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George L. Hardgrove and David H. Templeton
July 1958
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# THE CRYSTAL STRUCTURE OF RUTHENOCENE 

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July 1958

## ABSTRACT

Dicyclopentadienylruthenium, or ruthenocene, crystallizes in the orthorhombic space group Pnma (No. 62) with $\underline{a}=7.13, \underline{b}=8.99, \underline{c}=12.81 \AA$. . There are four $\mathrm{Ru}\left(\mathrm{C}_{5} \mathrm{H}_{5}\right)_{2}$ molecules per unit cell. The ruthenium atoms form approximately a face-centered lattice, and the cyclopentadienyl rings lie in an eclipsed configuration with respect to each other about each ruthenium atom. The structure was refined by Fourier and least-squares methods with 791 independent reflections. The ruthenium-carbon distance is $2.21 \AA$ and the carbon-carbon bond distance in the rings averages $1.43 \AA$.

# THE CRYSTAL STRUCTURE OF RUTHENOCENE* 

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$\square$
INTRODUCTION
X-ray investigation by Fischer and his collaborators (Pfab and Fischer, 1953, Weiss and Fischer, 1955 indicated that the dicyclopentadienyl compounds of iron, cobalt, nickel, chrom ium, vanadium, and magnesium are isomorphous, crystallizing in space group $\mathrm{P} 2_{1} / \mathrm{c}$ 。 Dunitz, Orgel, and Rich (1956) have reported a three-dimensional analysis of the iron compound. The present paper reports a three-dimensional analysis of dicyclopentadienylruthenium, which unexpectedly was found to have a quite different orthorhombic structure.

## EXPERIMENTAL

Ruthenocene crystals were kindly provided by Dr. J. H. Richards. The compound was prepared by reaction of ruthenium trichloride with sodium cyclopentadienide in tetrahydrofuran, was purified by chromatography over alumina, and was recrystallized from benzene-1igrain $\left(60-90^{\circ} \mathrm{C}\right)$.

A nearly cylindrical needle of ruthenocene was aligned about the [010] axis, and multiple-film Weissenberg photographs through the fifth layer were taken with Cu Ka . X ways. Additional reflections were observed on photographs taken of a crystal aligned about the [011] direction. The intensities on the multiple films were estimated by visual comparison with a standard. There were 586 observed reflections and 205 reflections too weak to be observed in the portion of the reciprocal lattice photographed.

An absorption correction was applied to the hOl data according to the method of Bradley (Klug and Alexander, 1954) for cylindrical crystals with $\mu^{r}=0.8$. The same absorption factor table was used for the higher layers, but the errors introduced by this method axe not expected to exceed $6 \%$ of the

[^0]$I_{o}$ values on the highest layers. Lorentz and polarization corrections were made in the usual manner.

## Unit cell and space group

The dimensions of the orthorhombic : unit cell were determined from measurements made on quartz calibrated zero layer films as suming $a=4.913 \AA$ for quartz. The standard quartz crystal was also checked with a precision of about one part in 3000 against a powder pattern of sodium chloride. For ruthenocene:

$$
\underline{a}=7.13, \underline{b}=8.99, \underline{c}=12.81 \AA, \text { each } \pm 0.02 \AA .
$$

The X-ray density is $1.876 \mathrm{~g} \mathrm{~cm}^{-3}$, assuming four molecules per unit cell.
The systematic absences suggested either Pnma (No. 62) or Pn2 ${ }_{1}{ }^{a}$ (No. 33) as possible space groups. The structure analysis proceeded on the assumption of the higher symmetry, and the final agreement justified this assumption.

## Determination of refinement of the structure

The strong reflections with $h, k$, and $\ell$ all even or all odd suggested that the ruthenium atoms lie in a face-centered lattice. In Pnma this is possible only with atoms on mirror planes in special positions 4(c):

$$
\mathrm{x}, 1 / 4, \mathrm{z} ; \overline{\mathrm{x}}, 3 / 4, \overline{\mathrm{z}} ; 1 / 2-\mathrm{x}, 3 / 4,1 / 2+\mathrm{z} ; 1 / 2+\mathrm{x}, 1 / 4,1 / 2-\mathrm{z},
$$

with special values of $x$ and $z$; for example at $1 / 4,1 / 4,1 / 2$ and its equivalent positions. An electron density projection using as coefficients the strong $\mathrm{h}=2 \mathrm{n}$ and $\mathrm{k}=2 \mathrm{n}$ reflections in the $\mathrm{h} O \ell$ layer have contours which suggested that the cyclopentadienyl rings are perpendicular to the mirror plane.

With this ruthenium structure and the rings perpendicular to the mirror plane, either a staggered carbon structure with a non-crystallographic center of symmetry at the ruthenium atom or an eclipsed structure with a non-crystallographic mirror plane between the rings is possible. In either case, the carbon atoms are distributed in two sets $4(\mathrm{c}$ ) (listed above) and four general sets $8(\mathrm{~d})$ :

$$
\pm\left(x, y, z ; x, 1 / 2-y, z ; 1 \_2+x, y, 1 / 2-z ; 1 / 2+x, 1 / 2-y, 1 / 2-z\right) .
$$

Sections of the three-dimensional electron density function were calculated

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using signs of the structure factors based on ruthenium alone. These sections showed maxima of electron density at positions consistent with an eclipsed structure and the absence of such maxima at positions corresponding to a staggered structure. These and subsequent Fourier calculations were made with the IBM 701 computer and the program completed by Dodge (1958).

Three-dimensional least-squares refinements were then carried out on the IBM 650 computer with the program known as LS-II (Senko, 1957). Structure factors were based, in the final set of calculations, on all atoms including hydrogen. Hydrogen was assumed to be $1.08 \AA$ from carbon in the plane of the ring. The carbon and ruthenium atomic parameters and individual isotropic temperature factors, and an over-all scale factor were refined. A weighting scheme similar to that of Hughes (1941) was used. The weight w was taken as $\left(16 \mathrm{~F}_{0}^{2}\right)^{-1}$ or as a constant $\left(16 \mathrm{~F}_{\mathrm{min}}^{2}\right)^{-1}$ if the uncorrected intensity was greater or less than 16 times the minimum observed value. For reflections too weak to be observed, the quantity $F_{o}-F_{C}$ was set equal to zero in the sums if $F_{c}<F_{\text {min }}$ or equal to $-F_{c}$ if $F_{c}>F_{\text {min }}$.

After the third cycle the calculated shifts were less than the standard deviations, and the refinement was concluded there. The coordinates, their standard deviations, and the temperature factors are listed in Table l(a). The "unreliability factors" at this point were:

$$
\begin{aligned}
& R_{1}=\Sigma| | F_{o}\left|-\left|F_{c}\right|\right| \div \Sigma\left|F_{o}\right|=0.098 \\
& R_{2}=\left(\Sigma\left(\left|F_{o}\right|-\left|F_{c}\right|\right)^{2} \div \Sigma F_{o}^{2}\right)^{1 / 2}=0.127 \\
& R_{3}=\left(\Sigma w\left(\left|F_{o}\right|-\left|F_{c}\right|\right)^{2} \div \Sigma w F_{o}^{2}\right)^{1 / 2}=0.162
\end{aligned}
$$

The atomic positions of carbon were also determined from a threedimensional difference Fourier series with coefficients $F_{o}-F_{R u}$ based on the best ruthenium position as determined from the least.-squares refinements. The signs of these coefficients were calculated from the best carbon and hydrogen structure. For the atoms in general positions, sections were calculated perpendicular to the [100] and [001] directions at the levels of the centers of the atoms. The two atoms in special positions were located from a section at $y=1 / 4$. Each maximum was located by a least-squares fit of a paraboloid to the logarithm of the electron density at the nine grid points nearest the peak. The values were corrected for series termination error by comparison with a similar Fourier calculation using the calculated structures for the carbon and
hydrogen positions as coefficients. The corrected coordinates are listed in Table $l(b)$. The simple average of the atomic parameters from the leastsquares and Fourier methods is given in Table $1(c)$. In twelve of the sixteen casës the two methods differ from the average by less than the standard deviation.

Projections of the electron density and of the difference function with ruthenium removed are shown in Fig. 1.

## Discussion of the structure

The carbon rings are the bases of a pentagonal prism with ruthenium at its center. The two rings are crystallographically independent, and each contains three independent carbon-carbon bonds. These bonds (Table 2 ) are within a standard deviation of the average bond distance in all cases except the bonds at $\mathrm{C}_{6}$. However, if $\mathrm{C}_{6}$ be moved one standard deviation in the appropriate direction, then the carbon-carbon bonds are all equal within the standard deviations. The deviations from five equal bonds in each ring are slightly less than those reported for ferrocene (Dunitz, Orgel, and Rich, 1956) and somewhat greater than those reported for bis-[ cyclopentadienyl molybdenum tricarbonyl] (Wilson and Shoemaker, 1957). To our accuracy the bond angles are consistent with the expected five-fold symmetry of the molecule.

The carbon-metal distance of 2.21 A in ruthenocene as determined by this research is larger than the $2.05 \AA$ reported for ferrocene, as is to be expected. The carbon-carbon distance of $1.43 \AA$ reported here is in agreement with the $1.42 \AA$ found in bis $-($ cyclopentadienyl molybdenum tricarbonyl) and the $1.41 \AA$ found in ferrocene. The average inter-ring distance in ruthenocene is 3.68 A compared to $3.32 \AA$ in ferrocene.

The packing of the molecules in layers perpendicular to the $\underline{b}$ axis is similar for ruthenocene and ferrocene. However, the stacking of the layers differs in the two compounds. In ruthenocene, Fig. 2, a hydrogen atom from one molecule appears surrounded by a cage of four hydrogens from a neighboring molecule as if the molecules were interlocking gears. The reason for the difference in arrangements may be that the smaller inter-ring distance in ferrocene with stronger carbon-carbon repulsions prevents the molecules from taking the eclipsed configuration required for this interlocking gear arrangement, which
presumably is a more favorable packing of the molecules.
We thank Dr. Richards for providing the crystals, Mrs. Helena W. Ruben for assistance in the laboratory, and Dr. Richard P. Dodge, Dr. Robert E. Jones, Dr. Michael E. Senko, and Dr. Allañ Zalkin for the use of their computer codes.

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Table 1. Atomic coordinates, standard deviations and temperature factors.

|  |  | (a) Re | of le | quare | fin |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | x | y | $z$ | ${ }^{\circ} \mathrm{x}$ | $\sigma_{\mathrm{y}}$ | $\sigma_{z}$ | B (A) |
| Ru | 0.23705 | 1/4 | 0.50419 | 0.00026 | J | 0.00010 | 1.36 |
| $\mathrm{C}_{1}$ | 0.5135 | 1/4 | 0.5779 | 0.0029 | -- | 0.0017 | 2.89 |
| $\mathrm{C}_{2}$ | 0.2529 | 0.3290 | 0.6711 | 0.0020 | 0.0024 | 0.0014 | 3.00 |
| $\mathrm{C}_{3}$ | 0.4125 | 0.3768 | 0.6147 | 0.0027 | 0.0012 | 0.0021 | 2.85 |
| $\mathrm{C}_{4}$ | 0.2485 | 1/4 | 0.3304 | 0.0027 | -- | 0.0019 | 2.63 |
| $\mathrm{C}_{5}$ | 0.9896 | 0.3315 | 0.4180 | 0.0017 | 0.0080 | 0.0010 | 2.28 |
| $\mathrm{C}_{6}$ | 0.1453 | 0.3806 | 0.3681 | 0.0019 | 0.0021 | 0.0011 | 2.70 |

(b) Results of Fourier difference sections.

|  | x | y | z |
| :---: | :---: | :---: | :---: |
| $\mathrm{C}_{1}$ | 0.5177 | $1 / 4$ | 0.5797 |
| $\mathrm{C}_{2}$ | 0.2455 | 0.3309 | 0.6655 |
| $\mathrm{C}_{3}$ | 0.4102 | 0.3797 | 0.6124 |
| $\mathrm{C}_{4}$ | 0.2553 | $1 / 4$ | 0.3316 |
| $\mathrm{C}_{5}$ | 0.9889 | 0.3298 | 0.4189 |
| $\mathrm{C}_{6}$ | 0.1510 | 0.3809 | 0.3688 |

(c) Final coordinates

|  | x | y | z |
| :--- | :--- | :--- | :--- |
| $\mathrm{Ru}^{*}$ | 0.2370 | $1 / 4$ | 0.5042 |
| $\mathrm{C}_{1}$ | 0.516 | $1 / 4$ | 0.579 |
| $\mathrm{C}_{2}$ | 0.249 | 0.330 | 0.668 |
| $\mathrm{C}_{3}$ | 0.411 | 0.378 | 0.614 |
| $\mathrm{C}_{4}$ | 0.252 | $1 / 4$ | 0.331. |
| $\mathrm{C}_{5}$ | 0.989 | 0.331 | 0.418 |
| $\mathrm{C}_{6}$ | 0.148 | 0.381 | 0.368 |

*Least squares only.

Table 2. Interatomic distances, standard deviations and bond angles.

(Table 2, continued)
(d) Carbon bond angles in the rings.
$\mathrm{C}_{3}-\mathrm{C}_{1}-\mathrm{C}_{3} \mathrm{l} \quad 106^{\circ} 9^{\prime}$
$\mathrm{C}_{1}-\mathrm{C}_{3}-\mathrm{C}_{2} \quad 109^{\circ} 5^{\prime}$
$\mathrm{C}_{3}-\mathrm{C}_{2} \mathrm{C}^{-\mathrm{C}_{2}} \quad 107^{\circ} 50^{\prime}$
$\mathrm{C}_{6}{ }^{-\mathrm{C}_{4}}{ }^{-\mathrm{C}_{6}} 6^{\prime} \quad 106^{\circ} 15^{\prime}$
$\mathrm{C}_{4}-\mathrm{C}_{6}-\mathrm{C}_{5} \quad 107^{\mathrm{O}} 45^{\prime}$
$\mathrm{C}_{6}-\mathrm{C}_{5}-\mathrm{C}_{5}, \quad 108^{\circ} 57^{\prime}$
Value for five-fold
symmetry: $108^{\circ} 0^{\prime}$
(e) Carbon-ruthenium-carbon angles.
$\mathrm{C}_{2}-\mathrm{Ru}-\mathrm{C}_{2} \quad 37^{\circ} 43^{\prime}$
$\mathrm{C}_{2}-\mathrm{Ru}-\mathrm{C}_{3} \quad 37^{\circ} 27^{\prime}$
$\mathrm{C}_{1}-\mathrm{Ru}-\mathrm{C}_{3} \quad 38^{\circ}$ 15 ${ }^{\mathrm{\prime}}$
$\mathrm{C}_{5}-\mathrm{Ru}-\mathrm{C}_{5}, \quad 38^{\circ} \quad 33^{\prime}$
$\mathrm{C}_{5}-\mathrm{Ru}-\mathrm{C}_{6} \quad 36^{\mathrm{O}} 32^{\prime}$
$\mathrm{C}_{4}-\mathrm{Ru}-\mathrm{C}_{6} \quad 38^{\circ} 54^{\prime}$
Value for five-fold symmetry
with the average distances:

$$
37^{\circ} \quad 54^{\prime}
$$


. mu-15,235

Fig. la. Projection in [010] direction of electron density. Contours are at intervals of 1 electron per $A^{2}$ except at the ruthenium atom, where the interval changes to 5 electrons per $A^{2}$. The zero contour is emitted and negative contours are broken. The carbon atoms in general positions are doubled in this projection by the mirror plane and are the only ones that are clearly shown.


Fig. lb. Projection in [010] direction of electron density with ruthenium effect subtracted from coefficients. Contours are at intervals of 1 electron per $A^{2}$. The zero contour is emitted and negative contours are broken. The carbon atoms in general positions are doubled in this projection by the mirror plane and are the only ones that are clearly shown.


Mu-15,234

Fig. 2. Crystal structure of ruthenocene.


MU- 15505

Fig. 3a. Distances in A, and angles, between carbon atoms.

(b)

MU-15506

Fig. 3b. Distances in $A$, and angles, between ruthenium and carbon in the ruthenocene molecule.

























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