Table 4. *Calculation of some structure factors in four hypotheses*

Hypothesis	Method of calculation of F	Result
(1) Tetragonal	$\frac{1}{2}$ C_5 placed in general position in $I4_1/amd$	$R = 0{\cdot}20$
(2) Orthorhombic pseudo-tetragonal	C_5 placed in general position in *Fddd* using coordinations corresponding to those in (1)	Calculated F's do not comply with observed Laue symmetry
(3) Orthorhombic twin	$\lvert F_c\rvert = (F_1^2+F_2^2)^{\frac{1}{2}}/\sqrt{2}$, where F_1 is calculated as in (2) and F_2 is calculated from the same structure reflected in (110)	$R = 0{\cdot}20$
(4) Combination (1) and (3)	F taken as average of that calculated from (1) and (3)	$R = 0{\cdot}17$

even when considerably reduced in magnitude by applying the abnormally large 'temperature corrections'. No coordinates for C_5 could be found which would remove the discrepancies between F_{H00} and F_{0H0}.

The above considerations suggest that twinning of the orthorhombic (pseudo-tetragonal) crystal, say by reflection in (110), might bring about the required tetragonal symmetry of the reflections. The orthorhombic-twin hypothesis implies perfectly ordered domains of at least a few hundred cells, in which the space group *Fddd* applies.

The tetragonal-crystal hypothesis implies random distribution of right-handed and left-handed molecules even within a single cell.

The structure factors obtained by averaging those from the two hypotheses correspond to a third possibility: a combination of the two, i.e. domains of orthorhombic individual 1 and of orthorhombic individual 2 with interspersed cells having the random disposition of C_5. Structure factors calculated for the various possibilities were compared for twenty reflections (Table 4).

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Reference

Dauben, C. H. & Templeton, D. H. (1955). *Acta Cryst.* 8, 841.

Acta Cryst. (1959). **12**, 28

The Crystal Structure of Ruthenocene*

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Dicyclopentadienylruthenium, or ruthenocene, crystallizes in the orthorhombic space group *Pnma* with $a = 7{\cdot}13$, $b = 8{\cdot}99$, $c = 12{\cdot}81$ Å. There are four $Ru(C_5H_5)_2$ 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 Å and the carbon–carbon bond distance in the rings averages 1·43 Å.

Introduction

X-ray investigation by Fischer and his collaborators (Pfab & Fischer, 1953, Weiss & Fischer, 1955) indicated that the dicyclopentadienyl compounds of iron, cobalt, nickel, chromium, vanadium and magnesium are isomorphous, crystallizing in space group $P2_1/c$. Dunitz, Orgel & 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.

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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–ligroin (60–90 °C.).

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 $K\alpha$ X-rays. 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 $h0l$ data according to the method of Bradley (Klug & Alexander, 1954) for cylindrical crystals with $\mu r = 0{\cdot}8$. The same absorption factor table was used for the higher layers, but the errors introduced by this method are not expected to exceed 6% of the I_0 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 assuming $a = 4{\cdot}913$ Å 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:

$$a = 7{\cdot}13, \quad b = 8{\cdot}99, \quad c = 12{\cdot}81 \text{ Å}, \quad \text{each} \quad \pm 0{\cdot}02 \text{ Å} .$$

The X-ray density is 1·876 g.cm.$^{-3}$, assuming four molecules per unit cell. The systematic absences suggested either $Pnma$ or $Pn2_1a$ as possible space groups. The structure analysis proceeded on the assumption of the higher symmetry, and the final agreement justified this assumption.

Determination and refinement of the structure

The strong reflections with h, k and l 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 $4(c)$:

$$x, \tfrac{1}{4}, z; \quad \bar{x}, \tfrac{3}{4}, \bar{z}; \quad \tfrac{1}{2}-x, \tfrac{3}{4}, \tfrac{1}{2}+z; \quad \tfrac{1}{2}+x, \tfrac{1}{4}, \tfrac{1}{2}-z ,$$

with special values of x and z; for example at $\frac{1}{4}, \frac{1}{4}, \frac{1}{2}$ and its equivalent positions. An electron-density projection using as coefficients the strong $h = 2n$ and $k = 2n$ reflections in the $h0l$ zone 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 $4(c)$ (listed above) and four general sets $8(d)$:

$$\pm(x, y, z; \quad x, \tfrac{1}{2}-y, z; \quad \tfrac{1}{2}+x, y, \tfrac{1}{2}-z; \quad \tfrac{1}{2}+x, \tfrac{1}{2}-y, \tfrac{1}{2}-z) .$$

Sections of the three-dimensional electron-density function were calculated 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).

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

(*a*) Results of least-squares refinement

	x	y	z	σ_x	σ_y	σ_z	B (Å^2)
Ru	0·23705	$\frac{1}{4}$	0·50419	0·00026	—	0·00010	1·36
C_1	0·5135	$\frac{1}{4}$	0·5779	0·0029	—	0·0017	2·89
C_2	0·2529	0·3290	0·6711	0·0020	0·0024	0·0014	3·00
C_3	0·4125	0·3768	0·6147	0·0021	0·0021	0·0012	2·85
C_4	0·2485	$\frac{1}{4}$	0·3304	0·0027	—	0·0019	2·63
C_5	0·9896	0·3315	0·4180	0·0017	0·0020	0·0010	2·28
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
C_1	0·5177	$\frac{1}{4}$	0·5797
C_2	0·2455	0·3309	0·6655
C_3	0·4102	0·3797	0·6124
C_4	0·2553	$\frac{1}{4}$	0·3316
C_5	0·9889	0·3298	0·4189
C_6	0·1510	0·3809	0·3688

(*c*) Final coordinates

	x	y	z
Ru*	0·2370	$\frac{1}{4}$	0·5042
C_1	0·516	$\frac{1}{4}$	0·579
C_2	0·249	0·330	0·668
C_3	0·411	0·378	0·614
C_4	0·252	$\frac{1}{4}$	0·331
C_5	0·989	0·331	0·418
C_6	0·148	0·381	0·368

* Least-squares only.

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 atoms were assumed to be 1·08 Å from carbon atoms 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 $(F_o^2)^{-1}$ or as a constant $(16\,F^2_{\text{min.}})^{-1}$ if the uncorrecte dintensity 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 1(a). The 'unreliability factors' at this point were:

$$R_1 = \Sigma||F_o| - |F_c|| \div \Sigma|F_o| = 0{\cdot}098\,.$$
$$R_2 = (\Sigma(|F_o| - |F_c|)^2 \div \Sigma F_o^2)^{\frac{1}{2}} = 0{\cdot}127\,.$$
$$R_3 = (\Sigma w(|F_o| - |F_c|)^2 \div \Sigma w F_o^2)^{\frac{1}{2}} = 0{\cdot}162\,.$$

The atomic positions of carbon were also determined from a three-dimensional difference Fourier series with coefficients $F_o - F_{\text{Ru}}$ 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 $y = \frac{1}{4}$. 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

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

(a) Ruthenium–carbon distances

Ru–C_1	2·205±0·021 Å	Ru–C_5	2·204–0·015
Ru–C_2	2·223±0·019	Ru–C_6	2·193±0·016
Ru–C_3	2·200±0·016	Average	2·21 ±0·01
Ru–C_4	2·220±0·024		

(b) Carbon–carbon distances in the rings

C_1–C_3	1·443±0·021 Å	C_5–C_6	1·378±0·018
C_2–C_3	1·420±0·021	C_5–$C_{5'}$	1·455±0·036
C_2–$C_{2'}$	1·437±0·044	Average	1·43 ±0·01
C_4–C_6	1·470±0·021		

(c) Carbon–carbon distances between the rings

C_1–C_4	3·689±0·031 Å	C_3–C_6	3·659±0·021
C_2–C_5	3·698±0·022	Average	3·68 ±0·01

(d) Carbon bond angles in the rings

C_3–C_1–$C_{3'}$	106° 9′	C_4–C_6–C_5	107° 45′
C_1–C_3–C_2	109 5	C_6–C_5–$C_{5'}$	108 57
C_3–C_2–$C_{2'}$	107 50	Value for five-fold symmetry:	108° 0′
C_6–C_4–$C_{6'}$	106 15		

(e) Carbon–ruthenium–carbon angles

C_2–Ru–$C_{2'}$	37° 43′	C_5–Ru–$C_{5'}$	38° 33′
C_2–Ru–C_3	37 27	C_5–Ru–C_6	36 32
C_1–Ru–C_3	38 15	C_4–Ru–C_6	38 54

Value for five-fold symmetry with the average distances: 37° 54′

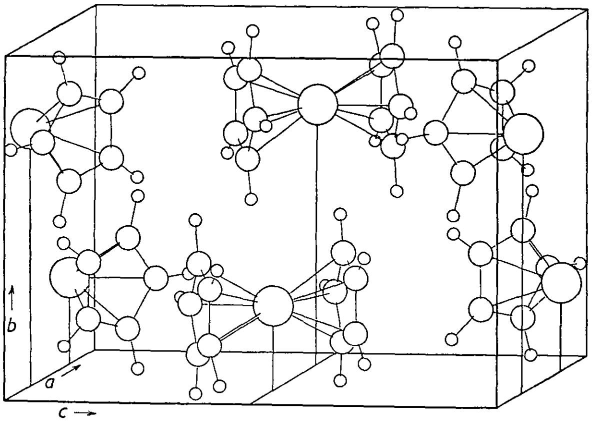

Fig. 1. Crystal structure of ruthenocene.

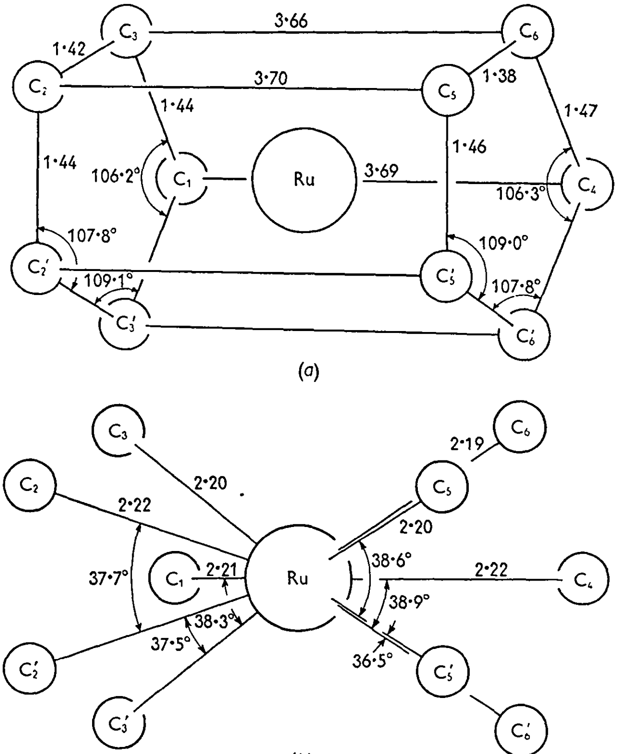

Fig. 2. Distances in Å and angles (a) between carbon atoms and (b) between ruthenium and carbon in the ruthenocene molecule.

Table 3. *Observed and calculated structure factors*

The unobserved reflections appear in the table with $F_o = 0$.

h	k	ℓ	F_o	F_c
0	0	2	119	164
0	0	4	39	36
0	0	6	116	114
0	0	8	105	93
0	0	10	82	80
0	0	12	82	73
0	0	14	52	49
0	0	16	36	42
1	0	1	22	21-
1	0	2	18	14-
1	0	3	15	10-
1	0	4	17	11-
1	0	5	18	12-
1	0	6	29	29-
1	0	7	0	5-
1	0	8	19	15-
1	0	9	0	1
1	0	10	13	12-
1	0	11	0	5-
1	0	12	27	28-
1	0	13	10	12-
1	0	14	23	22-
1	0	15	7	7-
1	0	16	11	12-
2	0	0	115	137-
2	0	1	35	35-
2	0	2	84	81-
2	0	3	36	31-
2	0	4	116	129-
2	0	5	41	36
2	0	6	155	165-
2	0	7	33	23
2	0	8	94	85-
2	0	9	15	11-
2	0	10	60	58-
2	0	11	10	7-
2	0	12	63	58-
2	0	13	0	9
2	0	14	42	39-
2	0	15	6	8
2	0	16	28	38-
3	0	1	38	36
3	0	2	7	3-
3	0	5	28	25
3	0	6	23	25
3	0	7	38	37
3	0	8	29	28
3	0	9	20	20
3	0	10	11	11
3	0	11	0	4
3	0	12	13	13
3	0	13	0	8
3	0	14	19	19
3	0	15	11	14
4	0	0	111	123
4	0	1	0	1
4	0	2	98	98
4	0	3	0	2-
4	0	4	89	91
4	0	5	0	3-
4	0	6	83	79
4	0	7	0	0
4	0	8	46	39
4	0	9	0	6-
4	0	10	57	60
4	0	11	11	12-
4	0	12	72	72
4	0	13	14	7-
4	0	14	39	39
5	0	1	50	47-
5	0	2	27	27-
5	0	3	25	28-
5	0	4	10	4-
5	0	5	21	18-
5	0	6	10	1
5	0	7	27	24-
5	0	8	15	15-
5	0	9	27	30-
5	0	10	14	18-
5	0	11	20	24-
5	0	12	13	14-
5	0	13	15	15-
6	0	0	62	68-
6	0	1	0	8
6	0	2	56	52-
6	0	3	10	13
6	0	4	62	59-
6	0	5	0	2
6	0	6	70	73-
6	0	7	0	1-
6	0	8	48	50-
6	0	9	0	6
6	0	10	38	43-
6	0	11	0	6
6	0	12	34	35-
7	0	1	21	21
7	0	2	10	9
7	0	3	34	41
7	0	4	0	2
7	0	5	35	41
7	0	6	0	4
7	0	7	24	24
7	0	8	10	10
7	0	9	16	19
7	0	10	11	11
8	0	0	46	58
8	0	1	0	2
8	0	2	36	40
8	0	3	0	3
8	0	4	28	32
8	0	5	0	0-
8	0	6	28	37
8	0	7	0	7-
8	0	8	22	26
9	0	1	22	29-
9	0	2	0	3
9	0	3	21	30-
0	1	3	7	2
0	1	5	12	11
0	1	7	26	25
0	1	9	22	18
0	1	11	29	25
0	1	13	28	25
0	1	15	17	12
1	1	1	151	202
1	1	2	85	81
1	1	3	80	70
1	1	4	51	40
1	1	5	135	131
1	1	6	21	17-
1	1	7	131	121
1	1	8	22	18-
1	1	9	80	75
1	1	10	0	7-
1	1	11	76	71
1	1	12	0	2-
1	1	13	61	53
1	1	14	0	1
1	1	15	38	40
2	1	0	27	22-
2	1	1	11	11-
2	1	2	19	17-
2	1	3	13	9-
2	1	4	23	19-
2	1	5	23	19-
2	1	6	31	25-
2	1	7	30	25-
2	1	8	18	15-
2	1	9	16	10-
2	1	10	0	5-
2	1	11	16	14-
2	1	12	11	8-
2	1	13	22	24-
2	1	14	11	12-
2	1	15	21	21-
3	1	1	120	125-
3	1	2	18	11
3	1	3	101	98-
3	1	4	29	25
3	1	5	123	121-
3	1	6	20	15
3	1	7	92	82-
3	1	8	14	11-
3	1	9	53	50-
3	1	10	16	12-
3	1	11	65	70-
3	1	12	10	4
3	1	13	59	56-
3	1	14	14	12
3	1	15	37	34-
4	1	0	53	50
4	1	1	0	8
4	1	2	35	34
4	1	3	0	1
4	1	4	20	18
4	1	5	0	2
4	1	6	29	24
4	1	7	20	21
4	1	8	28	30
4	1	9	22	22
4	1	10	21	22
4	1	13	15	12
4	1	14	13	12
5	1	1	81	80
5	1	2	0	4
5	1	3	68	66
5	1	4	0	7
5	1	5	77	83
5	1	6	0	3
5	1	7	66	66
5	1	8	13	11-
5	1	9	47	46
5	1	10	15	18-
5	1	11	52	53
5	1	12	12	9-
5	1	13	38	37
6	1	0	33	29-
6	1	1	13	14-
6	1	2	31	34-
6	1	3	16	16-
6	1	4	33	36-
6	1	5	0	2-
6	1	6	29	28-
6	1	7	0	4-
6	1	8	24	24-
6	1	9	12	11-
6	1	10	21	23-
6	1	11	11	14-
6	1	12	18	20-
7	1	1	56	63-
7	1	2	13	10
7	1	3	41	40-
7	1	4	0	10
7	1	5	44	46-
7	1	6	0	4
7	1	7	40	42-
7	1	8	0	2
7	1	9	29	33-
8	1	0	24	25
8	1	1	0	1-
8	1	2	28	31
8	1	3	0	2-
8	1	4	31	35
8	1	5	0	5
8	1	6	24	26
8	1	7	10	10
9	1	1	24	31
0	2	2	149	144-
0	2	4	127	115-
0	2	6	124	110-
0	2	8	86	72-
0	2	10	79	74-
0	2	12	81	76-
0	2	14	55	49-
0	2	16	32	37-
1	2	1	18	11
1	2	2	13	10
1	2	3	15	10
1	2	4	14	9
1	2	5	8	4
1	2	6	17	14
1	2	7	11	7
1	2	8	25	20
1	2	9	11	8
1	2	10	24	19
1	2	11	0	7
1	2	12	20	20
1	2	13	0	5
1	2	14	19	18
1	2	15	0	2
1	2	16	17	17
2	2	0	134	133
2	2	1	15	7-
2	2	2	112	101
2	2	3	14	8-
2	2	4	121	115
2	2	5	0	2-
2	2	6	135	131
2	2	7	0	1-
2	2	8	94	83
2	2	9	0	2-
2	2	10	72	64
2	2	11	0	3-
2	2	12	64	57
2	2	13	0	3-
2	2	14	41	38
2	2	15	0	3-
3	2	1	29	22-
3	2	2	13	10-
3	2	3	33	30-
3	2	4	13	11-
3	2	5	30	25-
3	2	6	17	15-
3	2	7	25	20-
3	2	8	19	16-
3	2	9	19	16-
3	2	10	18	17-
3	2	11	16	14-
3	2	12	18	18-
3	2	13	13	11-
3	2	14	19	16-
3	2	15	10	10-
4	2	0	129	127-
4	2	1	0	2-
4	2	2	101	93-
4	2	3	0	2-
4	2	4	77	74-
4	2	5	0	1
4	2	6	79	77-
4	2	7	0	6
4	2	8	64	55-
4	2	9	0	8
4	2	10	57	57-
4	2	11	0	7
4	2	12	57	58-
4	2	13	0	4
4	2	14	36	38-
5	2	1	37	34
5	2	2	0	3
5	2	3	36	32
5	2	4	0	7
5	2	5	33	28
5	2	6	13	12
5	2	7	26	25
5	2	8	11	12
5	2	9	22	24
5	2	10	14	13
5	2	11	20	20
5	2	12	15	14
5	2	13	15	17
6	2	0	64	64
6	2	1	0	2-
6	2	2	55	52
6	2	3	0	6-
6	2	4	58	58
6	2	5	0	7-
6	2	6	64	68
6	2	7	0	4-
6	2	8	47	48
6	2	9	0	3-
6	2	10	36	39
6	2	11	0	5-
6	2	12	30	35
7	2	1	27	32-
7	2	2	0	2-
7	2	3	27	31-
7	2	4	0	5-
7	2	5	25	30-
7	2	6	0	8-
7	2	7	24	27-
7	2	8	0	8-
7	2	9	21	23-
7	2	10	8	9-
8	2	0	39	50-
8	2	1	0	1-
8	2	2	33	39-
8	2	3	0	1-
8	2	4	29	34-
8	2	5	0	3
8	2	6	28	35-
0	3	1	0	2
0	3	3	27	24-
0	3	5	28	22-
0	3	7	21	16-
0	3	9	28	22-
0	3	11	19	15-
0	3	13	13	11-
0	3	15	21	22-
1	3	1	121	118-
1	3	2	25	18
1	3	3	125	127-
1	3	4	6	6-
1	3	5	137	127-
1	3	6	20	17-
1	3	7	95	87-
1	3	8	0	4
1	3	9	71	64-
1	3	10	16	14
1	3	11	74	71-
1	3	12	0	4
1	3	13	59	55-
1	3	14	0	4-
1	3	15	38	36-
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4	6	12	31	34-
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5	6	2	0	8-
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5	6	7	24	28
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6	7	2	20	25
6	7	3	17	2
6	7	4	21	23
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0	8	8	61	64
0	8	10	47	46
1	8	8	0	4-
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3	8	10	12	13
4	8	0	32	43
4	8	3	0	4-
4	8	4	62	59
4	8	8	41	37
5	8	3	14	17-
0	9	9	0	7
1	9	9	39	44

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 1(*b*). The simple average of the atomic parameters from the least-squares and Fourier methods is given in Table 1(*c*). In twelve of the sixteen cases the two methods differ from the average by less than the standard deviation.

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 C_6. However, if 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 & Rich, 1956) and somewhat greater than those reported for *bis*-[cyclopentadienyl molybdenum tricarbonyl] (Wilson & 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 Å in ruthenocene as determined by this research is larger than the 2·05 Å reported for ferrocene, as is to be expected. The carbon–carbon distance of 1·43 Å reported here is in agreement with the 1·42 Å found in *bis*-[cyclopentadienyl molybdenum tricarbonyl] and the 1·41 Å found in ferrocene. The average inter-ring distance in ruthenocene is 3·68 Å compared to 3·32 Å in ferrocene.

The packing of the molecules in layers perpendicular to the *b* axis is similar for ruthenocene and ferrocene. However, the stacking of the layers differs in the two compounds. In ruthenocene, Fig. 1, 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.

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References

DODGE, R. P. (1958). Ph.D. Dissertation, University of California, Berkeley.

DUNITZ, J. D., ORGEL, L. E. & RICH, A. (1956). *Acta Cryst.* **9**, 373.

HUGHES, E. (1941). *J. Amer. Chem. Soc.* **63**, 1737.

KLUG, H. P. & ALEXANDER, L. E. (1954). *X-Ray Diffraction Procedures*, p. 155. New York: Wiley.

PFAB, W. P. & FISCHER, E. O. (1953). *Z. anorg. Chem.* **274**, 317.

SENKO, M. E. (1957). Ph.D. Dissertation, University of California, Berkeley.

WEISS, E. & FISCHER, E. O. (1955). *Z. anorg. Chem.* **278**, 219.

WILSON, F. C. & SHOEMAKER, D. P. (1957). *J. Chem. Phys.* **27**, 809.

Acta Cryst. (1959). **12**, 32

Zur Polymorphie von Cäsiumchlorid in Aufdampfschichten

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Thin sheets of CsCl evaporated on an *amorphous* carrier film were shown by electron diffraction to have the NaCl-type structure. As in the deposition of CsCl on a single crystal carrier the NaCl-type structure was obtained only by slow evaporation at room temperature; it transforms by heating to the CsCl-type structure. The lattice constant of the NaCl-type was found to be 6·948 Å, that of the CsCl-type 4·120 Å. (*Note added in proof.*—Die NaCl-Modifikation ist also eine instabile Form, die entsteht, sobald geringere Energiemengen zur Verfügung stehen. Eine Unterlage vom NaCl-Gittertyp ist hingegen nicht Voraussetzung für die Entstehung der instabilen NaCl-Modifikation).

1. Problemstellung

Die Cäsium- und Thalliumhalogenide (CsCl, CsBr, CsJ, TlCl, TlBr und TlJ), die normalerweise im CsCl-Gittertyp auftreten, kristallisieren nach Elektroneninterferenz-Untersuchungen von Schulz (1951) beim Aufdampfen auf Einkristall-Spaltflächen vom NaCl-Typ (LiF, NaCl, KBr) im Gittertyp der Unterlage, sind also polymorph. Lüdemann (1957) hat die Bedingungen für das Auftreten des NaCl-Typs auf solchen Unterlagen genauer untersucht und folgendes