

Redetermination of the Ruthenocene Structure at Room Temperature and at 101 K: Molecular Internal Motion

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Abstract

$\text{Ru}(\text{C}_5\text{H}_5)_2$ is orthorhombic at room temperature [$a = 7.119$ (3), $b = 8.985$ (4), $c = 12.794$ (5) Å] and at 101 K [$a = 7.009$ (3), $b = 8.819$ (4), $c = 12.756$ (5) Å], space group $Pnma$, $Z = 4$. The refinement converged at $R = 0.034$ and 0.020 for the room temperature and 101 K data respectively. The structure found by Hardgrove & Templeton [*Acta Cryst.* (1959), **12**, 28–32] is confirmed. At 101 K the mirror-symmetric molecules have almost regular pentagonal cyclopentadienyl rings (C–C, 1.430 Å) and have approximate D_{5h} symmetry (eclipsed rings) with mean Ru–C = 2.186 Å. Both distances increase by 0.003 Å on application of libration corrections. Analysis of the atomic vibrational parameters shows that the molecule does not behave as a rigid body in the crystal at 101 K. Superimposed on the rigid-body motion is an additional libration of one ring with a mean-square amplitude of about 6 deg² relative to the other ring.

Introduction

The crystal structure of ruthenocene was determined by Hardgrove & Templeton (1959: hereinafter HT) from three-dimensional photographic X-ray data. We have recently redetermined the structure from new diffractometer data collected at 293 K (room temperature, RT) and at 101 K (LT) and report the results here.

Experimental

All X-ray measurements were made on an Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator (Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å) and a cooling device. Dimensions of the orthorhombic cell (space group $Pnma$) at 293 and at 101 K are:

	<i>a</i>	<i>b</i>	<i>c</i>
293 K	7.119 (3)	8.985 (4)	12.794 (5) Å
101 K	7.009 (3)	8.819 (4)	12.756 (5)

The former values agree closely with those given by HT. Complete sets of intensity measurements were made with a crystal ~ 0.18 mm in edge at 293 K (sin θ/λ limit 0.60 Å⁻¹, 949 independent reflexions, 626 with $I \geq 1.5\sigma_I$) and at 101 K (sin θ/λ limit 0.64 Å⁻¹, 1036 reflexions, 810 with $I \geq 1.5\sigma_I$). Intensities were converted to relative $|F|$ values, but absorption corrections ($\mu \sim 1.8$ mm⁻¹) were not applied.

The HT coordinates were used as the starting point for least-squares refinement of the RT data (final $R = 0.034$). The resulting coordinates were used in turn for refinement of the LT data (final $R = 0.020$ including an extinction correction). Scattering factors for neutral Ru and C were taken from Cromer & Mann (1968), those for H from Stewart, Davidson & Simpson (1965). Modified weighting systems (Dunitz & Seiler, 1973) with $r = 2$ Å² for the RT data and $r = 5$ Å² for the LT data were used in the later cycles. For the RT refinement H atoms were omitted from the least-squares model and inserted at calculated positions (C–H = 1.08 Å, C–H direction along bisector of the CCC angle) at the close of the analysis. With the LT data H positions could be successfully refined (C–H = 0.89–1.00 Å, $R = 0.019$) but for the final cycle they were moved along their respective C–H directions to a distance of 1.08 Å and held constant there. Final positional and vibrational parameters for both data sets are listed in Table 1.*

Molecular geometry

The ruthenocene molecule (Fig. 1) sits on a crystallographic mirror plane that passes through Ru, C(1) and C(4) and therefore has the eclipsed conformation of the two cyclopentadienyl rings, which are not related to each other by symmetry. However, as the rings are

* Lists of structure amplitudes measured at 101 and 293 K have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35480 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic positions and vibrational parameters (\AA^2) (with *e.s.d.*'s in parentheses) obtained from the X-ray analyses of ruthenocene at 101 K (upper entries) and at 293 K (lower entries)

Positional parameters are $\times 10^5$ for Ru, $\times 10^4$ for C and H; all vibrational parameters are $\times 10^4$.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru	23701 (3)	25000	50422 (1)	86 (2)	98 (2)	66 (2)	0	-1 (1)	0
	23754 (7)	25000	50399 (4)	279 (4)	315 (4)	190 (4)	0	-7 (3)	0
C(1)	5158 (4)	2500	5802 (2)	92 (13)	225 (15)	103 (11)	0	-30 (9)	0
	5107 (13)	2500	5809 (7)	344 (43)	753 (69)	336 (48)	0	-124 (39)	0
C(2)	2441 (3)	3315 (3)	6661 (1)	134 (10)	157 (14)	67 (9)	14 (7)	-18 (6)	-31 (7)
	2433 (8)	3308 (8)	6653 (4)	514 (37)	460 (38)	217 (28)	31 (21)	-106 (26)	-51 (26)
C(3)	4124 (3)	3814 (2)	6131 (1)	122 (9)	144 (9)	103 (7)	-32 (8)	-51 (7)	-6 (7)
	4096 (9)	3805 (8)	6127 (4)	459 (34)	534 (37)	269 (28)	-128 (32)	-124 (26)	6 (31)
C(4)	2546 (4)	2500	3330 (2)	143 (15)	213 (20)	67 (13)	0	5 (9)	0
	2546 (13)	2500	3340 (7)	521 (60)	878 (92)	171 (41)	0	-1 (36)	0
C(5)	-156 (3)	3311 (2)	4211 (1)	99 (9)	113 (10)	74 (7)	17 (7)	-30 (6)	3 (7)
	-123 (7)	3312 (6)	4208 (4)	332 (25)	334 (30)	309 (28)	-7 (23)	-108 (24)	37 (26)
C(6)	1510 (3)	3812 (2)	3667 (1)	158 (10)	156 (9)	65 (7)	-7 (9)	-28 (6)	42 (7)
	1532 (9)	3813 (8)	3672 (4)	495 (35)	507 (36)	228 (27)	-51 (31)	-59 (27)	118 (30)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}		<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}
H(1)	6491	2500	5378	317 (141)	H(4)	3872	2500	2898	174 (91)
	6427	2500	5393			3853	2500	2912	
H(2)	1360	4036	7000	127 (59)	H(5)	-1228	4030	4561	135 (60)
	1366	4013	6991			-1185	4016	4553	
H(3)	4542	4978	6003	197 (66)	H(6)	1918	4978	3533	139 (64)
	4511	4946	5996			1942	4955	3540	

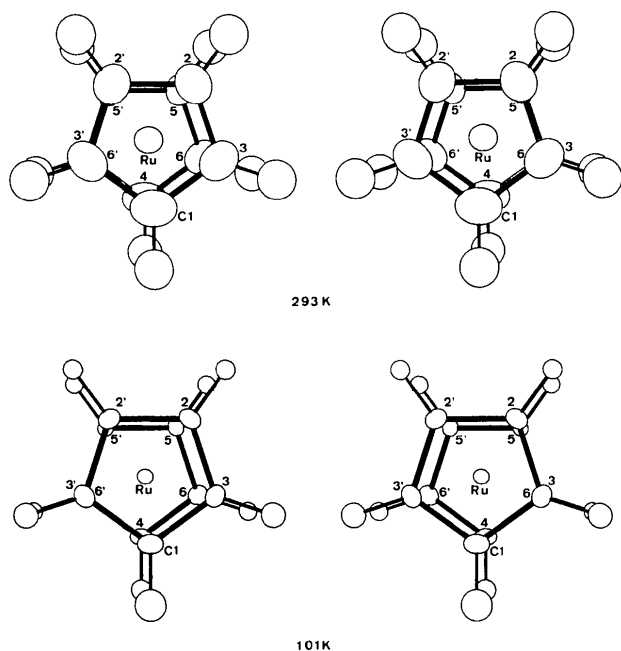


Fig. 1. Stereoscopic views of the ruthenocene molecule at 293 and 101 K. Vibrational ellipsoids (isotropic for H atoms, assumed values for 293 K, refined ones for 101 K) are at the 50% probability level (Johnson, 1965).

nearly regular pentagons, parallel to one another and equidistant from the Ru atom, the molecule has approximate D_{5h} symmetry. This was already known from the 1959 HT analysis, and our new RT study merely serves to confirm the essential correctness of the

earlier results. With the improved experimental data our RT analysis leads to a more regular molecular geometry (Table 2) than in the older work.

The molecular dimensions given by the LT analysis (Table 2) are still more regular with C—C = 1.428–1.438 \AA (average 1.430 \AA) and Ru—C = 2.181–2.188 \AA (average 2.186 \AA). On application of thermal-motion corrections derived from a rigid-body analysis these distances are increased by 0.003 \AA . The uncorrected RT bond distances tend to be slightly longer than the LT ones even when thermal-motion corrections are applied to the latter. The explanation is that

Table 2. Ruthenocene: bond distances (\AA) from the 101 and 293 K analyses

	101 K	293 K
Ru—C(1)	2.181	2.179
Ru—C(2)	2.186	2.188
Ru—C(3)	2.187	2.194
Ru—C(4)	2.188	2.179
Ru—C(5)	2.184	2.197
Ru—C(6)	2.187	2.195
C(2')—C(2)	1.438	1.452
C(2)—C(3)	1.428	1.433
C(3)—C(1)	1.429	1.435
C(5')—C(5)	1.430	1.458
C(5)—C(6)	1.429	1.436
C(6)—C(4)	1.432	1.447
Ru—C (mean)	2.186	2.191
C—C (mean)	1.430	1.441

The 101 K distances may be lengthened uniformly by about 0.003 \AA to allow for rigid-body libration effects. *E.s.d.*'s are about 0.002 for Ru—C, 0.003 \AA for C—C at 101 K (0.007 and 0.009 \AA respectively at 293 K).

omission of the H atoms from the RT analysis has led to slight displacements of the C positions towards the missing atoms, *i.e.* away from the centres of the rings; this apparent expansion of the C atom skeleton is more than enough to make up for the shortening effect due to increased thermal motion.

Thermal-motion analysis

The atomic vibrational parameters obtained for ruthenocene are smaller than those obtained for either ferrocene or nickelocene at the same temperature (Seiler & Dunitz, 1979, 1980). Results of rigid-body-motion analyses (*THMB*, Trueblood, 1978) are summarized in Table 3. The most striking difference with respect to the other two metallocenes is in the libration tensor: at 101 K the largest eigenvalue of **L** is only about 7 deg² for ruthenocene compared with 28 deg² for ferrocene and 45 deg² for nickelocene. Even at RT the ruthenocene value is only about 30 deg². The eigenvalues of the translational tensor are also markedly smaller than those for ferrocene and nickelocene at the same temperature. One eigenvector of **T** is parallel to **b** by symmetry and the other two are nearly parallel to the other crystal axes.

In the ruthenocene crystal the two cyclopentadienyl rings in a given molecule are crystallographically independent and they could have different rigid-body-motion parameters. The rigid-body test (Rosenfield, Trueblood & Dunitz, 1978) is not particularly informative here but it is at least compatible with rigidity of the individual rings as far as the LT data are concerned [$\chi^2 = \sum (\Delta_{C,C}^2)_i / \sigma_i^2 = 4.15$ for the eight symmetry-independent C,C directions in the two rings]. The possibility that the rings have different librational amplitudes can be tested in two ways. One is to calculate **L**, **T** and **S** for each ring separately. In such a calculation, to avoid the singularity associated with a regular pentagonal molecule (Cruickshank, 1956; Schomaker & Trueblood, 1968), the Ru atom has to be

included. With due allowance for symmetry constraints, there are then 20 observations (U^{ij} values) for each unit to which 12 non-zero parameters have to be fitted. The Ru atom contributes to **T** (indeed when properly weighted it practically determines **T**) but has no effect on the libration amplitude about the molecular fivefold axis. For the ring containing C(1) (ring I) the LT data give an **L** tensor with eigenvalues of 8.13, 1.87 and -1.19 deg², for the other ring (II) an **L** tensor with eigenvalues of 1.30, 1.24, -0.93 deg². The difference in L_1 is then 6.83 deg². The remaining components of **T** and **S** depend heavily on the Ru atom and the values obtained for the two rings separately are quite similar. We note that the agreement between observed and calculated U^{ij} values produced by this model is almost too good. For example, $\chi^2 = \sum \Delta^2(U) / \sigma^2(U)$ is 3.17 and 6.15 for rings I and II separately (with $20 - 12 = 8$ degrees of freedom we expect $\chi^2 \geq 7.34$ with 50% probability). For comparison, the rigid-body analysis summarized in Table 3 gave $\chi^2 = 47.6$ with 24 degrees of freedom (random sampling would produce $\chi^2 \leq 43$ with 99% probability). For ring I the principal libration axis L_1 (8.13 deg²) is within 5° of the corresponding axis calculated for the molecule as a whole. The calculation then suggests that ring I has a much larger librational amplitude than ring II, and this is confirmed by the second test.

The *THMB* program (Trueblood, 1978) contains the option of including allowance for internal torsion modes (Dunitz & White, 1973). Only one additional parameter, the mean-square librational amplitude about an axis in a specified direction, is added for each internal torsion mode considered; the set of atoms assumed to be affected by each such torsion mode can be chosen at will. For ruthenocene, the main torsional motion can be assumed to be about the fivefold axis. In this case, the axis of internal torsion happens to coincide nearly with the largest eigenvector of the rigid-body librational tensor and we were not sure in advance that the method would work under such circumstances. We need not have worried. The set of

Table 3. Results of rigid-body-motion analysis

All vectors are referred to Cartesian axes along **a**, **b**, **c**. The translation tensor is given in its reduced form (Schomaker & Trueblood, 1968). R' is $[\sum (\Delta U)^2 / \sum U^2]^{1/2}$.

	101 K			293 K				
	Eigenvalue	Eigenvector		Eigenvalue	Eigenvector			
Fivefold axis		0.5029	0	0.8644	0.5030	0	0.8643	
L_1 (deg ²)	7.33	0.6891	0	0.7247	30.77	0.6701	0	0.7420
L_2 (deg ²)	3.66	0.7247	0	-0.6891	14.04	0	1	0
L_3 (deg ²)	3.63	0	1	0	10.50	0.7420	0	-0.6701
T_1 (10 ⁻⁴ Å ²)	85	0	1	0	289	0.9889	0	0
T_2 (10 ⁻⁴ Å ²)	84	0.9955	0	-0.0946	270	0	1	0
T_3 (10 ⁻⁴ Å ²)	57	0.0946	0	0.9955	154	0.1487	0	0.9889
$\langle \Delta U^2 \rangle^{1/2}$ (Å ²)	11×10^{-4}				23×10^{-4}			
$\langle \sigma^2(U) \rangle^{1/2}$ (Å ²)	10×10^{-4}				36×10^{-4}			
R'	0.104				0.075			

atoms affected by the additional rotation can be taken in turn as those in ring I or II. When ring I is chosen, the mean-square amplitude for the additional internal rotation is calculated from the LT data to be 6.04 (2.50) deg^2 and the molecular libration tensor becomes more nearly isotropic (eigenvalues 4.74 , 3.78 , 2.98 deg^2 , compare Table 3). The reduced translation tensor is almost the same as in the rigid-body calculation, and the overall agreement between observed and calculated U^{ij} values is slightly improved ($R' = 0.087$, $\langle \Delta U^2 \rangle^{1/2} = 8 \times 10^{-4} \text{ \AA}^2$, compare Table 3). When the additional rotation is assumed to affect ring II instead of ring I its mean-square amplitude is calculated to be -6.04 deg^2 and the eigenvalues of the molecular libration tensor become 10.01 , 3.78 , 3.76 deg^2 . The other calculated quantities and also the calculated U^{ij} values are unchanged. The negative mean-square torsional amplitude for ring II is physically unreasonable, but the model works mathematically just as well as the physically reasonable one where the additional internal motion adds to, rather than subtracts from, the rigid-body motion.

Although the rigid-body test was rather non-committal about the possibility of internal molecular motion between the rings, both the new tests indicate clearly that the molecule does not behave as a rigid body in the crystal. Both tests show that ring I undergoes an additional rotation relative to ring II amounting to 6.8 deg^2 according to one test and 6.0 deg^2 according to the other.* The effective force constant for this motion can be estimated from $\langle \varphi^2 \rangle = RT/k$ to be about $130 \text{ J mol}^{-1} \text{ deg}^2$, corresponding to a barrier height V_0 of about 34 kJ mol^{-1} on the assumption of a fivefold sinusoidal potential $V = V_0(1 + \cos 5\varphi)/2$. This assumption is certainly not warranted for the molecule in its crystal environment and the estimate of V_0 can be considered only as an upper limit. The barrier to internal rotation in ruthenocene does not seem to be known.

Crystal packing

A stereopicture of the unit cell, viewed along a direction nearly perpendicular to the bc plane, is shown in Fig. 2.

* We have also applied these tests to the atomic vibrational parameters (at 101 K) in ferrocene where the normal rigid-body analysis yields mean-square libration amplitudes of 28.22 and 28.59 deg^2 for the two crystallographically independent molecules I and II, respectively (Seiler & Dunitz, 1979). For molecule I, the independent-motion model gives mean-square amplitudes of 36.3 and 21.2 deg^2 for rings C(1)–C(5) and C(6)–C(10) considered separately; the alternative non-rigid-body model leads to a rotation of the first ring relative to the second of 15.7 deg^2 , superimposed on a rigid-body motion with $L_1 = 21.4$ deg^2 . For molecule II, the independent-motion model gives values of 32.4 deg^2 for C(1)–C(5) and 28.6 deg^2 for C(6)–C(10); the non-rigid-body model gives 4.4 deg^2 for the additional rotation of C(1)–C(5) and 28.3 deg^2 for L_1 . The agreement between the two methods of calculation is excellent.

Table 4. Intermolecular H...H distances (\AA) calculated from atomic coordinates at 101 K

The last digit of the symmetry code specifies a given equivalent position:

- | | |
|---|---|
| (1) x, y, z | (5) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$ |
| (2) $x, \frac{1}{2} - y, z$ | (6) $-x, \frac{1}{2} + y, -z$ |
| (3) $-x, -y, -z$ | (7) $\frac{1}{2} - x, -y, \frac{1}{2} + z$ |
| (4) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$ | (8) $\frac{1}{2} + x, y, \frac{1}{2} - z$ |

and translations along a , b , c add or subtract one from the first three digits, which are 555.

Type	Distance	Number per molecule
H(1)...H(5)65501	2.34	2
H(2)...H(6)56507	2.46	4
H(2)...H(6)56603	2.55	4
H(2)...H(5)56603	2.62	4
H(3)...H(6)66603	2.55	4
H(3)...H(5)56603	2.58	4
H(3)...H(3)66603	2.64	2
H(5)...H(5)56603	2.67	2
H(5)...H(6)56603	2.63	4

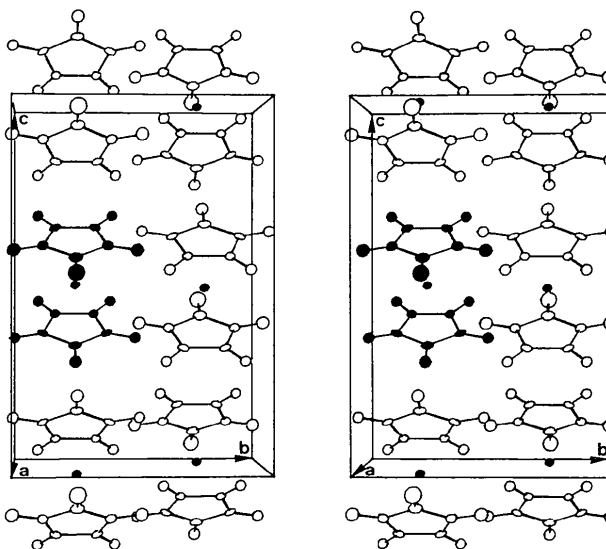


Fig. 2. Stereoscopic view of the packing of ruthenocene molecules at 101 K. The reference molecule is indicated.

Intermolecular H...H distances $< 2.8 \text{ \AA}$ are listed in Table 4 for the structure at 101 K (based on H positions given in Table 1). Each molecule is in contact with only 10 neighbouring molecules in comparison with 12 for the triclinic ferrocene structure and 14 for the monoclinic one (nickelocene). As Kitaigorodsky (1973) has pointed out, the space group $Pnma$ does not permit close packing of molecules but it does provide the densest possible packing for mirror-symmetric molecules that retain m symmetry in the crystal. Actually, the packing makes up for the lower number of nearest neighbours by having a higher number of

intermolecular H...H contacts $\leq 2.8 \text{ \AA}$ per molecule. This number is 30 in the ruthenocene structure compared with 23–25 in triclinic ferrocene and 22 in monoclinic nickelocene. Note that H(4), on the mirror plane, makes no intermolecular contact $< 2.8 \text{ \AA}$ (there are some just $> 2.8 \text{ \AA}$).

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Terminal Zinc–Hydrogen Bonding. X-ray and Neutron Diffraction Studies of the (2-Dimethylamino-*N*-methylethylamido)hydrido-zinc Dimer*

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Abstract

$C_{10}H_{28}N_4Zn_2$, $M_r = 670.2$, monoclinic, $P2_1/c$, at 293 K $a = 6.372$ (3), $b = 11.317$ (5), $c = 11.977$ (5) Å, $\beta = 111.75$ (8)°, $U = 802.1 \text{ \AA}^3$, $Z = 2$ dimer units, $D_m = 1.40$ (1), $D_c = 1.39 \text{ Mg m}^{-3}$, $\mu(\text{Cu } K\alpha) = 3.67 \text{ mm}^{-1}$, $F(000) = 352$. The structure was determined from photographic X-ray data. For the 1000 reflections classified as observed R converged to 0.109. Low-temperature (123 K) neutron diffraction yielded 337 independent reflections. All 14 H atoms showed up on a difference map obtained with neutron structure factors calculated from the Zn, N and C positions

found from the X-ray determination. The compound is dimeric in the solid as well as in benzene solution. A four-membered Zn_2N_2 ring links the two halves of the dimer round a centre of symmetry and a second, albeit weaker, dative bond involving the second N atom results in the formation of five-membered rings and brings the coordination number of the Zn atom to four. The H atom bonded to Zn occupies a terminal position.

Introduction

The preparation of $RMN(\text{Me})C_2H_4NMe_2$ ($R = \text{alkyl}$) has been reported for $M = \text{Be}$ (Coates & Roberts, 1968), Mg (Coates & Heslop, 1968) and Zn (Coates & Ridley, 1965). Such compounds are dimeric in benzene solution and structures have been suggested for them, but up to the time when the present work began no crystal structure data were available concerning either these compounds or the related species $HMN(\text{Me})C_2H_4NMe_2$ which has been reported for $M = \text{Be}$ and Zn (Bell & Coates, 1968). Furthermore no

* Bis[μ -(2-dimethylamino-*N*-methylethylamido)-*N'*, μ -*N*]-bis(hydrido-zinc).

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