JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

PHELPS, D. W., KAHN, E. M. & HODGSON, D. J. (1975). *Inorg. Chem.* **14**, 2486–2490.

RILLEMA, D. P., JONES, D. S. & LEVY, H. A. (1979). *J. Chem. Soc. Chem. Commun.* pp. 849–851.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

# Solid-State Structure of Ferrocenecarboxylic Acid, [Fe(C₅H₄CO₂H)(C₅H₅)]

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**Abstract.** $M_r = 230.05$, monoclinic, $P2_1/n$, $a = 5.797$ (1), $b = 12.896$ (3), $c = 12.586$ Å, $\beta = 96.96$ (1)°, $V = 934.1$ (3) Å³, $Z = 4$, $D_x = 0.818$ g cm⁻³, $\lambda(\text{Mo } K\bar{\alpha}) = 0.7107$ Å, $\mu = 7.889$ cm⁻¹, $F(000) = 236.0$, $T = 296$ K, $R = 0.053$ for 885 observed reflections. The structure consists of hydrogen-bonded pairs of molecules located so that the geometric center of the hydrogen-bonding framework coincides with a crystallographic center of inversion. The O⋯O distance is $2.714$ (14) Å and the $(C_5H_5)(C_5H_4)$Fe moieties are eclipsed. Comparisons are made between this structural determination and the study of ferrocene-1,1′-dicarboxylic acid reported by Takusagawa & Koetzle [*Acta Cryst.* (1979), B**35**, 2888–2896].

**Introduction.** The study of the chemistry of ferrocene and other metallocenes has become one of the largest areas of interest in the whole of organometallic chemistry since the first reports of this revolutionary compound and its congeners (Kealy & Pauson, 1951). One of the earliest evidences of the aromatic nature of ferrocene (Wilkinson, Rosenblum, Whiting & Woodward, 1952) was the dissociation constant of ferrocenecarboxylic acid (FCAH), after the determination of which studies of electrophilic substitution reactions and derivatizations followed rapidly (Pauson, 1977, and references therein). Despite the early recognition of the importance of the title compound (Benkesen, Goggin & Scholl, 1954), its structure in the single crystal has never been reported.

We have recently undertaken an exploration of the anion of the title compound as a ligand for the synthesis of mixed-metal species containing both iron and dimeric units made up of the Group VI transition elements (Cotton, Reid & Tocher, 1984). It was of interest to us to be able to make direct comparisons between the structure of the free acid and the structure of its anion upon ligation to such a dimetal unit. We have therefore carried out a single-crystal X-ray study of the free acid, the results of which we report here.

**Experimental.** Material studied was a recrystallized (tetrahydrofuran–hexane) commercial (Aldrich Chemical Company) sample. Well formed crystal, $0.40 \times 0.15 \times 0.15$ mm, Enraf–Nonius CAD-4 automated diffractometer, graphite monochromator, automatic search routine located and centered 25 intense reflections, $12 < 2\theta < 37°$, from which unit-cell dimensions derived; systematic absences uniquely defined space group as $P2_1/n$; 1214 unique reflections, $5 < 2\theta < 50°$, 885 $(I > 3\sigma)$ collected, $0 < h < 7$, $0 < k < 12$, $-12 < l < 12$, three intensity standards checked every hour of exposure time; no decay, random fluctuations of *ca* 3% during collection; empirical absorption correction, $\psi$ scan for each of nine reflections near $\chi = 90°$ measured, each reflection measured at 10° intervals from $\psi = 0$ to $\psi = 360°$, normalized transmission factors 0.98 to 0.82; structure solved by conventional heavy-atom methods (Bino, Cotton & Fanwick, 1979). All nonhydrogen atoms refined by full-matrix least squares using anisotropic and, for C(1′), isotropic thermal parameters, carboxylate hydrogen atom (from $F_o - F_c$ map) also with isotropic thermal parameter, $\sum w ||F_o| - |F_c||/\sum |F_o|$ minimized; $R = 0.053$, $wR = 0.064$, $w = 1/\sigma^2(|F_o|)$, scale factor = 0.971 (2), $\Delta_{max}/\sigma = 0.21$, $\Delta\rho$ excursion in final difference Fourier map $0.583$ e Å⁻³; neutral atomic scattering factors and $f'$, $f''$ values from *International Tables for X-ray Crystallography* (1974). All computations carried out on the departmental VAX-11/780 with Enraf–Nonius (1981) VAX-*SDP* software.

**Discussion.** The positional parameters and equivalent isotropic thermal parameters are given in Table 1. The structure of the molecule is given in Fig. 1, together with the numbering scheme used. Fig. 2 is an *ORTEP*

  

(Johnson, 1965) stereodiagram of the contents of the unit cell. The hydrogen-bonding framework is readily apparent, with its centroid coinciding with a center of inversion. The carbocyclic rings are coplanar and eclipsed within the limits of experimental error. Bond distances and angles are given in Table 2.*

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\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39963 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## Table 1. *Positional and equivalent isotropic thermal parameters and their e.s.d.'s*

Anisotropically refined atoms are given in the form of isotropic equivalent thermal parameter defined as $\frac{4}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

|       | $x$        | $y$         | $z$         | $B(\text{Å}^2)$ |
|-------|-----------|-------------|-------------|-----------------|
| Fe    | 0·6273 (2) | 0·18033 (8) | 0·32059 (9) | 1·94 (2)        |
| O(1)  | 0·757 (1)  | 0·4333 (5)  | 0·4615 (5)  | 4·4 (2)         |
| O(2)  | 0·383 (1)  | 0·4388 (5)  | 0·3922 (5)  | 4·4 (2)         |
| C(0)  | 0·586 (2)  | 0·4058 (6)  | 0·3890 (8)  | 3·1 (2)         |
| C(1)  | 0·642 (1)  | 0·3364 (5)  | 0·3098 (7)  | 2·4 (2)         |
| C(1') | 0·743 (2)  | 0·1018 (7)  | 0·4562 (8)  | 3·0 (2)*        |
| C(2)  | 0·868 (2)  | 0·2915 (6)  | 0·2992 (8)  | 2·8 (2)         |
| C(2') | 0·723 (2)  | 0·0323 (6)  | 0·3686 (8)  | 3·4 (2)         |
| C(3)  | 0·850 (2)  | 0·2226 (7)  | 0·2096 (8)  | 3·1 (2)         |
| C(3') | 0·486 (2)  | 0·0345 (6)  | 0·3207 (8)  | 4·4 (2)         |
| C(4)  | 0·598 (2)  | 0·2244 (7)  | 0·1641 (7)  | 3·4 (2)         |
| C(4') | 0·367 (2)  | 0·1038 (7)  | 0·377 (1)   | 3·5 (2)         |
| C(5)  | 0·485 (2)  | 0·2950 (6)  | 0·2202 (7)  | 2·4 (2)         |
| C(5') | 0·530 (2)  | 0·1490 (8)  | 0·4683 (9)  | 5·2 (3)         |
| H     | 0·67 (1)   | 0·487 (6)   | 0·504 (6)   | 2 (2)*          |

\* Refined isotropically.
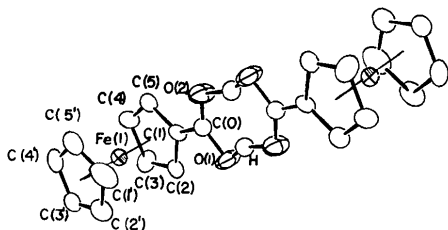


Fig. 1. *ORTEP* (Johnson, 1965) diagram of the [Fe($\eta^5$–C$_5$H$_4$-CO$_2$H)($\eta^5$–C$_5$H$_5$)]$_2$ dimer.
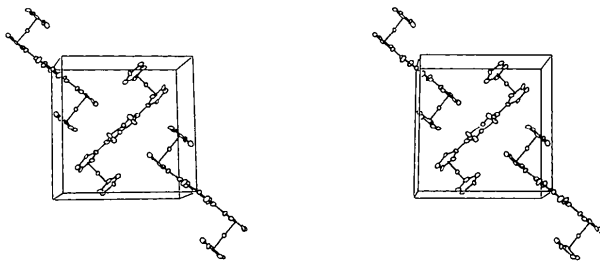


Fig. 2. *ORTEP* (Johnson, 1965) stereoview of the contents of the unit cell viewed along **a**.

## Table 2. *Molecular geometry*

(*a*) Bond distances (Å) and bond angles (°) and their e.s.d.'s for [Fe($\eta^5$–C$_5$H$_4$CO$_2$H)($\eta^5$–C$_5$H$_5$)]

| | | | |
|---|---|---|---|
| Fe–C(1)  | 2·020 (6)  | Fe–C(5)   | 2·052 (6)  |
| Fe–C(1') | 2·027 (8)  | Fe–C(5')  | 2·048 (18) |
| Fe–C(2)  | 2·041 (10) | C(0)–C(1) | 1·407 (15) |
| Fe–C(2') | 2·058 (7)  | C(0)–O(1) | 1·313 (8)  |
| Fe–C(3)  | 2·084 (14) | C(0)–O(2) | 1·261 (15) |
| Fe–C(3') | 2·052 (8)  | O(1)–H    | 1·03 (12)  |
| Fe–C(4)  | 2·037 (11) | O(1)···O(2) | 2·714 (14) |
| Fe–C(4') | 2·004 (14) |           |            |

| | | | |
|---|---|---|---|
| C(0)–C(1)–C(2) | 127·43 (7)  | C(1')–C(2')–C(3') | 107·32 (10) |
| C(1)–C(2)–C(3) | 109·78 (6)  | C(2')–C(3')–C(4') | 108·06 (7)  |
| C(2)–C(3)–C(4) | 105·50 (9)  | C(3')–C(4')–C(5') | 109·78 (9)  |
| C(3)–C(4)–C(5) | 108·47 (7)  | C(4')–C(5')–C(1') | 103·06 (11) |
| C(4)–C(5)–C(1) | 110·45 (8)  | C(5')–C(1')–C(2') | 111·78 (7)  |
| C(5)–C(1)–C(0) | 127·02 (9)  |                   |             |
| C(5)–C(1)–C(2) | 105·56 (9)  |                   |             |

| | |
|---|---|
| C(1)–C(0)–O(1) | 116·33 (10) |
|         –O(2)  | 122·42 (7)  |
| O(1)–C(0)–O(2) | 121·24 (11) |
| C(0)–O(1)–H    | 100·35 (37) |

(*b*) Comparison of selected bond distances (Å)

| Structural parameters | FCAH | FDAH[i] |
|---|---|---|
| C$_{(ring)}$–C$_{(ring)}$ (avg.)[ii] | 1·442 (13) | 1·429 (1) |
| C$_{(ring)}$–C$_{(carboxyl)}$        | 1·407 (15) | 1·466 (2) |
| C–O(H)                               | 1·313 (8)  | 1·313 (1) |
| C=O                                  | 1·261 (15) | 1·228 (3) |
| O–H                                  | 1·03 (12)  | 1·001 (3) |
| C$_{(ring)}$–C$_{(ring)}$[iii]       | 1·429 (13) | 1·429 (1) |

(i) Neutron data, *cf.* Takusagawa & Koetzle (1979). (ii) C$_5$H$_4$CO$_2$H ring. (iii) C$_5$H$_5$ ring.

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An interesting comparison may be drawn by consulting the reported structure (Takusagawa & Koetzle, 1979) of ferrocene-1,1'-dicarboxylic acid (hereafter FDAH). Our discussion will deal with the triclinic (Takusagawa & Koetzle, 1979) rather than the monoclinic (Palenik, 1969) polymorph, as the latter exhibits disorder in the carboxyl moiety. It should be mentioned at the outset that the triclinic structure cited was derived from neutron diffraction data recorded at low temperature and is therefore an inherently more precise study. A comparison of salient molecular dimensions for FCAH and FDAH is given in part (*b*) of Table 2. For FCAH the C$_5$H$_4$ ring possesses an average C$_{(ring)}$–C$_{(ring)}$ distance of 1·442 (13) Å, which is indistinguishable within the limits of experimental error from that of FDAH [1·429 (1) Å]. This distance is likewise comparable to the analogous distance within the C$_5$H$_5$ ring of FCAH, with an average C$_{(ring)}$–C$_{(ring)}$ distance of 1·429 (13) Å. The C$_{(ring)}$–C$_{(carboxylate)}$ distance of 1·407 (15) Å is noticeably shorter than the analogous distance in FDAH, *viz* 1·466 (2) Å; furthermore, the C=O distance of 1·261 (15) Å in the title compound is longer than that in FDAH [1·228 (3) Å], although the latter difference is at the limit of statistical significance. The differences in the C$_{(ring)}$–C$_{(carboxylate)}$ distances

could result from the higher degree of thermal motion present at ambient temperatures as compared to the low temperature at which the cited neutron study was performed. Still, the discrepancies may result from more subtle factors. The possibility of electronic perturbations resulting from interactions between neighboring dimers in FDAH is slight, as the contacts are rather long (*ca* 2·25 to 2·54 Å) and involve two crystallographically independent molecules. A further possibility is that the observed differences result from perturbations attributable to the presence of an 'extra' carboxylate group on the second ring in FDAH.

Ligation of the FCA⁻ anion to dimetal centers results in considerable changes in its molecular dimensions. These observations will be reported in detail in the near future (Cotton *et al.*, 1984).

**References**

BENKESEN, R. A., GOGGIN, D. & SCHOLL, G. (1954). *J. Am. Chem. Soc.* **76**, 4025–4026.
BINO, A., COTTON, F. A. & FANWICK, P. E. (1979). *Inorg. Chem.* **18**, 3558–3562.
COTTON, F. A., REID, A. H. JR & TOCHER, J. H. (1984). In preparation.
Enraf–Nonius (1981). *Structure Determination Package.* Enraf–Nonius, Delft.
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
KEALY, T. J. & PAUSON, P. L. (1951). *Nature (London)*, **168**, 1039–1040.
PALENIK, G. J. (1969). *Inorg. Chem.* **8**, 2744–2749.
PAUSON, P. L. (1977). *Coordination Chemistry*, Vol. 17, edited by E. WEISS, pp. 839–855 (first 25 years). IUPAC, Oxford: Pergamon Press.
TAKUSAGAWA, F. & KOETZLE, T. F. (1979). *Acta Cryst.* **B35**, 2888–2896.
WILKINSON, G., ROSENBLUM, M., WHITING, M. C. & WOODWARD, R. B. (1952). *J. Am. Chem. Soc.* **74**, 2125–2126.

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# Structure of the 2/1 Complex Dibenzotetrathiafulvalenium Hexabromodicuprate(II),*
## $2C_{14}H_8S_4^+.Cu_2Br_6^{2-}$

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**Abstract.** $M_r = 1215·49$, triclinic, $P\bar{1}$, $a = 9·982$ (1), $b = 12·122$ (1), $c = 7·893$ (1) Å, $\alpha = 83·70$ (1), $\beta = 112·80$ (1), $\gamma = 104·97$ (1)°, $V = 850·4$ (1) Å³, $Z = 1$, $D_x = 2·37$, $D_m = 2·36$ g cm⁻³, $\lambda(Cu\ K\alpha) = 1·5418$ Å, $\mu(Cu\ K\alpha) = 140·45$ cm⁻¹, $F(000) = 580$, $T = 293$ K, $R = 0·039$ for 2678 observed reflections. Cation radicals are stacked to form columns along **c** [interplanar distance 3·5 (5) Å]. Shortest contacts between adjacent cations in a column are S···S 3·391 (2) Å. The central C=C bond of the cation is 1·397 (6) Å.

**Introduction.** Organic charge-transfer radical salts consisting of the electron donor TTF (tetrathiafulvalene) and an electron acceptor such as TCNQ (tetracyano-*p*-quinodimethane) display high electrical conductivities (Cohen, Coleman, Garito & Heeger, 1974). The crystal structures of the organic conductors are composed of characteristic columns in which the donor cation and acceptor anion radicals are stacked separately. Electrons and holes are delocalized in the respective columns. This causes high anisotropy in the solid-state properties of the organic conductors, such as electrical, optical and magnetic ones. Many compounds analogous to TTF have been synthesized to obtain the radical salts with high electrical conductivity. Dibenzo-tetrathiafulvalene (DBTTF) is one of them and the direct oxidation of DBTTF by halogens and metal halides was reported to yield radical salts such as $(DBTTF)_2I_3$ (Shibaeva, Rozenberg, Aldoshina, Lubovskaya & Khidekel, 1979), $(DBTTF)_8(SnCl_6)_3$ and $(DBTTF)_3(SnBr_6)$ (Shibaeva, Rozenberg & Lubovskaya, 1980), and $(DBTTF)_2(Cu_2Cl_6)$ (Honda, Katayama, Tanaka & Tanaka, 1985). In this paper, we report the crystal structure of the complex of DBTTF with cupric bromide.