2)	0.1984(3)	0.1316(4)	0.4143(5)
C(3)	0.2849(4)	0.1053(3)	0.2916(5)
C(4)	0.3519(3)	0.1860(3)	0.1975(4)
C(5)	0.4041(4)	0.2500	0.7387(5)
C(6)	0.4573(3)	0.1448(3)	0.6674(4)
C(7)	0.5437(3)	0.1850(3)	0.5544(4)
H(1)	0.0913	0.2500	0.5677
H(2)	0.1561	0.0533	0.4739
H(3)	0.3002	0.0078	0.2699
H(4)	0.4133	0.1421	0.1109
H(5)	0.3333	0.2500	0.8314
H(6)	0.4356	0.0495	0.6957
H(7)	0.6006	0.1252	0.4802

[a] The numbers of the hydrogen atoms correspond with those of the carbon atoms to which they are linked.

For the H-atoms the f-curve calculated by Stewart[7] was used, while for the remaining atoms the analytical functions calculated by Doyle and Turner[8] were employed. The index $R=[\Sigma(\Delta F)^2/\Sigma(F_o)^2]^{\frac{1}{2}}$ decreased to 0.088 and the weighted index $R_W=[\Sigma W(\Delta F)^2/\Sigma W(F_o)^2]^{\frac{1}{2}}$ to 0.066. A list of observed and calculated structure factors is available on request.

The final coordinates and their standard deviations as calculated by the least-squares program are listed in Table 4. The standard deviations must be regarded as lower estimates of the errors occurring in the structure, as practical experience, such as comparison of atomic coordinates determined twice from independently observed X-ray data, has shown[10] that the standard deviations obtained from the least-squares program are generally too small.

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