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STRUCTURE OF CYCLOPENTADIENYLCYCLOOCTATETRAENE-TITANIUM

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SUMMARY

An X-ray diffraction study has shown the cyclooctatetraene ligand in cyclopentadienylcyclooctatetraenetitanium to be π-bonded to the metal.

RESULTS AND DISCUSSION

In a recent paper Van Oven and De Liefde Meyer[1] have described the synthesis and some properties of cyclopentadienylcyclooctatetraenetitanium C_5H_5Ti-C_8H_8. By comparison of its IR spectrum with those of other compounds containing a π-bonded cyclopentadienyl group, it could be concluded that the five-membered ring is π-bonded to the metal. No conclusive evidence about the kind of bonding of the cyclooctatetraene ligand to the titanium atom could be obtained in this way, because of the diffculties encountered in interpreting the infrared spectra. The present authors were therefore asked to determine the structure of $C_5H_5TiC_8H_8$ by means of X-ray diffraction.

The structure of the molecule as found by the present X-ray study is shown in

TABLE 1

MOLECULAR GEOMETRY

Bond lengths (Å)[a]				Bond angles (°)[b]	
C(1')–C(1)	1.393(8)	Ti–C(1)	2.318(4)	C(1')–C(1)–C(2)	135.3
C(1)–C(2)	1.381(8)	Ti–C(2)	2.325(4)	C(1)–C(2)–C(3)	135.3
C(2)–C(3)	1.399(8)	Ti–C(3)	2.328(4)	C(2)–C(3)–C(4)	134.7
C(3)–C(4)	1.398(8)	Ti–C(4)	2.321(4)	C(3)–C(4)–C(4')	134.7
C(4)–C(4')	1.414(10)				
C(5)–C(6)	1.395(8)	Ti–C(5)	2.345(4)	C(6')–C(5)–C(6)	108.1
C(6)–C(7)	1.392(8)	Ti–C(6)	2.350(4)	C(5)–C(6)–C(7)	108.1
C(7)–C(7')	1.406(9)	Ti–C(7)	2.359(5)	C(6)–C(7)–C(7')	107.8

[a] The standard deviations (in parentheses) are in units of the last decimal place. For numbering of atoms see Fig. 1. [b] Standard deviations 0.2°.

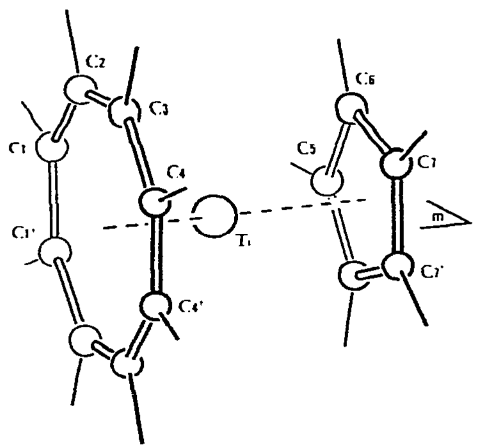

Fig. 1. The cyclopentadienylcyclooctatetraenetitanium molecule.

Fig. 1. The molecule has a crystallographic mirror plane which is indicated by m in the Figure. The bond lengths and angles are given in Table 1. The interaction between the molecules in the crystal is small, none of the intermolecular distances is shorter than the sum of the respective conventional Van der Waals radii.

Fig. 1 and Table 1 show that both the eight- and the five-membered ring are π-bonded to the metal. The Ti-atom is "sandwiched" between the cyclopentadiene and the cyclooctatetraene groups which are both planar within the experimental error. The rings are approximately parallel to each other, the angle between the planes is $1.9 \pm 0.2°$. No significant differences have been observed between the lengths of the C–C bonds (Table 1). The weighted average value is 1.395 Å for the eight-membered ring and 1.396 Å for the five-membered ring (values not corrected for libration). The distances between the Ti-atom and the C-atoms of the eight- and the five-membered rings average to 2.323 and 2.353 Å respectively.

The length of the C–C bond in the eight-membered ring of $C_5H_5TiC_8H_8$, 1.395 Å, shows good agreement with the C–C bond lengths observed in tris(cyclooctatetraene)dititanium[2], average value 1.399 ± 0.012 Å, (the standard deviation refers to the average value). The Ti–C distances in the latter compound, average value 2.350 ± 0.008 Å, are slightly larger than the Ti–C (8-ring) distances in $C_5H_5TiC_8H_8$, 2.323 Å. The values for the C–C bond lengths in cyclopentadienyl rings of several Ti-compounds range from 1.39 to 1.44 Å.

A rigid body analysis of the molecule according to Cruickshank[3], has shown that the thermal motion of the atoms can be described in good approximation in terms of rigid body translations and librations. The largest libration axis is approximately perpendicular to the planes of the rings. It should be noted, however, that the results of the X-ray study cannot distinguish between a rigid body libration and an intramolecular ring torsion about this axis. The libration corrections in the bond lengths are estimated at +0.01 Å for C–C and at +0.008 Å for Ti–C. In Table 1 the uncorrected values are given.

EXPERIMENTAL

The compound was prepared by H. O. van Oven in the Laboratory of Inorganic Chemistry of the Rijksuniversiteit in Groningen. Because of the sensitivity of the compound to oxygen the crystals had to be coated with a thin layer of plastic spray to prevent them from oxidation by the air during the measurements. For the determination of the unit cell dimensions crystals measuring 0.15 mm in each direction were used. The intensity measurements were done with a larger crystal of 0.65 × 0.35 × 0.35 mm. The crystallographic data are listed in Table 2. Corrections for absorption were calculated by a program based on procedures suggested by Busing and Levy[4].

TABLE 2

CRYSTALLOGRAPHIC DATA AND DETAILS OF EXPERIMENTAL METHODS

Data	Method
Space group *Pnma* $Z=4$	Weissenberg photographs of zero and higher layer lines
$a=11.178\pm0.003$ Å[a] $b=10.993\pm0.003$ Å[a] $c=\ 8.469\pm0.002$ Å[a]	Weissenberg photographs of zero layer lines $\lambda(\text{CuK}\alpha)=1.5418$, $\lambda(\text{CuK}\alpha_1)=1.54051$ and $\lambda(\text{CuK}\alpha_2)=1.54433$ Å. Calibration with NaCl reflection spots. Least squares adjustment of 45 $0kl$ and 30 $h0l$ reflections
2328 reliable intensities	Automatic Nonius diffractometer, Mo-radiation, Zr-filter, θ–2θ scan, $(\sin\theta)/\lambda < 0.847$ Å^{-1}
2328 reliable $F(hkl)$ values	Corrections for L.P. and absorption ($\mu=8.0$ cm^{-1})

[a] Estimated standard deviation.

The general position in space group *Pnma* is eightfold, so that the four molecules in the unit cell have to lie at special positions with multiplicity four. In view of the possible symmetry of the molecules they were assumed to lie on the mirror planes of the unit cell. This assumption, and thus the choice of the centrosymmetric space group *Pnma* rather than the non-centrosymmetric group $Pna2_1$, has been confirmed by the results of the refinement. The position of the one independent Ti-atom could be found from a three-dimensional Patterson synthesis. After refinement of this position with isotropic least-squares methods, a Fourier map was calculated with the reflections with reliable sign. This map clearly revealed the positions of the carbon atoms. The parameters of Ti and C were refined by anisotropic least squares methods on a TR4 computer. After this refinement a $[F_o\text{–}F_c(\text{Ti,C})]$ map including the low angle reflections only, was calculated, which clearly showed positive regions at the positions expected for the hydrogen atoms. In the final cycles of the least squares refinement the hydrogen atoms were taken into account with fixed parameters at 1.08 Å from their respective carbon atoms. The weighting scheme $W=[W_c^{-1}+0.0004\ F^2]^{-1}$ was applied, W_c being the weight based on counting statistics. For the H-atoms the *f*-curve calculated by Stewart[5] was used and for the remaining atoms the *f*-curve calculated by Doyle and Turner[6]. The index $R=[\Sigma(\Delta F)^2/\Sigma(F_o)^2]^{\frac{1}{2}}$ decreased to 0.076 and $R_W=[\Sigma(W\Delta F)^2)/\Sigma(F_o)^2]^{\frac{1}{2}}$ to 0.064. The final coordinates and standard deviations as calculated by the least squares program are given in Table 3. A list of observed and

TABLE 3

FINAL COORDINATES FOR THE INDEPENDENT PART OF ONE OF THE MOLECULES[a]

Atom	x/a	y/b	z/c
Ti	0.34622(4)	0.25000(0)	0.54152(5)
C(1)	0.1498(2)	0.1866(2)	0.5108(3)
C(2)	0.2083(3)	0.0974(2)	0.5957(3)
C(3)	0.2932(2)	0.0962(2)	0.7170(3)
C(4)	0.3540(2)	0.1857(2)	0.8023(3)
C(5)	0.4016(3)	0.2500(2)	0.2745(4)
C(6)	0.4531(2)	0.1473(2)	0.3433(3)
C(7)	0.5365(2)	0.1861(2)	0.4544(3)
H(1)	0.0886	0.1515	0.4239
H(2)	0.1831	0.0070	0.5604
H(3)	0.3174	0.0054	0.7517
H(4)	0.4151	0.1471	0.8876
H(5)	0.3354	0.2500	0.1834
H(6)	0.4323	0.0541	0.3167
H(7)	0.5914	0.1287	0.5272

[a] The standard deviations as calculated by the least squares program are given in parentheses, in units of the last decimal place. The numbers of the hydrogen atoms correspond with those of the carbon atoms to which they are linked. These atoms were given fixed positions during the last few cycles of the refinement.

calculated structure factors is available on request. The standard deviations given in the bond lengths in Table 1 are twice the values calculated from the standard deviations in Table 3, as experience has shown that in many cases the standard deviations obtained by the least squares program are lower estimates of the errors in the atomic parameters.

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