

& Rohmer, 1969). The two water molecules form intramolecular hydrogen bonds $\text{O}(11) \cdots \text{Cl}(21)$ and $\text{O}(21) \cdots \text{Cl}(11)$ and intermolecular hydrogen bonds $\text{O}(11) \cdots \text{Cl}(12)'$ and $\text{O}(21) \cdots \text{Cl}(22)'$ (Table 7) which link neighbouring dimers, making a chain along the [011] axis, Fig. 4.

In the cyclopentadienyl rings the average C—C length is 1.392 Å and the average C—C—C angle 108.0°. The Nb—C distances lie in the range 2.402 to 2.481 Å and the lengths of the normals to the rings at the Nb atoms are 2.133 and 2.126 Å respectively, surprisingly rather longer than in (I).

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The Crystal and Molecular Structure of 1,1'-Ferrocenedicarboxylic Acid (Triclinic Modification): Neutron and X-ray Diffraction Studies at 78 K and 298 K*

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Abstract

The crystal structure of the triclinic modification of 1,1'-ferrocenedicarboxylic acid, $\text{C}_{12}\text{H}_{10}\text{FeO}_4$, $[\text{Fe}(\eta^5\text{-C}_6\text{H}_5\text{O}_2)_2]$, has been determined from X-ray diffraction

data measured at room temperature (298 K). Refinements based upon neutron diffraction data measured at a temperature of 78 K have provided a highly precise model. Crystal data: space group $P\bar{1}$, $Z = 4$, $a = 7.424$ (2), $b = 7.809$ (2), $c = 18.118$ (4) Å, $\alpha = 98.79$ (2), $\beta = 91.07$ (2), $\gamma = 97.21$ (3)° at $T = 78$ K. For the neutron diffraction data, the final unweighted R value based on F^2 is 0.043 for 3856 unique reflections, and all bond distances have been determined to better

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than 0.003 Å. The structure is composed of hydrogen-bonded dimers, each related internally by a center of inversion, and there are two crystallographically independent dimers per unit cell. The C and H atoms attached to the cyclopentadienyl rings are displaced significantly out of the ring planes toward the Fe atoms [mean displacement = 0.030 (4) Å]. The major difference between the 1,1'-ferrocenedicarboxylic acid molecules in the triclinic and monoclinic modifications concerns the positions of the acidic protons. In the triclinic form, the protons are ordered, while in the monoclinic form, they are equally distributed over two sites displaced approximately symmetrically from the midpoint of the O...O hydrogen bonds.

Introduction

Ferrocene and other metallocenes have been the subject of numerous structural investigations during the past 25 years. Gas-phase electron diffraction studies of these systems have been reviewed by Haaland (1975), and the literature describing X-ray and neutron diffraction studies is covered by Seiler & Dunitz (1979*a*). The present work has been undertaken as part of a study of the distribution of valence-electron density in 1,1'-ferrocenedicarboxylic acid by combined X-ray and neutron diffraction (*X-N*) techniques.

The carboxyl groups of the title compound are hydrogen bonded to form dimers, thus preventing large-amplitude rotations or disorder of the cyclopentadienyl rings as seen in the structure of ferrocene above 164 K (Dunitz, Orgel & Rich, 1956; Seiler & Dunitz, 1979*a*; Takusagawa & Koetzle, 1979*a*). At this temperature, ferrocene undergoes a first-order phase transition to an ordered low-temperature form (Seiler & Dunitz, 1979*b*). 1,1'-Ferrocenedicarboxylic acid also crystallizes in two different modifications. The structure of the monoclinic form was determined at room temperature by Palenik (1969) and we have examined its charge density based on X-ray data measured at 78 K (Takusagawa & Koetzle, 1979*b*). In the present paper we report the determination of the structure of the triclinic form, and its refinement based on neutron diffraction data measured at 78 K, providing a highly precise model for use in the subsequent *X-N* analysis.

Data collection

Samples of 1,1'-ferrocenedicarboxylic acid used in this work were recrystallized from glacial acetic acid by means of slow evaporation at room temperature.

(a) Neutron diffraction

A crystal of approximate dimensions 1.5 × 1.5 × 0.5 mm was mounted on an aluminum pin, the end of

which was made hollow in order to reduce the amount of metal in the neutron beam, and was oriented approximately along the crystallographic [4 $\bar{1}$ 1] direction. The sample was placed in a closed-cycle helium refrigerator* and mounted on an automated four-circle diffractometer (Dimmler, Greenlaw, Kelley, Potter, Rankowitz & Stubblefield, 1976; McMullan, Andrews, Koetzle, Reidinger, Thomas & Williams, 1976) at the Brookhaven High Flux Beam Reactor. A beryllium (002) crystal monochromator was employed to obtain a neutron beam of wavelength 1.1302 (2) Å (based upon KBr, $a = 6.600$ Å at $T = 298$ K). The temperature recorded during data collection was 78 ± 1 K.† Cell dimensions, refined by a least-squares procedure based on $\sin \theta$ values of 32 reflections ($40.0^\circ \leq 2\theta \leq 50.0^\circ$), are listed in Table 1. Reflection intensities were measured in one hemisphere of reciprocal space with $2\theta \leq 90^\circ$, employing a $\theta/2\theta$ step-scan technique. The scan range was varied according to $\Delta 2\theta = 2.44^\circ + 1.76^\circ \tan \theta$ for the high-angle data ($60^\circ \leq 2\theta \leq 90^\circ$) and $\Delta 2\theta = 3.0^\circ$ for the low-angle data. The step size was adjusted to give between 60 and 75 steps in each scan. At each point, counts were accumulated for approximately 5 s, with the exact time interval being determined by monitoring the incident-beam intensity. As a general check on experimental stability, the intensities of two reflections were monitored every 100 measurements. These did not vary to any significant degree during the entire period of data collection.

Integrated intensities of reflections were obtained by a modification of the Lehmann & Larsen (1974) method, with a program that employs an interactive CRT display (Takusagawa, 1977). Individual profiles

* Air Products and Chemicals, Inc. DISPLEX® Model CS-202.

† Calibration with reference to a magnetic phase transition in FeF₂ at $T_N = 78.38$ (1) K indicated that the recorded temperature is within 3 K of the correct value.

Table 1. *Crystal data for 1,1'-ferrocenedicarboxylic acid*

	78 K Neutron ($\lambda = 1.1302$ Å)	298 K X-ray‡	78 K* X-ray‡	298 K† X-ray‡
<i>a</i>	7.424 (2) Å	7.477 (1) Å	8.330 (2) Å	8.403 (10) Å
<i>b</i>	7.809 (2)	7.895 (1)	8.750 (1)	8.910 (10)
<i>c</i>	18.118 (4)	18.235 (3)	14.123 (2)	14.192 (18)
α	98.79 (2)°	99.04 (1)°	90.0°	90.0°
β	91.07 (2)	91.35 (3)	90.76 (3)	90.41 (8)
<i>y</i>	97.21 (3)	97.41 (2)	90.0	90.0
<i>V</i>	1029.1 (5) Å ³	1053.0 (3) Å ³	1029.3 (3) Å ³	1062 (2) Å ³
<i>Z</i>	4	4	4	4
$D_{n,x}$	1.769 Mg m ⁻³	1.729 Mg m ⁻³	1.769 Mg m ⁻³	1.714 Mg m ⁻³
Space group	<i>P</i> 1	<i>P</i> 1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
μ §	0.1634 mm ⁻¹	1.4686 mm ⁻¹	1.5026 mm ⁻¹	1.4559 mm ⁻¹

* Takusagawa & Koetzle (1979*b*).

† Palenik (1969).

‡ Mo *K* α , $\lambda = 0.71069$ Å.

§ Mass-absorption coefficients of C, N, and O atoms were obtained from *International Tables for X-ray Crystallography* (1962). For H atoms in the neutron case, 2390 mm² g⁻¹ was used for the effective mass-absorption coefficient due to incoherent scattering, corresponding to an incoherent cross-section of 4×10^3 fm².

were displayed in order to check the automatic integration, especially for weak reflections and those with unusual backgrounds. (During the subsequent refinements, reflections with large discrepancies between observed and calculated structure factors were rechecked on the CRT.) Absorption corrections for observed intensities were made by means of numerical integration over a Gaussian grid of points (Busing & Levy, 1957). Calculated transmission coefficients range from 0.74 to 0.90. The variance of the net intensity of each reflection was estimated as $\sigma^2(I) = T + B + [0.03(T - B)]^2 + (0.03B)^2$, where T and B are total background counts, respectively, and the factor 0.03 represents an estimate of non-Poisson errors. Squared observed structure factors were obtained as $F_o^2 = I \sin 2\theta$ and averaged for Friedel-related reflections. Agreement factors (R_c) are included in Table 2, which gives some experimental details and summarizes the subsequent refinement.

(b) X-ray diffraction

X-ray data were collected in order to allow solution of the structure by heavy-atom methods. Measurements were made at 298 ± 3 K on a Picker diffractometer using graphite (002) monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). Intensities were sampled over a hemisphere in reciprocal space, out to $2\theta = 50^\circ$, with a $\theta/2\theta$ step-scan technique. A correction was applied for a small amount of decay (*ca* 5.5%) in the intensities of two monitor reflections observed during the period of data collection.

Integrated intensities were obtained by an analogous procedure to that followed for the neutron data. Intensities were corrected for absorption, Lorentz and polarization factors (ideally imperfect crystal approximation assumed for the monochromator), and averaged

for Friedel-related reflections. Details are presented in Table 2.

Structure determination and refinements

(a) X-ray diffraction

The Fe atom positions were deduced from a three-dimensional Patterson function. Lighter atoms were located in subsequent difference and observed Fourier syntheses. All positional parameters, anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for H atoms were refined by a full-matrix least-squares procedure, minimizing $\sum w(F_o^2 - k^2 F_c^2)^2$ and using *LINEX* 79, a modified version of *ORFLS* (Busing, Martin & Levy, 1962). Weights were taken as $w = 1/\sigma^2(F_o^2)$. A scale factor and type I isotropic extinction parameter (Becker & Coppens, 1975) were varied together with the atomic positional and thermal parameters. X-ray scattering factors for neutral Fe, O and C atoms were taken from the relativistic Hartree-Fock values of Doyle & Turner (1968) given in *International Tables for X-ray Crystallography* (1974); those for H atoms were from Stewart, Davidson & Simpson (1965). For Fe atoms, the anomalous-dispersion factors of Cromer & Liberman (1970) were applied.

(b) Neutron diffraction

The atomic coordinates from the X-ray determination were used as initial values for a full-matrix least-squares refinement. A scale factor, coherent neutron scattering lengths of Fe atoms and a type I isotropic extinction parameter (Becker & Coppens, 1975) were varied, together with positional and anisotropic thermal parameters for all atoms. Neutron scattering lengths used are $b_c = 0.665$, $b_H = -0.374$, and $b_o = 0.580 \times 10^{-14}$ m (Shull, 1972). For the two crystallographically independent Fe atoms, refined values are $b_{Fe} = 0.948$ (4) and 0.951 (4) $\times 10^{-14}$ m, which agree to within experimental error with the value of 0.954 (6) given by Koester (1977).

Third- and fourth-order thermal tensors were introduced for the Fe atoms using an expansion developed by Johnson (1970*a,b*), and these higher-order terms were refined together with other parameters for the Fe atoms, in order to assess the importance of anharmonic thermal motion. The weighted R value after this refinement is 0.0013 lower than for the conventional refinement, and Hamilton's (1965) R -value test indicates that the model including higher-order terms gives significantly better fit to the data than does the conventional model at the 99.5% confidence level. However, there is no third- or fourth-order term with magnitude greater than 2.3σ .

Table 2. *Experimental and refinement parameters*

	78 K (neutron)	298 K (X-ray)
Crystal weight	3.2 mg	0.04 mg
Crystal volume (at room temperature)	1.83 mm ³	0.022 mm ³
Number of faces*	12	12
Number of reflections measured	4479	4118
Number of independent reflections†	3894	3110
Number of reflections used in refinement (n)‡	3856	3093
$R_c = \sum (\sum_{hkl} F_o^2 - F_c^2) / \sum n' \langle F_o^2 \rangle$	0.028	0.026
Number of variable parameters (m)	490	388
$R = \sum F_o^2 - k^2 F_c^2 / \sum F_o^2$	0.0428	0.0371
$wR = [\sum w(F_o^2 - k^2 F_c^2)^2 / \sum w F_o^4]^{1/2}$	0.0487	0.0590
$S = [\sum w(F_o^2 - k^2 F_c^2)^2 / (n - m)]^{1/2}$	1.1898	1.5719

* Forms {010}, {001}, {112}, {101}, {203}, {032}.

† Reflections with negative or zero intensities were eliminated.

‡ A few reflections with differences of more than 50% between intensities of symmetry-related observations were eliminated (38 neutron reflections and 17 X-ray reflections).

Final discrepancy factors are summarized in Table 2, while positional parameters for all atoms from the conventional refinement are listed in Table 3.*

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34687 (45 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion

Bond distances and angles are given in Figs. 1 and 2, respectively. Fe...C distances are listed in Table 4. It is somewhat difficult to compare the values obtained from the X-ray diffraction analysis with those from the neutron analysis because there are expected to be two sources of systematic differences between the results,

Table 3. *Fractional atomic coordinates*
Neutron values at 78 K X-ray values at 298 K

	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
Fe(<i>AB</i>)	0.0986 (1)	-0.31425 (9)	0.34744 (4)	0.09992 (4)	-0.31658 (4)	0.34865 (2)
C(1 <i>A</i>)	0.2476 (2)	-0.1521 (1)	0.43196 (6)	0.2536 (3)	-0.1562 (3)	0.4316 (1)
C(2 <i>A</i>)	0.0584 (2)	-0.1583 (1)	0.44565 (6)	0.0666 (3)	-0.1570 (3)	0.4455 (1)
C(3 <i>A</i>)	-0.0262 (2)	-0.0984 (2)	0.38478 (6)	-0.0159 (3)	-0.0988 (3)	0.3857 (1)
C(4 <i>A</i>)	0.1094 (2)	-0.0568 (1)	0.33351 (6)	0.1179 (3)	-0.0620 (3)	0.3345 (1)
C(5 <i>A</i>)	0.2797 (2)	-0.0898 (1)	0.36209 (6)	0.2839 (3)	-0.0974 (3)	0.3621 (1)
C(6 <i>A</i>)	0.3792 (2)	-0.2099 (1)	0.48049 (6)	0.3848 (3)	-0.2131 (3)	0.4803 (1)
O(1 <i>A</i>)	0.5445 (2)	-0.2057 (2)	0.45703 (8)	0.5467 (2)	-0.2133 (3)	0.4567 (1)
O(2 <i>A</i>)	0.3355 (2)	-0.2581 (2)	0.54032 (8)	0.3401 (2)	-0.2548 (2)	0.54067 (9)
C(1 <i>B</i>)	0.1617 (2)	-0.5626 (1)	0.34272 (6)	0.1565 (3)	-0.5640 (3)	0.3439 (1)
C(2 <i>B</i>)	-0.0259 (2)	-0.5586 (2)	0.35677 (7)	-0.0295 (3)	-0.5558 (3)	0.3585 (2)
C(3 <i>B</i>)	-0.1059 (2)	-0.4959 (2)	0.29515 (7)	-0.1073 (4)	-0.4940 (3)	0.2979 (2)
C(4 <i>B</i>)	0.0335 (2)	-0.4597 (2)	0.24430 (7)	0.0278 (4)	-0.4627 (3)	0.2470 (2)
C(5 <i>B</i>)	0.1995 (2)	-0.5000 (2)	0.27335 (6)	0.1913 (4)	-0.5056 (3)	0.2747 (1)
C(6 <i>B</i>)	0.2930 (2)	-0.6153 (1)	0.39365 (6)	0.2867 (3)	-0.6181 (3)	0.3941 (1)
O(1 <i>B</i>)	0.4586 (2)	-0.6138 (2)	0.37011 (8)	0.4481 (2)	-0.6220 (3)	0.3702 (1)
O(2 <i>B</i>)	0.2478 (2)	-0.6615 (2)	0.45307 (8)	0.2407 (2)	-0.6594 (2)	0.45411 (9)
Fe(<i>CD</i>)	-0.2793 (1)	0.00991 (9)	0.14632 (4)	-0.27841 (3)	0.00710 (4)	0.14627 (1)
C(1 <i>C</i>)	-0.4918 (1)	-0.1570 (1)	0.17436 (6)	-0.4898 (3)	-0.1573 (3)	0.1737 (1)
C(2 <i>C</i>)	-0.5508 (1)	0.0080 (1)	0.16729 (6)	-0.5465 (3)	0.0052 (3)	0.1676 (1)
C(3 <i>C</i>)	-0.4451 (2)	0.1374 (1)	0.21972 (6)	-0.4410 (3)	0.1334 (3)	0.2195 (1)
C(4 <i>C</i>)	-0.3211 (2)	0.0535 (1)	0.25908 (6)	-0.3195 (3)	0.0513 (3)	0.2582 (1)
C(5 <i>C</i>)	-0.3483 (2)	-0.1290 (1)	0.23048 (6)	-0.3477 (3)	-0.1289 (3)	0.2301 (1)
C(6 <i>C</i>)	-0.5633 (1)	-0.3220 (1)	0.12666 (6)	-0.5622 (3)	-0.3217 (3)	0.1268 (1)
O(1 <i>C</i>)	-0.4795 (2)	-0.4567 (2)	0.13584 (8)	-0.4837 (2)	-0.4556 (2)	0.13671 (9)
O(2 <i>C</i>)	-0.6939 (2)	-0.3317 (2)	0.08336 (8)	-0.6903 (2)	-0.3300 (2)	0.08221 (9)
C(1 <i>D</i>)	-0.1785 (1)	-0.0890 (1)	0.04728 (6)	-0.1797 (3)	-0.0910 (3)	0.0473 (1)
C(2 <i>D</i>)	-0.2449 (2)	0.0736 (1)	0.04174 (6)	-0.2425 (3)	0.0701 (3)	0.0423 (1)
C(3 <i>D</i>)	-0.1448 (2)	0.2038 (1)	0.09568 (6)	-0.1423 (3)	0.1979 (3)	0.0960 (1)
C(4 <i>D</i>)	-0.0187 (2)	0.1222 (1)	0.13456 (6)	-0.0184 (3)	0.1169 (3)	0.1346 (1)
C(5 <i>D</i>)	-0.0382 (1)	-0.0595 (1)	0.10486 (6)	-0.0409 (3)	-0.0612 (3)	0.1050 (1)
C(6 <i>D</i>)	-0.2489 (2)	-0.2561 (1)	0.00128 (6)	-0.2507 (3)	-0.2571 (3)	0.0014 (1)
O(1 <i>D</i>)	-0.1671 (2)	-0.3902 (2)	0.01366 (8)	-0.1727 (2)	-0.3889 (2)	0.01364 (9)
O(2 <i>D</i>)	-0.3738 (2)	-0.2676 (2)	-0.04501 (8)	-0.3733 (2)	-0.2658 (2)	-0.04578 (9)
H(1 <i>A</i>)	0.6236 (4)	-0.2539 (4)	0.4916 (2)	0.607 (5)	-0.262 (5)	0.484 (2)
H(2 <i>A</i>)	-0.0096 (4)	-0.2061 (4)	0.4923 (1)	0.011 (3)	-0.192 (3)	0.491 (1)
H(3 <i>A</i>)	-0.1705 (4)	-0.0919 (4)	0.3788 (2)	-0.135 (4)	-0.095 (3)	0.383 (1)
H(4 <i>A</i>)	0.0850 (4)	-0.0119 (4)	0.2805 (1)	0.111 (3)	-0.020 (3)	0.293 (1)
H(5 <i>A</i>)	0.4095 (4)	-0.0729 (4)	0.3362 (2)	0.391 (4)	-0.085 (3)	0.342 (1)
H(1 <i>B</i>)	0.5380 (4)	-0.6590 (4)	0.4065 (2)	0.523 (5)	-0.654 (5)	0.403 (2)
H(2 <i>B</i>)	-0.0941 (4)	-0.5949 (4)	0.4054 (2)	-0.086 (3)	-0.591 (3)	0.401 (1)
H(3 <i>B</i>)	-0.2463 (4)	-0.4758 (4)	0.2909 (2)	-0.225 (4)	-0.475 (4)	0.296 (2)
H(4 <i>B</i>)	0.0170 (5)	-0.4065 (4)	0.1933 (1)	0.016 (4)	-0.421 (4)	0.205 (2)
H(5 <i>B</i>)	0.3304 (4)	-0.4850 (4)	0.2491 (2)	0.290 (4)	-0.507 (4)	0.248 (2)
H(1 <i>C</i>)	-0.5355 (4)	-0.5626 (3)	0.1004 (1)	-0.524 (4)	-0.549 (4)	0.108 (2)
H(2 <i>C</i>)	-0.6505 (3)	0.0306 (3)	0.1266 (1)	-0.633 (3)	0.022 (3)	0.132 (1)
H(3 <i>C</i>)	-0.4534 (4)	0.2773 (3)	0.2279 (1)	-0.451 (3)	0.255 (3)	0.225 (1)
H(4 <i>C</i>)	-0.2229 (4)	0.1188 (3)	0.3016 (1)	-0.232 (3)	0.111 (3)	0.296 (1)
H(5 <i>C</i>)	-0.2739 (4)	-0.2275 (3)	0.2482 (1)	-0.290 (3)	-0.212 (3)	0.244 (1)
H(1 <i>D</i>)	-0.2192 (3)	-0.4957 (3)	-0.0220 (1)	-0.222 (4)	-0.477 (4)	-0.013 (2)
H(2 <i>D</i>)	-0.3519 (4)	0.0932 (3)	0.0040 (1)	-0.333 (3)	0.086 (3)	0.009 (1)
H(3 <i>D</i>)	-0.1659 (4)	0.3400 (3)	0.1073 (1)	-0.162 (3)	0.309 (4)	0.106 (1)
H(4 <i>D</i>)	0.0731 (4)	0.1888 (3)	0.1806 (1)	0.065 (3)	0.174 (3)	0.174 (1)
H(5 <i>D</i>)	0.0385 (3)	-0.1590 (3)	0.1212 (2)	0.023 (3)	-0.145 (3)	0.120 (1)

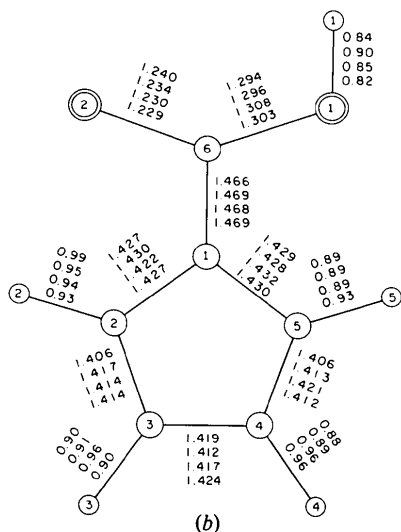
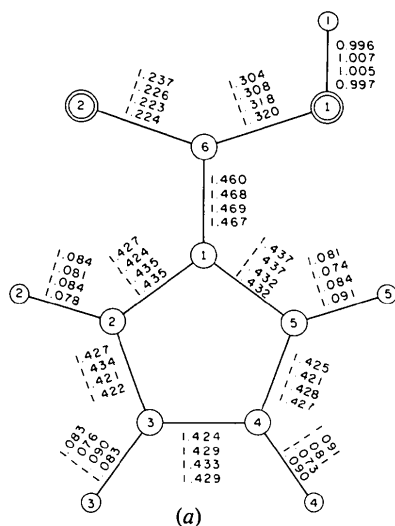


Fig. 1. Bond distances (Å) in the carboxycyclopentadienyl ligands. The four values for each bond correspond to the distances in rings A, B, C, and D, respectively. Double circles denote O atoms. (a) Neutron diffraction analysis at 78 K. Estimated standard deviations are 0.002 ~ 0.003 Å in all bonds. (b) X-ray diffraction analysis at 298 K. Estimated standard deviations are 0.003 Å for C—C and C—O, and 0.03 ~ 0.04 Å for C—H and O—H bonds.

viz the two experiments were carried out at different temperatures, and the effects of non-spherical charge density may cause the X-ray atomic positions to deviate from the locations of the nuclei. In this paper we have chosen to use mainly the results of the neutron diffraction analysis for purposes of discussion, because these are more accurate than the X-ray results, especially for parameters involving H atoms. The overall agreement between the two analyses is, however, quite good.

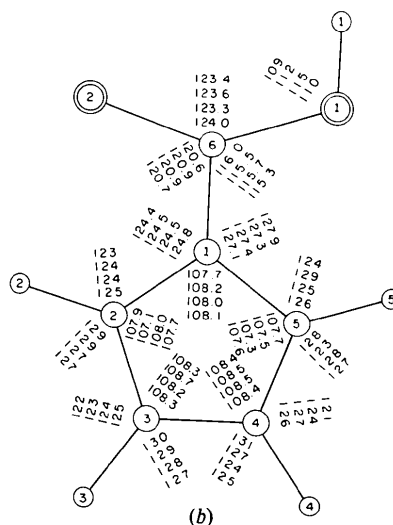
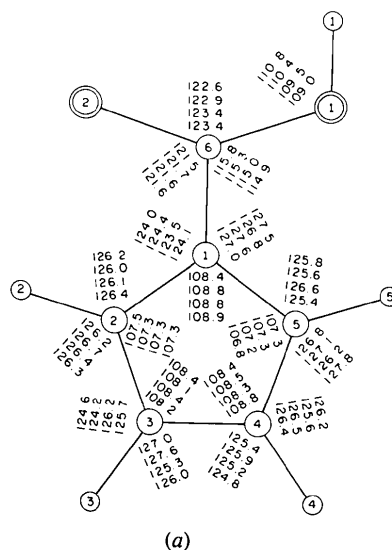


Fig. 2. Bond angles (°) in the carboxycyclopentadienyl ligands, with values shown in the same order as in Fig. 1. (a) Neutron diffraction analysis at 78 K. Estimated standard deviations are 0.1° for C—C—C and C—C—O, and 0.2° for C—C—H and C—O—H angles. (b) X-ray diffraction analysis at 298 K. Estimated standard deviations are 0.2 ~ 0.3° for C—C—C and C—C—O, and 1.0 ~ 2.0° for C—C—H and C—O—H angles.

Dimensions of the four independent carboxycyclopentadienyl (C_5H_4COOH) ligands are quite similar. Average distances are C(ring)—C(ring) = 1.429 (1), C(ring)—C(carboxyl) = 1.466 (2), C—O(H) = 1.313 (1), C=O = 1.228 (3), C—H = 1.083 (1) and O—H = 1.001 (3) Å.* Interior angles of Cp^\dagger rings show that the rings are slightly distorted from an ideal pentagonal shape. Also, the angles C(2)—C(1)—C(6)

* Standard deviations of mean values have been estimated as $\sigma(\bar{x}) = [\sum_{i=1}^n (x_i - \bar{x})^2 / n(n-1)]^{1/2}$. Neutron results are quoted.

† Abbreviations: Cp = cyclopentadienyl; Me = methyl.

Table 4. Fe...C distances (Å)

(a) Neutron at 78 K

	A ring	B ring	C ring	D ring
Fe...C(1)	2.041 (1)	2.042 (2)	2.040 (1)	2.037 (1)
Fe...C(2)	2.046 (1)	2.046 (2)	2.057 (1)	2.044 (1)
Fe...C(3)	2.055 (2)	2.052 (2)	2.059 (1)	2.052 (1)
Fe...C(4)	2.056 (1)	2.048 (1)	2.055 (1)	2.050 (1)
Fe...C(5)	2.050 (1)	2.045 (2)	2.040 (1)	2.057 (1)

Overall mean Fe...C 2.049 (2)

(b) X-ray at 298 K

	A ring	B ring	C ring	D ring
Fe...C(1)	2.038 (2)	2.041 (2)	2.036 (2)	2.042 (2)
Fe...C(2)	2.042 (2)	2.044 (2)	2.050 (2)	2.050 (2)
Fe...C(3)	2.052 (3)	2.046 (3)	2.056 (2)	2.057 (2)
Fe...C(4)	2.054 (3)	2.043 (3)	2.052 (2)	2.054 (2)
Fe...C(5)	2.045 (2)	2.046 (3)	2.041 (2)	2.048 (2)

Overall mean Fe...C 2.047 (1)

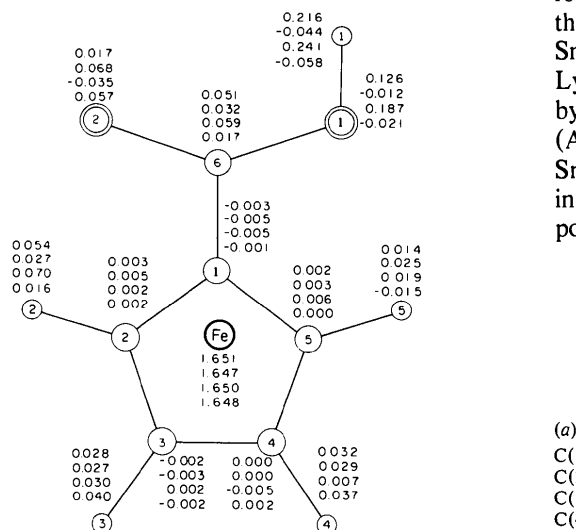


Fig. 3. Displacements (Å) from the least-squares plane through the five C atoms of the Cp rings A, B, C, and D, respectively, as determined in the neutron diffraction analysis at 78 K.

are significantly smaller than C(5)—C(1)—C(6). However, none of the mean distances O(1)...C(5) = 2.895 (4), O(2)...C(2) = 2.914 (3), O(1)...H(5) = 2.765 (12) and O(2)...H(2) = 2.797 (4) Å is unusually short, suggesting that it is difficult to explain these distortions by means of intramolecular steric interactions.

The mean Fe—ring distance of 1.649 (1) Å is essentially the same as that of 1.645 (2) Å found by neutron diffraction in ferrocene (Takusagawa & Koetzle, 1979a). These dimensions are only very slightly smaller than the value of 1.661 (4) Å calculated from the electron diffraction results for ferrocene in the gas phase at 410 K (Haaland & Nilsson, 1968). The Cp rings in 1,1'-ferrocenedicarboxylic acid are nearly

planar, but show marginally significant distortions toward C₂ (twist) forms as indicated in Fig. 3. The atoms attached to the Cp rings, except for H(5D), are displaced out of the ring planes toward the Fe atoms. The mean displacement is 0.030 (4) Å, corresponding to an inclination of the C—H or C—C (exocyclic) vectors to the plane of 1.5 (3)°. In ferrocene, our neutron diffraction analysis (Takusagawa & Koetzle, 1979a) indicated a mean displacement toward the Fe atom of 0.030 (7) Å or 1.6 (4)°, while the electron diffraction study (Haaland & Nilsson, 1968) indicated a displacement of 0.07 (2) Å, corresponding to an inclination of the C—H vector to the plane of 3.7 (9)°. The same sense of displacement has been measured by electron diffraction in several unsubstituted metallocenes (Haaland, 1975). By contrast, in X-ray studies of the octa- and decamethyl derivatives (Me₅Cp)₂Mn, (Me₄Cp)₂Fe, and (Me₅Cp)₂Fe, the methyl C atoms are found to be displaced approximately 0.06 Å away from the metal atoms (Freyberg, Robbins, Raymond & Smart, 1979; Struchkov, Andrianov, Sal'nikova, Lyatifov & Materikova, 1978). This result is confirmed by a recent electron diffraction study of (Me₅Cp)₂Fe (Almenningen, Haaland, Samdal, Brunvoll, Robbins & Smart, 1979). The opposite sense of the displacements in these substituted systems has been described as possibly due to intra-ring steric effects.

Table 5. Ring-orientation parameters

	Neutron at 78 K	X-ray at 298 K	X-ray at 78 K*
(a) Torsion angles defined by C—(ring center 1)—(ring center 2)—C†			
C(1A)...C(1B)	1.6 (1)°	1.2 (1)°	1.7 (1)°
C(2A)...C(2B)	1.4 (1)	1.1 (1)	1.5 (1)
C(3A)...C(3B)	1.6 (1)	1.5 (1)	1.3 (1)
C(4A)...C(4B)	1.8 (1)	1.1 (1)	1.6 (1)
C(5A)...C(5B)	1.5 (1)	1.3 (1)	1.4 (1)
C(1C)...C(1D)	−0.8 (1)	−0.6 (1)	
C(2C)...C(2D)	−0.7 (1)	−0.4 (1)	
C(3C)...C(3D)	−0.7 (1)	−0.6 (1)	
C(4C)...C(4D)	−0.8 (1)	−0.2 (1)	
C(5C)...C(5D)	−0.8 (1)	−0.6 (1)	
(b) Angles defined by (ring center 1)—Fe—(ring center 2)			
(A ring)—Fe(AB)—(B ring)	177.1 (1)°	176.9 (1)°	177.3 (1)°
(C ring)—Fe(CD)—(D ring)	176.4 (1)	176.4 (1)	
(c) Dihedral angles between the pairs of Cp rings and the maximum and minimum distances from the least-squares plane of one Cp ring to the C atoms of another ring			
(A ring)—(B ring)	2.3 (2)°	2.4 (2)°	1.5 (1)°
Maximum distance‡	3.314 (3) Å	3.320 (4) Å	3.302 (2) Å
Minimum distance‡	3.268 (3)	3.271 (4)	3.273 (2)
(C ring)—(D ring)	2.5 (2)°	2.4 (2)°	
Maximum distance‡	3.323 (3) Å	3.331 (4) Å	
Minimum distance‡	3.270 (3)	3.266 (4)	
(d) Distances between ring centers			
(A ring)...(B ring)	3.296 (2) Å	3.301 (2) Å	3.290 (1) Å
(C ring)...(D ring)	3.297 (2)	3.306 (2)	

* Monoclinic form (P2₁/c; Z = 4) (Takusagawa & Koetzle, 1979b).

† Calculated according to the IUPAC—IUB (1970) conventions.

‡ Maximum distance = [C(1) + C(2) + C(5)]/3.0; minimum distance = [C(3) + C(4)]/2.0.

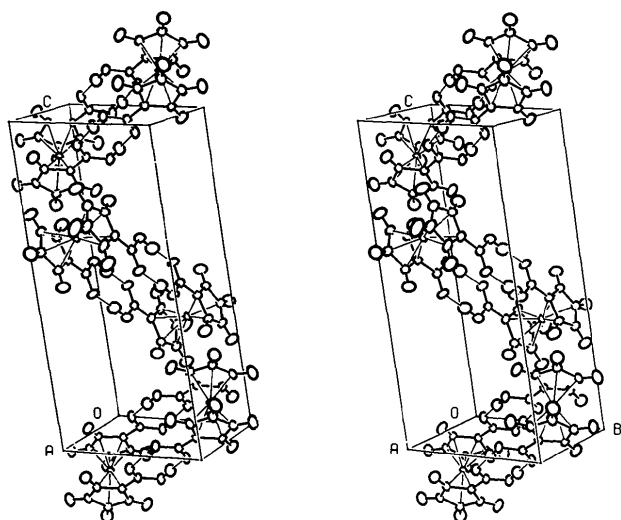


Fig. 4. Stereoscopic view (Johnson, 1976) of the crystal structure of 1,1'-ferrocenedicarboxylic acid in the triclinic modification.

The 1,1'-ferrocenedicarboxylic acid molecules take an almost totally eclipsed configuration. The angles of twist, defined as the torsion angle between one C atom, the two ring centers, and a second C atom, are given in Table 5. A quite similar configuration has been found in the monoclinic form (Palenik, 1969). In both modifications the angles defined by (ring center)—Fe—(ring center) deviate significantly from 180° , with the Fe atoms being moved toward C(1) by $0.013(2)$ Å (mean value). The Cp ring planes are tilted slightly with the opening in the C(1) direction, as one might expect.

Two molecules of 1,1'-ferrocenedicarboxylic acid related by a center of symmetry form a hydrogen-bonded dimer. Fig. 4 illustrates the packing of these dimers in the unit cell. The hydrogen-bonding geometry is illustrated in Fig. 5, where it is apparent that $H\cdots O$ distances correlate inversely with $O-H$ covalent-bond distances. Neighboring dimers are joined *via* weak $C-H\cdots O$ -type interactions which are found only around carbonyl oxygens.* It should be noted that the donor groups in $C-H\cdots O$ interactions are H(2) and H(5) which are electronically poorer than the H(3) and H(4) atoms. The $H\cdots O$ vectors are in reasonable alignment with the expected direction of the lone-pair electrons on the carbonyl oxygens. The $C(5D)-H(5D)\cdots O(2C)$ interaction could be responsible for the atypical displacement of H(5D) from the Cp ring plane that was mentioned earlier. If H(5D) were displaced out of the Cp ring by 0.03 Å toward the Fe atom, as is the case for the other H atoms, the $H(5D)\cdots O(2C)$ distance would be increased from 2.584 to 2.611 Å.

* Curiously, these interactions occur between dimers of the same type; they do not link the *AB* molecules to *CD* molecules. The interactions involving the *CD* molecules are somewhat weaker than those involving *AB*.

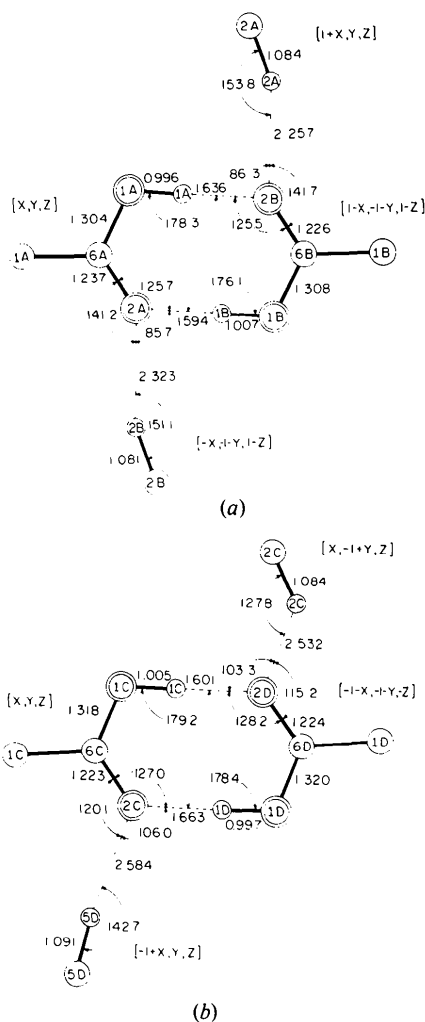


Fig. 5. Hydrogen-bonding geometry (lengths in Å, angles in deg) (a) around rings A and B; (b) around rings C and D.

The observed thermal parameters from the low-temperature neutron study have been fitted to general rigid-body motions described by T, L, and S tensors (Schomaker & Trueblood, 1968). When one entire molecule (except for H atoms) is taken as a rigid body, the r.m.s. error of fit is $\langle \Delta U_{ij}^2 \rangle^{1/2} = 0.0024$ Å², and no special trend shows in the tensor components. The large apparent libration (L) around the direction perpendicular to the Cp rings that is observed in ferrocene itself does not occur in this material. Bond distances corrected for effects of thermal motion are longer than uncorrected distances by *ca* $0.001-0.004$ Å.

It is interesting to compare the molecular and crystal structure of the triclinic form ($P\bar{1}$) with that of the monoclinic form ($P2_1/c$). The major difference between the molecular structures in the two modifications is found in the dimensions of the carboxyl groups. In the triclinic form, the groups are ordered, *i.e.* C—O(H)

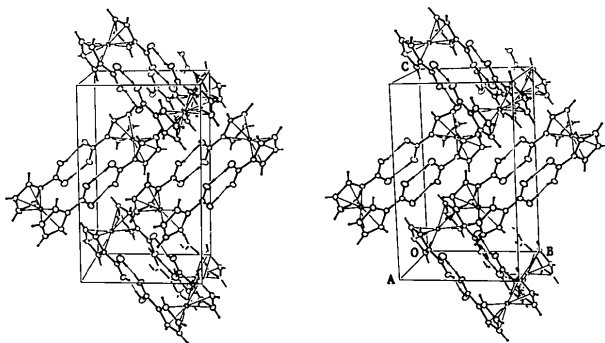


Fig. 6. Stereoscopic view of the crystal structure of 1,1'-ferrocenedicarboxylic acid in the monoclinic modification.

and C=O distances are significantly different from one another, and the acidic proton is covalently bonded to the O atom on one side of the hydrogen bond only. On the other hand, in the monoclinic form the carboxyl groups are disordered, *i.e.* the difference between the two C—O distances is much smaller than that observed in a normal carboxyl group, and the acidic proton is found to be assigned approximately 50% to each O atom on the basis of a low-temperature (78 K) X-ray diffraction analysis (Takusagawa & Koetzle, 1979*b*). As mentioned above in the experimental section, the triclinic modification is recrystallized by slow evaporation of solvent at room temperature. On the other hand, the monoclinic modification is only obtainable from hot solution (≥ 333 K). Therefore, the triclinic modification may be considered to be recrystallized under conditions of lower entropy than the monoclinic modification, and in turn would be expected to show more complete ordering. It is naturally recognized that the monoclinic crystal consists of molecular dimers in two different orientations, which are mirror images of one another and distributed approximately in a random fashion.

The crystal structure in the monoclinic form is shown in Fig. 6, and a superposition of the structures in both crystal forms is illustrated in Fig. 7. The cell parameters as given in Table 1 are quite different, but unit-cell volumes ($Z = 4$) for the two modifications are essentially the same. As seen in Fig. 7, the molecular packing in the two forms differs considerably, but in both structures pairs of molecules are hydrogen bonded around an inversion center to form dimers. These dimers are joined in a three-dimensional fashion by weak C—H \cdots O interactions. In the triclinic form, acceptors in the C—H \cdots O interactions are always carbonyl oxygens, while in the monoclinic form, the disordered packing geometry is such that both carbonyl and hydroxyl oxygens may serve as acceptors, as can be seen in Fig. 6. The H \cdots O distances in question are similar for both forms, and range from 2.25 to 2.6 Å.

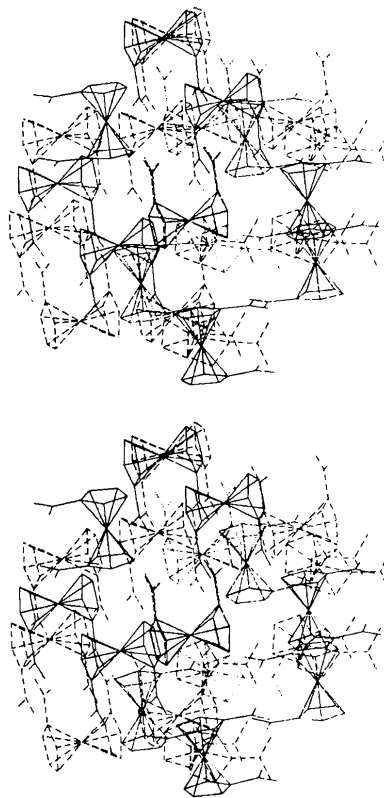


Fig. 7. Superimposed view of the two crystalline modifications, in which the relative orientation has been adjusted so that the two images are coincident for the central molecule. The molecules drawn with solid and dashed lines belong to the monoclinic and triclinic forms, respectively.

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Structure Cristalline de l'Hexachlorotellurate(IV) de Bis(pyridinium)

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Abstract

$[\text{C}_5\text{H}_6\text{N}]_2[\text{TeCl}_6]$ is monoclinic, space group $B2/m$. $a = 12.882$ (6), $b = 8.004$ (3), $c = 8.470$ (2) Å and $\gamma = 96.84$ (4)°. $Z = 2$. $D_m = 1.92$ (2), $D_c = 1.91$ Mg m⁻³. The crystal structure was determined from single-crystal Enraf–Nonius CAD-4 diffractometer data. The final R is 0.034 for 1091 independent reflections. The TeCl_6^{2-} ions constitute layers which alternate with double layers of $\text{C}_5\text{H}_6\text{N}^+$ ions. The position of the nitrogen atom in the pyridinium ring is discussed.

Introduction

L'hexachlorotellurate de bis(pyridinium) a été préparé par action de l'acide chlorhydrique concentré sur le

dioxyde de tellure TeO_2 , et addition de pyridine à la solution ainsi obtenue. Il cristallise dans le système monoclinique. Les dimensions de la maille indiquées ci-dessus ont été déterminées à l'aide d'un diffractomètre automatique Enraf–Nonius CAD-4 utilisant le rayonnement $\text{Mo } K\alpha$. Elles sont relativement voisines des dimensions indiquées par Aynsley & Hazell (1963) et par Khodadad (1965).

Les extinctions systématiques autorisent les trois groupes spatiaux $B2$, Bm et $B2/m$. L'étude de monocristaux à l'aide d'un goniomètre optique à deux cercles a permis de montrer que les faces se correspondent deux à deux, d'une part par un axe binaire, d'autre part par un plan de symétrie perpendiculaire à l'axe binaire. Le groupe spatial le plus vraisemblable est donc le groupe $B2/m$. Ce groupe a d'abord été confirmé, comme cela sera précisé ci-après, par le fait que les