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# Crystal and Molecular Structure of 1,2-Bis(ferrocenyl)ethane

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The crystal structure of 1,2-bis(ferrocenyl)ethane, $(C_5H_5)Fe(C_5H_4)CH_2CH_2(C_5H_4)Fe(C_5H_5)$, has been determined from three-dimensional X-ray data collected on an automatic four-circle diffractometer at room temperature. The compound crystallizes in the orthorhombic space group *Pbca* with four molecules in a cell of dimensions $a = 10.063$ (8) Å, $b = 10.434$ (4) Å, and $c = 16.226$ (5) Å. The experimental density was found to be 1.45 g/cm$^3$. Least-squares refinement of absorption-corrected intensity data lead to a final value for the conventional $R$ factor of 0.045 based on 1202 present reflections. The molecular structure of the compound is such that the two ferrocene moieties are symmetrically equivalent by virtue of an inversion center at the midpoint of the carbon–carbon bond in the ethane fragment. Thus, the compound adopts a transoid configuration in the solid state. The cyclopentadienyl rings in the respective ferrocene moieties are parallel and separated by 3.34 Å. Iron–ring carbon distances are equivalent and equal to 2.030 Å while inner ring carbon–carbon distances are also equal and average 1.413 Å. The cyclopentadienyl rings are rotated 8.5° from the fully eclipsed configuration.

## Introduction

Ferrocene and formaldehyde undergo reaction in either concentrated sulfuric acid[2] or liquid hydrogen fluoride[3] to yield 1,2-Bis(ferrocenyl)ethane, $(C_5H_5)FeC_5H_4CH_2CH_2C_5H_4Fe(C_5H_5)$. The compound was initially assigned the structure illustrated by Figure 1(a).[2,3] Later Nesmeyanov and coworkers revised the predicted structure to that illustrated in Figure 1(b).[4] In 1959 Rinehart and coworkers[5] reported infrared, synthetic, and general chemical evidence in strong support of the structure illustrated in Figure 1(c).

In an effort to determine the correct structure for the compound, a single-crystal X-ray study was begun in this laboratory. Approximately 1900 independent reflections were measured by standard moving-film and visual techniques and standard heavy-atom methods were used to solve the structure which was refined by conventional least-squares methods to a final $R$ value of 0.166. This refinement was based on unit weights and anisotropic temperature factors for carbon and iron atoms. The results of the study indicated that the molecular structure was that illustrated by Figure 1(c) as Rinehart and coworkers had claimed,[5] but the high $R$ value prevented the definitive assignment of accurate bond distances as well as the relative configuration of the cyclopentadienyl rings (staggered or eclipsed). The low accuracy of these results was not surprising since many X-ray structural investigations involving ferrocene and ferrocene derivatives have been characterized by high standard errors ($R$ generally greater than 0.10). These high errors have generally been attributed to extinction, absorption, and possible disorder factors.

The advent of the common usage of automated X-ray diffractometers has served to improve greatly the quality of data obtained in single-crystal X-ray diffraction studies over that previously obtainable with standard moving-film techniques and visual estimation of intensity data. The possibility of obtaining significantly improved X-ray intensity data through the use of an automated X-ray diffractometer and subsequent additional refinement of the data obtained in this manner from a single crystal of 1,2-bis(ferrocenyl)ethane was thought to be useful in two respects. First, improved data would result in a more accurate assignment for the crystal and molecular structure of 1,2-bis(ferrocenyl)ethane. Second, if the $R$ factor dropped to a low level, significant disorder and extinction problems as properties of the crystalline state could be ruled out for this ferrocene derivative. Instead, some indication would exist that the inherent errors in visually measured X-ray intensities might be partially responsible for the generally high standard errors noted in crystallographic studies involving ferrocene and ferrocene derivatives.

Such reasoning has recently been supported by the appearance of two X-ray crystallographic studies involving ferrocene compounds. In each case intensity data were obtained using modern automated data collection techniques. The first, $[Fe(C_5H_5)_2]^+[(CCl_3CO_2H)_3]^-$, was refined to an $R$ value of 0.05[6a] and the second, diiodocarbonylferrocene-1,1-bis(dimethylarsine)nickel(II), to an $R$ value of 0.038.[6b] Both studies illustrate that extinction and disorder phenomena are not inherent properties of ferrocene compounds and that low standard errors are obtainable for X-ray studies involving ferrocene derivatives when modern automated intensity data collection techniques are employed.

## Experimental Section

Crystals of 1,2-bis(ferrocenyl)ethane suitable for X-ray analysis were obtained by recrystallizing the compound from dichloromethane. *Anal.* Calcd for $Fe_2C_{22}H_{22}$: C, 66.37; H, 5.57. Found: C, 66.32; H, 5.29. The crystals formed in this manner were deep orange rhombohedrons elongated along $a$. The crystal of 1,2-bis(ferrocenyl)ethane selected for X-ray analysis measured 1.28 × 0.17 × 0.07 mm along the $a$, $b$, and $c$ unit cell axes, respectively.

Preliminary Weissenberg and precession photographs of the compound showed orthorhombic diffraction symmetry and exhibited the following systematic absences: $0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$. These absences allowed the unambiguous assignment of the *Pbca* space group to the compound. The cell dimensions were determined on the Picker four-circle automated diffractometer using zirconium-filtered Mo K$\alpha_1$ radiation (λ 0.7107 Å). The results were $a = 10.063$ (8) Å, $b = 10.434$ (4) Å, and $c = 16.226$ (5) Å. The measurement temperature was 24°.

The density calculated from X-ray data is 1.53 g/cm$^3$ (mol wt 398.10, $Z = 4$). The measured density obtained by pycnometric techniques is 1.45 ± 0.03 g/cm$^3$.

Three-dimensional intensity data were obtained by mounting the crystal onto a Picker four-circle automated diffractometer with the $a^*$ axis approximately coincident with the spindle axis ($\phi$ axis) of the diffractometer. Intensity data were collected using the $\theta$–$2\theta$ scan mode to $(\sin\theta)/\lambda = 0.676$ and zirconium-filtered molybdenum radiation. The scan rate was 1°/min and the scan range was 1.5° for each reflection observed. Background intensity was determined by mak-

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[1] Based in part on the Ph.D. thesis of R. L. D., 1972.

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[5] K. L. Rinehart, Jr., C. J. Michejda, and P. A. Kittle, *J. Amer. Chem. Soc.*, 81, 3162 (1959).

[6] (a) A. W. Schlueter and H. B. Gray in "Program and Abstracts of the American Crystallographic Association Summer Meeting, August 15-20, 1971," Iowa State University, Ames, Iowa, p 41; (b) C. G. Pierport and R. Eisenberg, *Inorg. Chem.*, 11, 828 (1972).

Table II. Fractional Atomic Coordinates and Mean-Square Amplitude Tensors

| | $x^a$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Fe | 9956 (0.8) | 1964 (0.6) | 1291 (0.4) | 32 (1) | 35 (1) | 33 (1) | 6 (1) | 2 (1) | 13 (1) |
| C(1) | 253 (5) | 4622 (5) | 371 (3) | 44 (4) | 44 (3) | 37 (3) | −9 (5) | −17 (5) | 19 (5) |
| C(2) | 9492 (5) | 3389 (5) | 489 (3) | 43 (3) | 34 (3) | 31 (3) | 7 (5) | −11 (5) | 18 (5) |
| C(3) | 8418 (5) | 3174 (5) | 1053 (3) | 31 (3) | 43 (3) | 43 (3) | 17 (5) | 2 (4) | 13 (6) |
| C(4) | 8008 (5) | 1882 (5) | 974 (3) | 32 (3) | 50 (3) | 48 (3) | 1 (6) | 2 (5) | 15 (6) |
| C(5) | 8814 (5) | 1294 (5) | 352 (3) | 46 (3) | 43 (3) | 37 (3) | −3 (6) | −15 (5) | −4 (6) |
| C(6) | 9718 (5) | 2231 (5) | 61 (3) | 39 (3) | 44 (3) | 36 (3) | 10 (5) | −3 (5) | 7 (5) |
| C(7) | 1496 (7) | 2590 (7) | 1979 (4) | 63 (4) | 57 (4) | 69 (5) | −22 (7) | −71 (8) | 29 (8) |
| C(8) | 447 (7) | 2172 (7) | 2498 (4) | 69 (4) | 75 (4) | 40 (3) | 24 (8) | −36 (6) | 1 (7) |
| C(9) | 217 (8) | 883 (7) | 2323 (4) | 81 (6) | 70 (4) | 49 (4) | −7 (9) | −29 (8) | 53 (7) |
| C(10) | 1108 (8) | 483 (6) | 1699 (4) | 89 (6) | 50 (4) | 62 (4) | 50 (8) | −39 (9) | 28 (7) |
| C(11) | 1875 (6) | 1534 (8) | 1491 (4) | 44 (4) | 103 (6) | 52 (4) | 53 (8) | −18 (6) | 32 (9) |
| H(1) | 134 | 5215 | 919 | | | | | | |
| H(2) | 1302 | 4397 | 285 | | | | | | |
| H(3) | 7986 | 3877 | 1471 | | | | | | |
| H(4) | 7219 | 1422 | 1327 | | | | | | |
| H(5) | 8750 | 306 | 136 | | | | | | |
| H(6) | 470 | 2083 | 4585 | | | | | | |
| H(7) | 1929 | 3547 | 1959 | | | | | | |
| H(8) | 9912 | 2741 | 2953 | | | | | | |
| H(9) | 9467 | 290 | 2623 | | | | | | |
| H(10) | 1189 | 9532 | 1426 | | | | | | |
| H(11) | 2649 | 1530 | 1021 | | | | | | |

[a] Fractional coordinates with standard deviations in parentheses ($\times 10^4$). The $U_{ij}$'s (Å$^2$) are given together with standard deviations in parentheses ($\times 10^3$) and defined such that the atomic temperature factor is given by $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$. The isotropic temperature factor $B = 3.5$ Å$^2$ was assigned to hydrogens H(1)-H(6) and $B = 5.0$ Å was assigned to hydrogens H(7)-H(11).

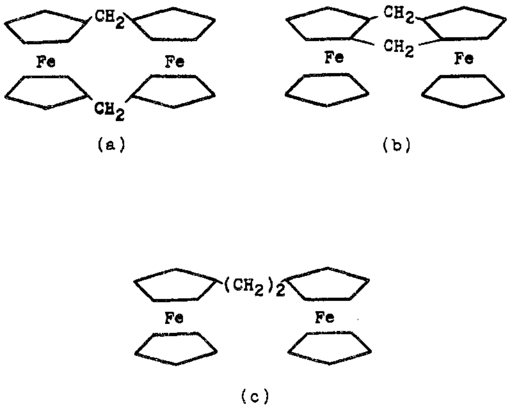

Figure 1. (a) Initial proposed structure for bis(ferrocenyl)ethane. (b) Revised structure proposed by Nesmeyanov and coworkers.[4] (c) Structure proposed by Rinehart and coworkers.[5]

ing 10-sec counts at each end of the scan range. In this manner 15,394 reflections were measured, 2542 of which were independent and 2215 of which were symmetry allowed. Of these 2215 symmetry-allowed reflections, 1202 were actually observed. Inspection showed that the intensities of each of the 327 reflections not allowed in the *Pbca* space group were within three standard deviations of the background. Three relatively high-intensity reflections (400, 080, and 008) were measured at regular intervals (every 60 reflections) and served as standards. The variance in the intensities of these standards over the entire data collection period was as follows: 400, 12%;[7] 080, 2%; 008, 1%.

The standard deviation ($S$) of a reflection was determined by two procedures: (1) from counting statistics alone

$$S^2 = \left[\sum_{i=1}^{N} (I_i + B_i)\right]/N$$

where $I_i$ is the total measured intensity for one reflection, $B_i$ is the measured background adjusted for length of scan time, and the sum is over the $N$ symmetry-equivalent or duplicately measured reflections; (2) from the equivalent reflections

$$S^2 = \left[\sum_{i=1}^{N}(C_i - C_{\mathrm{av}})^2\right]/(N-1)$$

where $C_i = I_i - B_i$ and $C_{\mathrm{av}} = [\Sigma_{i=i}{}^N C_i]/N$. The largest value of $S$ was chosen. Method (2) was used only if $N > 2$. A reflection was considered to be unobserved if $C_{\mathrm{av}} \leqslant 3S_{\mathrm{B}}$, where $S_{\mathrm{B}}{}^2 = [\Sigma_{i=1}{}^N B_i]/N$.

Each reflection was weighted by the procedure outlined by Grant, Killean, and Lawrence[8] where $w = 1/(S^2 + c^2F_{\mathrm{o}}{}^2)$. The term $c$ was adjusted to give the error-fit function a value of 1.0 and in the final refinement cycle $c^2 = 0.0002$, where the (error-fit function)$^2$ = $[\Sigma w(\Delta F)^2]/(M - N)$, $M$ is the number of reflections, $N$ is the number of parameters varied, and $\Delta F = F_{\mathrm{o}} - F_{\mathrm{c}}$.

The X-ray intensity data obtained in the above manner were corrected for Lorentz and polarization effects[9] using the IBM 360/65 computer facilities at the University Computer Center, University of Iowa, Iowa City, Iowa. The data were corrected for absorption based upon $\mu = 17.5$ cm$^{-1}$ using the method of Alberti and Gottardi.[10] The value of the absorption correction varied from 0.616 to 0.864.

The atom scattering factors and dispersion corrections used in the structure factor computations were obtained from ref 11; both real and imaginary dispersion corrections were used for iron during the refinement. All atoms were assumed to be neutrally charged.

The general structure of the compound had been solved previously in this laboratory using photographic data and conventional heavy-atom techniques. Thus, the atomic coordinates for the iron and carbon atoms determined previously were used for the initial cycle of

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(7) The relatively high per cent standard deviation (12%) for the (400) standard reflection was ignored for the following reasons. A partial data set was collected on the crystal ($\theta$ = 3-17°), and subsequently a more complete data set was collected ($\theta$ = 3-28.8°) on the same crystal. The magnitude of the intensity of (400) reflection increased during the collection of the first data set and eventually reached a stable value. The per cent standard deviation for the first data set was 5.6% for the (400) reflection; the other standard reflections did not show this trend. When the (400) reflection stabilized, a second set of data was collected and the per cent standard deviation for the (400) reflection in this set was 3.8%. Examination of both data sets indicated that the major discrepancy occurred with the (400) reflection and the two data sets were then combined and averaged. The average per cent standard deviation of the combined data for all reflections larger than $F_{\mathrm{max}}/5$ was 4.45%, and the combined data set was used for the solution of the structure. The average standard deviation of 12% was due to the larger fluctuation in intensity of (400) in the first data set and the difference in the intensity for this reflection between data sets. We can only speculate that the observed increase in the value of the (400) reflection as the data collection proceeded may have been due to decrease in primary extinction which particularly influenced the (400) reflection.

(8) D. F. Grant, R. C. G. Killean, and J. L. Lawrence, *Acta Crystallogr., Sect. B*, **25**, 374 (1969).

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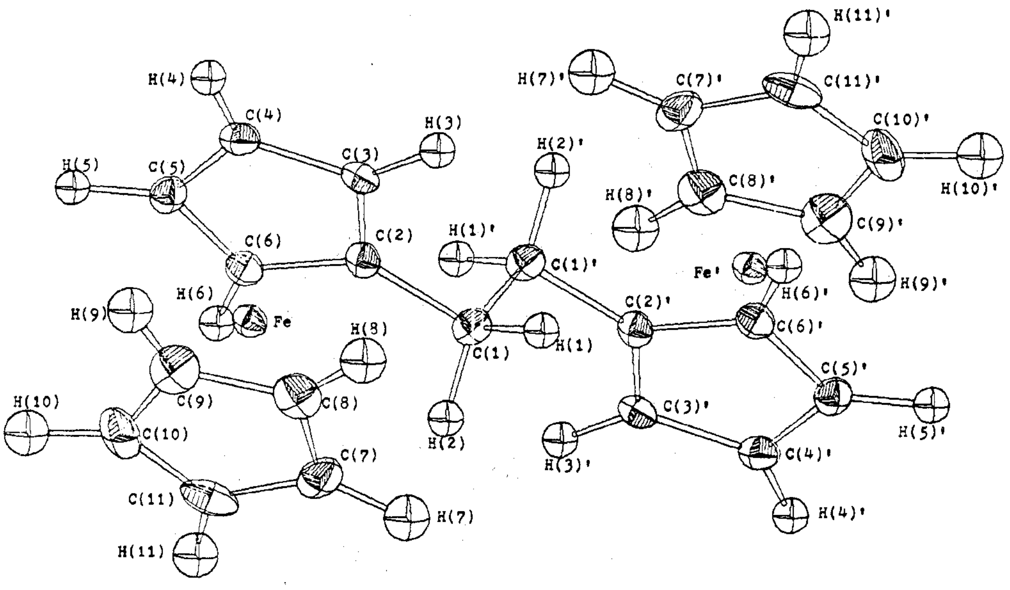

Figure 2. ORTEP plot of 1,2-bis(ferrocenyl)ethane. Thermal ellipsoids are plotted at the 20% probability contour. The projection is basically on the 001 plane but has been rotated 10° about the *a* and *b* axes to avoid overlap of atoms.

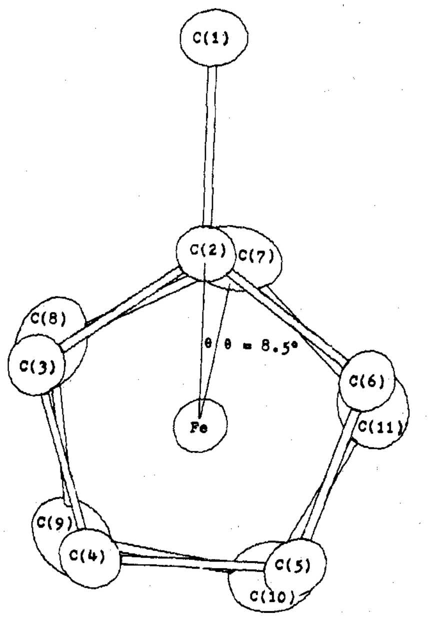

Figure 3. ORTEP plot of the symmetrically unique atoms (hydrogen atoms omitted) in 1,2-bis(ferrocenyl)ethane as viewed along the normal to the cyclopentadienyl rings.

Table III. Bond Lengths and Angles[a]

| | | Distances, Å | |
|---|---|---|---|
| Fe–Fe′ | 7.599 (1) | C(1)–C(1)′ | 1.528 (9) |
| Fe–C(2) | 2.030 (5) | C(1)–C(2) | 1.509 (7) |
| Fe–C(3) | 2.034 (5) | C(2)–C(3) | 1.433 (7) |
| Fe–C(4) | 2.028 (5) | C(3)–C(4) | 1.417 (7) |
| Fe–C(5) | 2.033 (5) | C(4)–C(5) | 1.433 (7) |
| Fe–C(6) | 2.029 (5) | C(5)–C(6) | 1.416 (7) |
| Fe–C(7) | 2.018 (6) | C(6)–C(2) | 1.413 (7) |
| Fe–C(8) | 2.033 (6) | C(7)–C(8) | 1.419 (9) |
| Fe–C(9) | 2.037 (6) | C(8)–C(9) | 1.393 (9) |
| Fe–C(10) | 2.042 (6) | C(9)–C(10) | 1.416 (9) |
| Fe–C(11) | 2.009 (6) | C(10)–C(11) | 1.382 (10) |
| | | C(11)–C(7) | 1.410 (9) |

| | | Bond Angles, Deg | |
|---|---|---|---|
| C(1)′–C(1)–C(2) | 111.78 (35) | C(3)–C(4)–C(5) | 107.77 (50) |
| C(1)–C(2)–C(3) | 126.66 (60) | C(4)–C(5)–C(6) | 107.66 (49) |
| C(1)–C(2)–C(6) | 125.82 (61) | C(7)–C(8)–C(9) | 107.43 (86) |
| C(2)–C(3)–C(4) | 108.16 (55) | C(7)–C(11)–C(10) | 109.34 (73) |
| C(2)–C(6)–C(5) | 108.88 (55) | C(8)–C(7)–C(11) | 107.13 (56) |
| C(3)–C(2)–C(6) | 107.51 (48) | C(8)–C(9)–C(10) | 108.95 (75) |
| | | C(9)–C(10)–C(11) | 107.14 (81) |

[a] The estimated standard deviation in the last digit is given in parentheses.

full-matrix least-squares refinement.[9] The previously determined anisotropic temperature factors for the iron and carbon atoms were also used in the initial refinement. The progress of the refinement was followed using the $R_2$ factor: $R_2 = [\Sigma w(\Delta F)^2/\Sigma w(F_o)^2]^{1/2}$, where $\Delta F = F_c - F_o$. The function minimized was $\Sigma w(\Delta F)^2$ and any intensity below the minimum observable intensity was assigned $w = 0.0$ (unless $F_o < F_c$ in which case it was assigned $w = 1.0$). The conventional $R$ factor ($R_1$), where $R_1 = \Sigma\Delta F/\Sigma F_o$, was also calculated and observed as the refinement progressed.

The initial refinement cycles used experimentally determined weights and did not include positional parameters for hydrogen atoms. $R_2$ was found to be 0.0629 and $R_1$ was 0.0586. Experimentally determined weights were then replaced by weights determined by the method of Grant, Killean, and Lawrence[8] as described above and the refinement was resumed. The new $R_2$ value was 0.0875 and $R_1$ = 0.0775.

An electron density difference map was then computed and the positions of only two hydrogen atoms were apparent; consequently, the positions of these and the other nine hydrogen atoms were calculated based on an assumed carbon–hydrogen bond distance of 1.09 Å. Ideal trigonal and tetrahedral coordinations were assumed for the aromatic and methylene carbon atoms, respectively. The positional parameters for the hydrogen atoms were fixed and when added to the least-squares refinement $R_2$ became 0.0814 while $R_1$ became 0.0737. The final refinement step involved the removal of the 1013 absent reflections. The new value of $R_2$ became 0.0534 whereas $R_1$ became 0.045. The ratio of the largest shift in the last refinement cycle to the standard deviation in the positional parameters was 3%. The average change in all parameters was 1%.

A final electron density difference map based on parameters obtained from the final refinement cycle showed two weak peaks. The fractional coordinates of the peaks were 0.50, 0.19, and 0.37 (1 e/Å$^3$) and 0.47, 0.22, and 0.86 (1 e/Å$^3$). Both sets of coordinates lay near the positions of iron atoms. This "excess" electron density cannot be assigned to any such species as hydrogen atoms but more likely represents some error in the assumption of completely neutral iron and carbon atoms or simply residual error in the fit between the data and the proposed model.

The observed and calculated structure factors for each reflection, as well as their relative weights, are seen in Table I.[12]

## Results

The final positional parameters are summarized in Table II and final bond angles in Table III. Iron to ring carbon

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(12) See paragraph at end of paper regarding supplementary material.

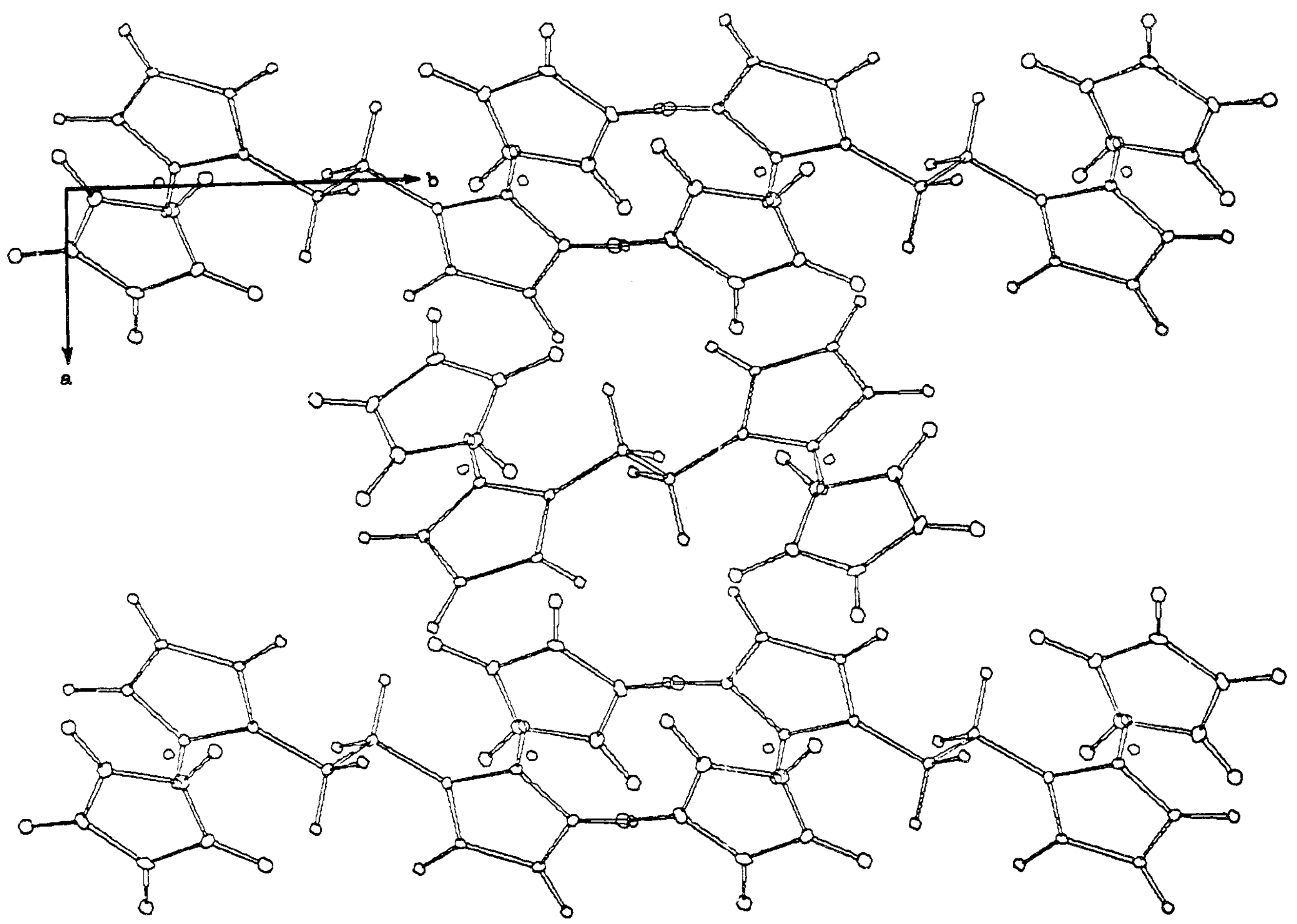

**Figure 4.** ORTEP plot of the molecular packing in the unit cell of 1,2-bis(ferrocenyl)ethane as projected onto the 001 plane. The upper layer is omitted for clarity.

distances average 2.031 (5) Å for the unsubstituted cyclopentadienyl ring. The individual bond distances differ by less than one standard deviation and can be considered equal. The distance between the cyclopentadienyl rings along a line normal to both $C_5$ planes is 3.34 Å. This distance is similar to the ring spacing noted for other ferrocene derivatives, *e.g.*, 3.32 Å in both biferrocenyl[13,14] and ferrocene itself.[15] The five carbon atoms of the respective cyclopentadienyl rings were fitted to the best plane passing through them by the method of Blow.[16] The equations of the planes are $-0.65835i + 0.27449j - 0.70088k = -5.87012$ for the substituted cyclopentadienyl ring and $-0.66849i + 0.26242j - 0.69579k = -2.5284$ for the unsubstituted cyclopentadienyl ring, where $i$, $j$, and $k$ are unit vectors of the $a$, $b$, and $c$ unit cell axes, respectively. These planes intercept the $a$, $b$, and $c$ axes at the angles 131.57, 74.42, and 134.29°. The two cyclopentadienyl rings are thus parallel with the calculated angle between their normals being less than 1°. The nonaromatic carbon atom, C(1), is virtually coplanar with the cyclopentadienyl ring to which it is bonded, the calculated perpendicular distance between C(1) and the plane of that cyclopentadienyl ring being 0.02 Å.

All carbon-carbon bond distances within both cyclopentadienyl rings differ by no more than $3\sigma$ and can be considered equal. However, the thermal parameters listed in Table II clearly show that the carbon atoms comprising the unsubstituted cyclopentadienyl ring are undergoing considerably more thermal motion than those carbon atoms contained in the substituted cyclopentadienyl ring. This motion accounts for the slightly larger standard errors associated with the carbon atoms of the unsubstituted cyclopentadienyl ring.

Using the data contained in Tables II and III in conjunction with the ORTEP computer program[17] a diagram of the molecule was produced and is seen in Figure 2. Twenty per cent of the root-mean-square displacement is shown. The configuration of the molecule includes an inversion center at the midpoint of the carbon-carbon bond in the ethane fragment. It is noteworthy that the general configuration of the molecule is not unlike that found for dibenzyl.[18]

Figure 3 views the symmetrically unique half of the molecule along the normal to the cyclopentadienyl rings (hydrogen atoms omitted). This view illustrates that the cyclopentadienyl rings are in neither a fully eclipsed nor a fully staggered configuration, the calculated angular rotation from the fully eclipsed configuration being 8.5 ± 0.8°. This value compares with the fully staggered configuration (36°) in ferrocene and diindenyliron,[19] 17° in biferrocenyliron,[13,14] 10° in 1,1′-tetramethylethyleneferrocene,[20] 8.8° in diiodocar-

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bonylferrocene-1,1′-bis(dimethylarsine)nickel(II),[7] 5° in diferrocenyl ketone[21] and dichlorodiferrocenyl,[22] 4° in diethyldiferrocenyl,[23] and the fully eclipsed configuration in 1,1′,3,3′-bis(trimethylene)ferrocene[24] and the ferrocenium ion.[6] Figure 4 illustrates the packing of the molecule in the unit cell.

In conclusion it should be reemphasized that the initial intensity data collected by standard moving-film techniques and refined to an *R* value of 0.166 led to the consideration of inherent disorder and large extinction effects as properties of 1,2-bis(ferrocenyl)ethane and such possible properties have been reported for other related ferrocene compounds.[13,15,19,25] The intensity data obtained during this study through the use of the automated diffractometer clearly exclude these phenomena as properties of this compound. Instead, those errors inherent to visually obtained intensity data resulted in the initial inability to assign accurately and refine the structure 1,2-bis(ferrocenyl)ethane. Furthermore, this study and the other recent[6,7] X-ray studies involving ferrocene derivatives are indicative that low standard errors may be obtainable for ferrocene compounds when modern automated intensity data collection techniques are employed.

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**Registry No.** 1,2-Bis(ferrocenyl)ethane, 12156-05-7.

**Supplementary Material Available.** Table I, a listing of structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-101.

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# Crystal and Molecular Structure of Potassium Heptacyanovanadate(III) Dihydrate

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The structure of potassium heptacyanovanadate(III) dihydrate, $K_4[V(CN)_7]\cdot 2H_2O$, consists of discrete pentagonal-bipyramidal $V(CN)_7^{4-}$ anions. The molecular structure was determined by a single-crystal X-ray crystallographic study using Mo K$\alpha$ radiation. The space group was chosen as $I1$ with lattice constants $a = 9.229$ (1), $b = 9.097$ (1), $c = 9.341$ (1) Å; $\alpha = 90.02$ (1), $\beta = 92.49$ (1), $\gamma = 90.00$ (1)°. The observed and calculated densities are $1.77 \pm 0.02$ and 1.80 g cm$^{-3}$, respectively, for $Z = 2$. A total of 824 independent nonzero reflections were collected by the stationary-crystal, stationary-counter method with a General Electric XRD-7 manual diffractometer equipped with balanced zirconium–yttrium filters ($\sin \theta_{max} = 0.38$). The structure was solved by conventional Patterson, Fourier, and least-squares refinement techniques, the final atom (conventional) $R$ value being 2.5%. The central vanadium(III) atom is coordinated to seven cyanide anions in a linear fashion to produce a structure of approximate $D_{5h}$ symmetry. The averaged V–C distance is 2.15 (1) Å, there being no significant difference between equatorial and axial V–C distances. The two axial cyanides give rise to $C_{ax}$–V–$C_{ax}$ = 171.0°. The average $C_{eq}$–V–$C_{eq}$ = 72.0 (6)°. The standard deviation of the distances of the vanadium and the five equatorial carbons from a least-squares plane is 0.03 Å with the greatest distance from the plane being 0.05 Å for one of the carbon atoms. A discussion of the bonding and the factors pertaining to this geometry is presented.

## Introduction

There are relatively few examples of seven-coordinate complexes containing only simple monodentate ligands. Among structures proposed as being ideal for this coordination number are the pentagonal bipyramid (of symmetry $D_{5h}$), the monocapped trigonal prism ($C_{2v}$), the monocapped octahedron ($C_{3v}$), and the tetragonal base–trigonal base structure. Factors which may influence the geometry any given compound assumes have been discussed by Muetterties.[2] Definitive structures of seven-coordinate compounds as determined by X-ray crystallography include very few in which there are seven identical ligands. To date, the only discrete (*i.e.*, mononuclear) $ML_7$ (L = monodentate ligand) compounds which are known are those for which L equals fluoride. Among these are $UF_7^{3-}$ ($D_{5h}$)[3a] and $NbF_7^{2-}$ ($C_{2v}$).[3b] Other seven-coordinate structures contain either more than one type of ligand (*e.g.*, $UO_2F_5^{3-}$ ($D_{5h}$)[4]) or multidentate ligands (*e.g.*, $Zr(acac)_3Cl$[5] and the $[Fe^{III}(OH_2)EDTA]^-$ anion[6]). In these latter examples, because of ligand complexities, it is difficult to assess the relative merits of the several seven-coordinate geometries. In addition, $MF_7$ complexes reported to date have had $d^0$ electronic configurations, and thus no assessment of ligand–electron repulsive effects for seven-coordination has been possible.

The nature of the cyano complex of vanadium(III) has been

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