Contribution from the Department of Chemistry, Northeastern University, Boston, Massachusetts 02115,
and Experimental Station E328, Central Research and Development Department,
E. I. du Pont de Nemours and Company, Inc., Wilmington, Delaware 19898

Structural and ^{57}Fe Mössbauer Characterization of 1:1 and 2:3 Ferrocenium Salts of 7,7,8,8-Tetracyanoperfluoro-*p*-quinodimethane

Joel S. Miller,*[1a] Jian H. Zhang, and William M. Reiff*[1b]

Received May 23, 1986

The reaction of ferrocene and 7,7,8,8-tetracyanoperfluoro-*p*-quinodimethane, $(TCNQ)F_4$, results in the formation of purple reflecting crystals of $[Fe(C_5H_5)_2][(TCNQ)F_4]$ and $[Fe(C_5H_5)_2]_2[(TCNQ)F_4]_3$ composition. Crystals of the 1:1 salt belong to the centrosymmetric monoclinic $P2_1/n$ space group [a = 6.886 (6) Å, b = 13.774 (7) Å, c = 21.085 (11) Å, β = 93.87 (5)°, V = 1995.3 Å^3, Z = 4]. The unit cell is comprised of segregated one-dimensional chains of $S = {}^1/_2$ cations and $S = {}^1/_2$ anions stacked along a. The parallel anions form a dimerized chain along the a axis with intra- and interdimer spacings of 3.225 and 3.675 Å, respectively. Each anion chain is surrounded by six cation chains with the interchain $Fe^{III}—Fe^{III}$ distance of 6.886 Å. The shortest intrachain Fe—Fe distance is 7.679 Å. The cation possesses one ordered and one disordered C_5H_5 ring. The average Fe—C and C—C distances for the ordered C_5H_5 ring are 2.094 and 1.438 Å, respectively, which are typical of the cation. The cyano groups of the anion form a plane that forms a 4.9° dihedral angle with the C_6F_4 ring. The ring C═C, C—C(C(CN)$_2$), and C—F distances average 1.36, 1.42, and 1.35 Å, respectively. The average ring—C(CN)$_2$, C—CN, and C≡N distances are 1.42, 1.43, and 1.14 Å, respectively. The average ring—C—CN and NC—C—CN angles are 123 and 113.5°, respectively. The structure was refined to R = 6.3% and R_w = 6.8% at room temperature. Crystals of the 2:3 salt belong to the centrosymmetric monoclinic $C2/c$ space group [a = 26.885 (11) Å, b = 14.591 (5) Å, c = 13.901 (4) Å, β = 116.97 (2)°, V = 4859.9 Å^3, Z = 4]. The unit cell is complex and is comprised of 1 and 0.5 unique $(TCNQ)F_4$ moieties and a unique ferrocenium cation. The anions are distributed as a $[(TCNQ)F_4]_2^{2-}$ dimer and a neutral $(TCNQ)F_4$ molecule perpendicular to the 2− dimer separated by a short intermolecular N···C contact of 3.14 Å. The cation also possesses one ordered and one disordered C_5H_5 ring. The average Fe—C and C—C distances for the ordered ring are 2.091 and 1.414 Å, respectively, which are typical of the cation. The ring C═C, C—C(C(CN)$_2$), and C—F distances average 1.345, 1.419, and 1.353 Å for the anion and 1.331, 1.439, and 1.333 Å for $(TCNQ)F_4$, respectively. For the anion the average ring—C(CN)$_2$, C—CN, and C≡N distances are 1.419, 1.423, and 1.148 Å, respectively, whereas $(TCNQ)F_4$ possesses average ring—C(CN)$_2$, C—CN, and C≡N distances of 1.373, 1.438, and 1.149 Å, respectively. The structure was refined to R = 5.4% and R_w = 6.8% at −97 °C. The ^{57}Fe Mössbauer spectra of both the 1:1 and 2:3 phases between 1.6 and 300 K correspond to singlets (e.g.: 1:1 phase, $\delta_{1.6K}$ = 0.530 mm/s and Γ = 0.512 mm/s; 2:3 phase, $\delta_{1.6K}$ = 0.559 mm/s and Γ = 0.734 mm/s), suggesting rapid paramagnetic relaxation at the low-spin Fe(III) sites. The infrared ν(C≡N) for $(TCNQ)F_4$ is 2225 m cm^{-1}, whereas it occurs at 2179 s and 2195 s cm^{-1} for $[(TCNQ)F_4]^{\bullet-}$.

Introduction

Linear-chain, 1-D, charge-transfer complexes have been characterized to frequently exhibit unusual electrical properties.[2–5] In contrast, the study of the magnetic properties particularly with the focus toward highly magnetic materials has not been intensive.[6] However, since we reported[7] on the metamagnetic behavior observed for the 1-D phase of $[Fe(C_5Me_5)_2]^{\bullet+}[TCNQ]^{\bullet-}$ (TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane), we have purposely sought to prepare charge-transfer complexes possessing a ferromagnetic ground state. Thus, we have undertaken the systematic study of the structure–function relationship between salts primarily comprising metallocenium cations and planar polycyano anions with the goal of elucidating the electronic and steric requirements for the stabilization of the ferromagnetic state in a molecular material. Previously we have reported that $[Fe(C_5Me_5)_2]^{\bullet+}$ salts of 2,3-dichloro-4,5-dicyanobenzoquinone [DDQ],[8] $[C_3(CN)_5]^-$,[9] $[C(CN)_3]^-$,[10] $[p\text{-}(NC)_2C_6H_4C(O)CN]^-$,[9] $[FeCl_4]^-$,[11] and $[FeBr_4]^-$ [12] are paramagnetic at the lowest temperatures measured, typically <4.2 K. Utilizing the tetracyanoethylenide[9,13] and hexacyanobutadienide[14] anions as the $[Fe(C_5Me_5)_2]^{\bullet+}$ salts, we have demonstrated the occurrence of ferromagnetic exchange in a charge-transfer salt and moreover a 3-D ferromagnetic ground state. The former charge-transfer complex possesses a spontaneous magnetic moment at zero applied field. With our observation of meta- and ferromagnetic behavior in 1-D charge-transfer complexes, and the theoretical encouragement supplied McConnell[15] and later by Breslow,[6a] we are continuing our efforts to prepare new materials exhibiting ferromagnetic coupling. We specifically aim to prepare complexes with higher transition temperatures, stable under ambient conditions, and form large single crystals enabling the detailed study to the physical properties of oriented single-crystal samples. With the goal of preparing materials with a greater spin concentration, we have sought to prepare highly magnetic compounds based on ferrocene instead of its permethylated analogue, as it is smaller and its cation radical would have a greater spin density on a volume basis. The 1:1 salt with TCNQ has yet to be reported;[16] however, the 1:1 complex with TCNE was reported in 1962.[17] Consistent with the redox potentials, the latter complex has been characterized not to exhibit charge transfer.[18] Anticipating a stronger acceptor might enable

---

(1) (a) Du Pont; Contribution No. 4100. (b) Northeastern University.

(2) Simon, J.; André, J. J. *Molecular Semiconductors*; Springer-Verlag: New York, 1985.

(3) Epstein, A. J.; Miller, J. S. *Sci. Am.* **1979**, *240*(4), 52–61. Bechgaard, K.; Jerome, D. *Sci. Am.* **1982**, *247*(2), 52–61.

(4) Miller, J. S., Ed. *Extended Linear Chain Compounds*; Plenum: New York, 1982, 1983; Vols. 1–3.

(5) For a detailed overview, see the proceedings of recent series of international conferences: (a) Pecile, C., Zerbi, G., Bozio, R., Girlando, A., Eds. *Mol. Cryst. Liq. Cryst.* **1985**, *117–121*. (b) Comes, R., Bernier, P., Andre, J. J., Rouxel, J., Eds. *J. Phys., Colloq.* **1983**, 44-C3. (c) Epstein, A. J., Conwell, E. M., Eds. *Mol. Cryst. Liq. Cryst.* **1981**, *77, 79, 82, 83, 85, 86*. (d) Carneiro, K., Ed. *Chem. Scr.* **1981**, *17*. (e) Bartsic, S., Bjelis, A., Cooper, J. R., Leontic, B. A., Eds. *Lecture Notes Phys.* **1979**, *95, 96*. (f) Miller, J. S., Epstein, A. J., Eds. *Ann. N.Y. Acad. Sci.* **1978**, *313*.

(6) (a) Breslow, R. *Pure Appl. Chem.* **1982**, *54*, 927–938. (b) Iwamura, H. *Pure Appl. Chem.* **1986**, *58*, 187–196. (c) Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Isr. J. Chem.*, in press.

(7) Candela, G. A.; Swarzendruber, L.; Miller, J. S.; Rice, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 2755–2756.

(8) (a) Gebert, E.; Reis, A. H., Jr.; Miller, J. S.; Rommelmann, H.; Epstein, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 4403–4410. (b) Miller, J. S.; Krusic, P. J.; Dixon, D. A.; Reiff, W. M.; Zhang, Z. H.; Anderson, E. C.; Epstein, J. *J. Am. Chem. Soc.* **1986**, *108*, 4459–4466.

(9) Miller, J. S.; Calabrese, J. C.; Rommelmann, H.; Epstein, A. J.; Zhang, J. H.; Chittipeddi, S. R.; Reiff, W. M. *J. Am. Chem. Soc.*, in press.

(10) Dixon, D. A.; Calabrese, J. C.; Miller, J. S. *J. Am. Chem. Soc.* **1986**, *108*, 2582–2586.

(11) Reiff, W. M.; Zhang, J. H.; Calabrese, J. C.; Miller, J. S., manuscript in preparation.

(12) Reiff, W. M.; Zhang, J. H.; Miller, J. S., manuscript in preparation.

(13) Miller, J. S.; Calabrese, J. C.; Epstein, A. J.; Bigelow, R. W.; Reiff, W. M.; Zhang, J. H. *J. Chem. Soc., Chem. Commun.* **1986**, 1026–1027.

(14) Miller, J. S.; Zhang, J. H.; Reiff, W. M., submitted for publication.

(15) McConnell, H. M. *Proc. Robert A. Welch Found. Chem. Res.* **1967**, *11*, 144–145.

(16) Miller, J. S., unpublished results.

(17) Webster, O. W.; Mahler, W.; Benson, R. E. *J. Am. Chem. Soc.* **1962**, *84*, 3678. Rosenblum, M.; Fish, R. W.; Bennett, C. *J. Am. Chem. Soc.* **1964**, *86*, 5166–5170.

(18) $E°_{1/2}(TCNE^0 + e^- = [TCNE]^{\bullet-})$ = +0.15 V; $E°_{1/2}\{[Fe(C_5H_5)_2]^{\bullet+} + e^- = Fe(C_5H_5)_2\}$ = +0.28 V; $E°_{1/2}((TCNQ)F_4{}^0 + e^- = [(TCNQ)F_4]^-)$ = +0.53 V vs. SCE.

0020-1669/87/1326-0600$01.50/0

the preparation of a highly magnetic charge-transfer complexes, we have studied the chemistry of perfluorinated TCNQ, $(TCNQ)F_4$,[19] with ferrocene. Herein we report the preparation and ESR and ^{57}Fe Mössbauer spectral properties of $[Fe(C_5Me_5)_2][(TCNQ)F_4]$ and $[Fe(C_5Me_5)_2]_2[(TCNQ)F_4]_3$.

Experimental Section

$[Fe(C_5H_5)_2]^{\bullet+}[(TCNQ)F_4]^{\bullet-}$ was prepared from $Fe(C_5H_5)_2$ and $(TCNQ)F_4$[19] in an inert-atmosphere glovebox. Ferrocene (Aldrich, Inc.) (100 mg; 0.538 mmol) was dissolved in 5 mL of acetonitrile (distilled under argon from P_2O_5 and subsequently CaH_2). This solution was added to 149 mg (0.540 mmol) of $(TCNQ)F_4$ also dissolved in 10 mL of MeCN. Upon refrigeration at −25 °C overnight, 129 mg of the purple product (52%) was collected via vacuum filtration. Anal. Calcd for $C_{22}H_{10}FeF_4N_4$: C, 57.17; H, 2.18; Fe, 12.08; F, 16.44; N, 12.12. Found: C, 57.34; H, 2.10; N, 12.38 (Galbraith, Knoxville, TN). Infrared spectra (Nujol): $\nu(C{\equiv}N)$ 2179 s, 2195 s cm^{-1}.

$[Fe(C_5H_5)_2]_2[(TCNQ)F_4]_3$ was prepared from $Fe(C_5H_5)_2$ and $(TCNQ)F_4$[19] in an inert-atmosphere glovebox. Ferrocene (100 mg; 0.538 mmol) dissolved in 5 mL of acetonitrile was added to a solution containing 300 mg (1.087 mmol) of $(TCNQ)F_4$ dissolved in 8 mL of MeCN. Upon cooling to room temperature and vacuum filtration, 280 mg of the purple product (70%) was collected. Anal. Calcd for $C_{56}H_{20}Fe_2F_{12}N_{12}$: C, 56.03; H, 1.68; Fe, 9.30; F, 18.99; N, 14.00. Found: C, 56.20; H, 1.68; N, 13.99 (Galbraith, Knoxville, TN). Infrared spectra (Nujol): $\nu(C{\equiv}N)$ 2179 s, 2195 s, 2225 s cm^{-1}.

X-ray Data Collection and Data Reduction.[20] Crystals of either $[Fe(C_5H_5)_2][(TCNQ)F_4]$ or $[Fe(C_5H_5)_2]_2[(TCNQ)F_4]_3$ were mounted on a glass fiber with its long axis roughly parallel to the φ axis of the goniometer. Preliminary examination and data collection were performed with Mo K$\bar{\alpha}$ radiation (λ = 0.71073 Å) on an Enraf-Nonius CAD4 computer-controlled κ-axis diffractometer equipped with a graphite-crystal, incident-beam monochromator.

Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $3 < \theta < 13°$ and $2 < \theta < 7°$ for the 1:1 and 2:3 salts, respectively, measured by the computer-controlled diagonal-slit method of centering. The key crystallographic parameters are summarized in Table I. As a check on crystal quality, ω scans of several intense reflections were measured; the width at half-height was ≤0.30° with a takeoff angle of 2.8°, indicating good crystal quality. From the systematic absences (i.e., $0k0$ ($k = 2n + 1$) and $h0l$ ($h + l = 2n + 1$) for the 1:1 salt and hkl ($h + k = 2n + 1$) and $h0l$ ($l = 2n + 1$) for the 2:3 salt) and from subsequent least-squares refinement, the space groups were determined to be $P2_1/n$ (No. 14) and $C2/c$ (No. 15) for the 1:1 and 2:3 salts, respectively.

The data were collected by using the ω–θ scan technique. The scan rate varied from 2 to 20°/min (in ω). The variable rate ensures good counting statistics for weak reflections where a slow scan rate is used. Data were collected to a maximum 2θ of 40.0° for the 1:1 salt of 52.0° for the 2:3 salt. The scan range (in degrees) was determined as a function of θ to correct for the separation of the K$\bar{\alpha}$ doublet;[21] the scan width was calculated as $x + 0.350 \tan \theta$ (x = 0.7 or 0.6 for the 1:1 and 2:3 salts, respectively).

Moving-crystal, moving-counter background counts were made by scanning an additional 25% above and below this range. Thus, the ratio of peak-counting time to background-counting time was 2:1. The counter aperture was also adjusted as a function of θ. The horizontal aperture width ranged from 2.0 to 2.5 mm; the vertical aperture was set at 2.0 mm. The diameter of the incident beam collimator was 0.7 mm, and the crystal to detector distance was 21 cm. For intense reflections an attenuator was automatically inserted in front of the detector; the attenuator factor was 20.7.

For the 1:1 salt a total of 2037 reflections were collected, of which 1854 were unique and not systematically absent. For the 2:3 salt a total of 5413 reflections were selected, of which 4747 were unique and not systematically absent. As a check on crystal and electronic stability, three representive reflections were measured every 41 min (15 min for the 2:3 salt). The intensities of these standards remained constant within experimental error throughout data collection. No decay correction was applied.

Table I. Summary of Crystallographic Data

	$[Fe(C_5H_5)_2]$-$[(TCNQ)F_4]$	$[Fe(C_5H_5)_2]_2$-$[(TCNQ)F_4]_3$
cation:anion	1:1	2:3
formula	$C_{22}H_{10}FeF_4N_4$	$C_{56}H_{20}Fe_2F_{12}N_{12}$
fw	462.19	1200.56
cryst dimens, mm	0.05 × 0.08 × 0.35	0.07 × 0.12 × 0.35
peak width at half-height, deg	0.30	0.20
radiation	Mo K$\bar{\alpha}$	Mo K$\bar{\alpha}$
temp, °C	23	−97
space group	$P2_1/n$	$C2/c$
a, Å	6.886 (6)	26.885 (11)
b, Å	13.774 (7)	14.591 (5)
c, Å	21.085 (11)	13.901 (4)
β, deg	93.87 (5)	116.97 (2)
V, Å^3	1995.3	4859.9
Z	4	4
density, g/cm^3	1.54	1.64
μ, cm^{-1}	8.3	7.2
attenuator	Zr foil, factor 20.7	Zr foil, factor 20.7
takeoff angle, deg	2.8	2.8
detector aperture, mm: horiz; vert	2.0–2.4; 2.0	2.0–2.5; 2.0
cryst–detector dist, cm	21	21
scan type	ω–θ	ω–θ
scan rate, deg/min (in ω)	2–20	2–20
scan width, deg	40.0	52.0
no. of reflcns measd	2037 total, 1854 unique	5413 total, 4747 unique
corr	Lorentz–polarizn	Lorentz–polarizn
soln	direct methods	direct methods
H atoms	not included	not included
refinement	full-matrix least squares	full-matrix least squares
minimizn function	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
least-squares weights	$4F_o^2/\sigma^2(F_o^2)$	$4F_o^2/\sigma^2(F_o^2)$
"Ignorance," p factor	0.050	0.060
anomalous dispersion	all non-H atoms	all non-H atoms
no. of reflcns included	899 with $F_o^2 > 2.0\sigma(F_o^2)$	2163 with $F_o^2 > 3.0\sigma(F_o^2)$
no. of params refined	275	365
unweighted agreement factor, R	0.063	0.054
weighted agreement factor, R_w	0.068	0.068
factor including unobsd data	0.236	0.194
esd of observed of unit weight	1.48	1.49
convergence, largest shift	0.02σ	0.60σ
high peak in final diff map	0.34 (9) e/Å^3	1.04 (9) e/Å^3

Lorentz and polarization corrections were applied to the data. The linear absorption coefficients are 8.3 and 7.2 cm^{-1} for Mo K$\bar{\alpha}$ radiation for the 1:1 and 2:3 salts, respectively. No absorption correction was made. An extinction correction was not necessary.

Structure Solution and Refinement. $[Fe(C_5H_5)_2][(TCNQ)F_4]$. The structure was solved by using direct methods. One of the cyclopentadienyl rings is disordered. A 50:50 rotational disorder was assumed, and atoms C(18)–C(22) were refined at half-occupancy. The thermal parameters and positions of the disordered carbon atoms showed some unexpected variations, which are ascribed to the relatively low resolution of the data. Hydrogen atoms were not included in the calculations. The structure was refined in full-matrix least-squares where $\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$ was minimized and the weight w is defined as $4F_o^2/\sigma^2(F_o^2)$. The standard deviation on intensities, $\sigma(F_o^2)$, is defined as $\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/L_p^2$ where S is the scan rate, C is the total integrated peak count, R is the ratio of scan time to background counting time, B is the total background count, L_p is the Lorentz–polarization factor, and p is introduced to downweight intense reflections. Here p was set to 0.050.

Scattering factors were taken from Cromer and Waber.[22a] Anomalous dispersion effects were included in F_c;[23] the values for $\Delta f'$ and $\Delta f''$

---

[19] Wheland, R. C.; Martin, E. L. *J. Org. Chem.* **1975**, *40*, 1301.

[20] These services were performed by the Molecular Structure Corp. All calculations were performed on a PDP-11/60-based TEXRAY system, which includes the Enraf-Nonius SDP and proprietary crystallographic software of Molecular Structure Corp.

[21] *CAD4 Operation Manual*; Enraf-Nonius: Delft, 1977.

[22] (a) Cromer, D. T.; Waber, J. T. In *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B. (b) Cromer, D. J. In *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

[23] Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

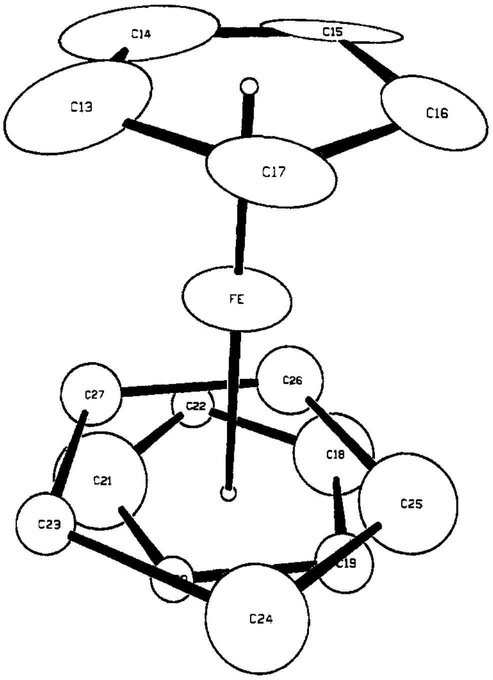


Figure 1. Atom labeling for the $[Fe(C_5H_5)_2]^{\cdot+}$ cation in $[Fe(C_5H_5)_2][(TCNQ)F_4]$.

were those of Cromer.[22b] For the 1:1 salt only the 889 reflections having intensities greater than 2.0 times their standard deviation were used in the refinements. The final cycle of refinement included 275 variable parameters and converged (largest parameter shift was 0.02 times its esd) with unweighted, R, and weighted, R_w, agreement factors of

$$R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.063$$

$$R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2} = 0.068$$

The standard deviation of an observation of unit weight was 1.48. The highest peak in the final difference Fourier had a height of 0.34 e/Å^3 with an estimated error based on ΔF[24] of 0.09. Plots of $\sum w(|F_o| - |F_c|)^2$ vs. $|F_o|$, reflection order in data collection, $(\sin \theta)/\lambda$, and various classes of indices showed no unusual trends.

$[Fe(C_5H_5)_2]_2[(TCNQ)F_4]_3$. The structure was solved by direct methods. An E map yielded the positions of most of the non-hydrogen atoms. The remaining atoms were located in succeeding difference Fourier syntheses. The structure contains a $Fe(C_5H_5)_2$ on a general position, a $(TCNQ)F_4$ on a general position, and a second $(TCNQ)F_4$ molecule on a twofold axis. Thus, the Fe to $(TCNQ)F_4$ ratio is 2:3. One of the cyclopentadienyl ligands is disordered. A twofold rotational disorder was assumed with atoms C(6)–C(15) refined at 0.5 occupancy. Hydrogen atoms were not included in the calculations. The structure was refined in full-matrix least-squares where $\sum w(|F_o| - |F_c|)^2$ was minimized and the weight, w, is defined as $4F_o^2/\sigma^2(F_o^2)$.

Scattering factors were taken from Cromer and Waber.[22a] Anomalous dispersion effects were included in F_c;[23] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[22b] For the 2:3 salt only the 2163 reflections having intensities greater than 3.0 times their standard deviation were used in the refinements. The final cycle of refinement included 265 variable parameters and converged (largest parameter shift was 0.60 times its esd) with unweighted, R, and weighted, R_w, agreement factors of 5.4 and 6.8%, respectively.

The standard deviation of an observation of unit weight was 1.49. The highest peak in the final difference Fourier had a height of 1.04 e/Å^3 with an estimated error based on ΔF[24] of 0.109. Plots of $\sum w(|F_o| - |F_c|)^2$ vs. $|F_o|$, reflection order in data collection, $(\sin \theta)/\lambda$, and various classes of indices showed on unusual trends.

Physical Properties—^{57}Fe Mössbauer Spectra. Zero-field Mössbauer spectra were determined by using a conventional constant-acceleration spectrometer with a 50-mCi ^{57}Co source electroplated onto the surface and annealed into the body of a 6 μm thick foil of high-purity rhodium under a hydrogen atmosphere. The details of cryogenics, temperature control, etc. have been described previously.[25]

Table II. Positional Parameters and Their Estimated Standard Deviations[a,b] for $[Fe(C_5H_5)_2][(TCNQ)F_4]$

atom	x	y	z
Fe	0.7407 (3)	1.0371 (2)	0.3303 (1)
F1	0.672 (1)	0.4892 (6)	0.6295 (3)
F2	0.673 (1)	0.6602 (6)	0.5729 (4)
F3	0.813 (1)	0.5075 (5)	0.3801 (3)
F4	0.810 (1)	0.3399 (6)	0.4352 (4)
N1	0.708 (2)	0.2788 (9)	0.6843 (5)
N2	0.772 (2)	0.1468 (8)	0.5102 (5)
N3	0.780 (2)	0.7161 (10)	0.3240 (5)
N4	0.720 (2)	0.8527 (9)	0.4999 (6)
C1	0.740 (2)	0.4038 (10)	0.5366 (6)
C2	0.702 (2)	0.4921 (9)	0.5678 (6)
C3	0.713 (2)	0.5792 (10)	0.5396 (6)
C4	0.742 (2)	0.5957 (11)	0.4737 (6)
C5	0.773 (2)	0.5081 (10)	0.4419 (5)
C6	0.774 (2)	0.4187 (10)	0.4714 (6)
C7	0.732 (2)	0.3096 (10)	0.5651 (6)
C8	0.755 (2)	0.2216 (11)	0.5320 (6)
C9	0.722 (2)	0.2989 (10)	0.6324 (6)
C10	0.737 (2)	0.6884 (11)	0.4451 (6)
C11	0.724 (2)	0.7795 (11)	0.4774 (6)
C12	0.766 (2)	0.7005 (10)	0.3771 (7)
C13	0.995 (2)	1.1084 (13)	0.3683 (8)
C14	0.982 (2)	1.1102 (15)	0.3006 (8)
C15	0.981 (2)	1.0136 (14)	0.2762 (7)
C16	0.989 (2)	0.9482 (13)	0.3323 (8)
C17	0.992 (2)	1.0089 (11)	0.3868 (7)
C18	0.483 (4)	0.984 (2)	0.2943 (13)
C19	0.493 (3)	0.962 (2)	0.3525 (10)
C20	0.490 (3)	1.045 (2)	0.3782 (9)
C21	0.485 (4)	1.106 (2)	0.3383 (14)
C22	0.476 (3)	1.075 (2)	0.2814 (10)
C23	0.511 (3)	1.118 (2)	0.3748 (11)
C24	0.509 (4)	0.996 (2)	0.3915 (14)
C25	0.499 (4)	0.936 (3)	0.3180 (14)
C26	0.502 (4)	1.021 (2)	0.2639 (12)
C27	0.501 (4)	1.132 (2)	0.2985 (12)

[a] Estimated standard deviations in the least significant digits are shown in parentheses. [b] The carbon atoms C18–C27 were refined at half-occupancy.

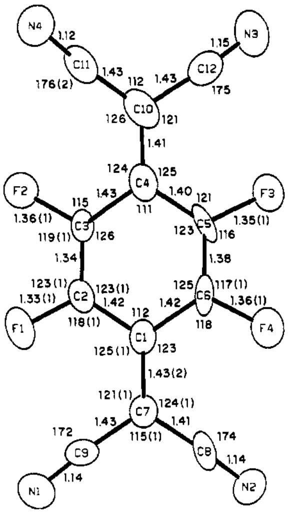


Figure 2. Atom labeling and bond distances and angles for the $[(TCNQ)F_4]^{\cdot-}$ anion in $[Fe(C_5H_5)_2][(TCNQ)F_4]$ (esd's are (2) unless noted).

Spectroscopic Measurements. The infrared spectra were recorded on a Nicolet 7199 Fourier transform spectrometer. The UV-visible spectra were recorded on a Cary 2390 spectrometer. The ESR spectra were recorded on an IBM/Bruker ER 200 D-SRC spectrometer.

---

(24) Cruickshank, D. W. J. *Acta Crystallogr.* **1949**, *2*, 154.

(25) Cheng, C.; Reiff, W. M. *Inorg. Chem.* **1977**, *16*, 2097.

(26) Sullivan, B. W.; Foxman, B. M. *Organometallics* **1983**, *2*, 187–189. Rheingold, A. L.; Uhler, A. D.; Landers, A. G. *Inorg. Chem.* **1983**, *22*, 3255–3258. Mammano, N. T.; Zalkin, A.; Landers, A.; Rheingold, A. L. *Inorg. Chem.* **1977**, *6*, 297–305. Churchill, M. R.; Landers, A. G.; Rheinhold, A. L. *Inorg. Chem.* **1981**, *20*, 849–853.

Table III. Bond Distances (Å) for $[Fe(C_5H_5)_2][(TCNQ)F_4]$[a]

Fe–C13	2.12 (2)	F1–C2	1.331 (14)	C5–C6	1.38 (2)	C19–C24	0.95 (4)
Fe–C14	2.08 (2)	F1–C3	1.356 (14)	C7–C8	1.41 (2)	C19–C25	0.82 (4)
Fe–C15	2.097 (15)	F3–C5	1.350 (13)	C7–C9	1.43 (2)	C20–C21	1.18 (5)
Fe–C16	2.10 (2)	F4–C6	1.360 (14)	C10–C11	1.43 (2)	C20–C23	1.02 (4)
Fe–C17	2.07 (2)	N1–C9	1.140 (15)	C10–C12	1.47 (2)	C20–C24	0.74 (4)
Fe–C18	2.02 (3)	N2–C8	1.14 (2)	C13–C14	1.42 (2)	C21–C22	1.27 (5)
Fe–C19	2.07 (3)	N3–C12	1.15 (2)	C13–C17	1.43 (2)	C21–C23	0.80 (4)
Fe–C20	2.06 (2)	N4–C11	1.12 (2)	C14–C15	1.43 (3)	C21–C27	0.93 (4)
Fe–C21	2.01 (4)	C1–C2	1.42 (2)	C15–C16	1.49 (3)	C22–C26	0.86 (4)
Fe–C22	2.10 (3)	C1–C6	1.42 (2)	C16–C17	1.42 (2)	C22–C27	0.88 (4)
Fe–C23	2.20 (3)	C1–C7	1.43 (2)	C18–C19	1.26 (5)	C23–C24	1.72 (5)
Fe–C24	2.19 (4)	C2–C3	1.34 (2)	C18–C22	1.28 (5)	C23–C27	1.62 (4)
Fe–C25	2.17 (4)	C3–C4	1.43 (2)	C18–C25	0.82 (5)	C24–C25	1.75 (5)
Fe–C26	2.10 (3)	C4–C5	1.40 (2)	C18–C26	0.83 (5)	C25–C26	1.63 (5)
Fe–C27	2.17 (3)	C4–C10	1.41 (2)	C19–C20	1.26 (5)	C26–C27	1.70 (4)

[a] Numbers in parentheses are estimated standard deviations in the least signficant digits.

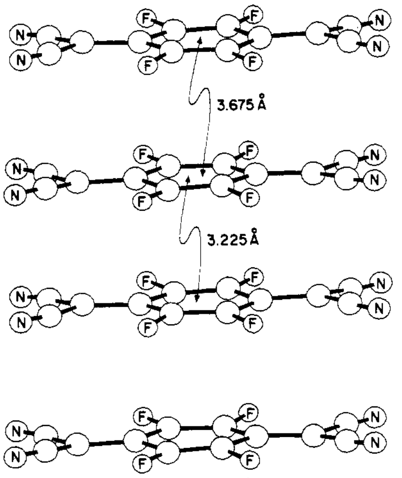


Figure 3. Parallel segregated dimer chains of $[(TCNQ)F_4]^{\bullet-}$.

Results and Discussion

Crystal Structure. $[Fe(C_5H_5)_2][(TCNQ)F_4]$. The monoclinic unit cell is comprised of a cation with one ordered and one disordered C_5H_5 ring and a half-anion. The fractional atomic coordinates and interatomic distances and angles are located in Tables II–IV, respectively. Atom labeling for the cation and anion can be found in Figures 1 and 2, respectively.

$[Fe(C_5H_5)_2]^{\bullet+}$ possesses one disordered and essentially one ordered C_5H_5 ring. For the ordered ring the Fe–C and C–C distances range from 2.07 (2) to 2.12 (2) Å and from 1.42 (2) to 1.49 (3) Å and average 2.094 and 1.438 Å, respectively. These values are in accord with those previously reported for ferrocene and its cation;[9] however, the anisotropic nature of the thermal parameters suggests that there is unresolved disorder in this ring as well. The other C_5H_5 ring can be refined via a disorder model comprised of equal contributions from rings C18–C22 and C23–C27 (Figure 1). The average Fe–C distances for these rings are 2.052 and 2.166 Å, which deviate from 2.07 Å previously reported for $[Fe(C_5H_5)_2]^{\bullet+}$.[9] Larger deviations from the expected 1.40 Å are observed for the C–C bond. The average C–C distances for each ring are 1.25 and 1.68 Å, respectively. The cations form chains along *a* with an intrachain Fe^{III}–Fe^{III} separation of 6.886 Å. The shortest interchain Fe^{III}–Fe^{III} separations are 7.679 and 8.139 Å.

$[(TCNQ)F_4]^{\bullet-}$'s structure is summarized in Table V. This planar anion possesses local crystallographic C_{2v} symmetry, and the bond distances and angles are summarized in Figure 3. The angles are essentially identical with those previously reported[27-29] and, like TCNQ, cannot be used to ascertain the degree of charge transfer.[30-32] In accord with TCNQ salts, the bond distances vary significantly with charge. The average bond distances are in excellent agreement with those previously reported for the *N*-butylphenazenium salt of (TCNQ)F$_4$, which also possesses $[(TCNQ)F_4]_2^{2-}$ dimers.[27] Except for the C—CN bond, which differs by -0.012 Å, the remaining distances are <0.005 Å smaller. With respect to $(TCNQ)F_4{}^{\circ}$,[29] the central and exo C═C bonds are ~0.02 and ~0.04 Å longer, while the C—C(CN)$_2$ and C—CN bonds constrict by ~0.02 and ~0.01 Å, respectively. C≡N remains essentially invariant in length. These trends are seen for TCNQ and are expected upon adding an extra electron to the b_{3g} π^* orbital.[33]

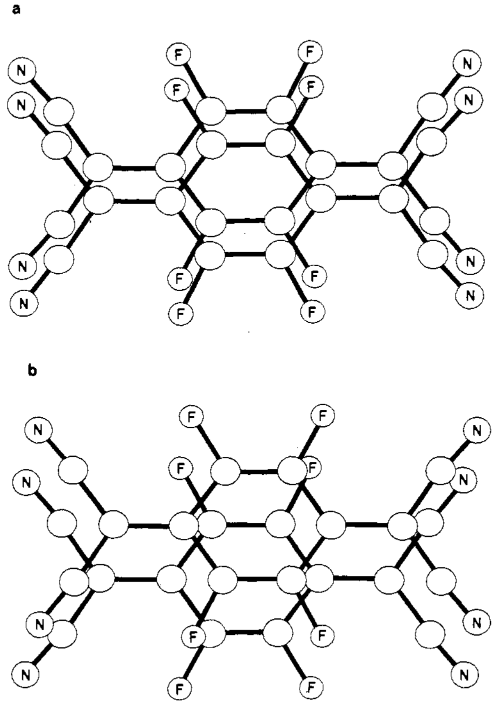


Figure 4. Normal projection of adjacent $[(TCNQ)F_4]^{\bullet-}$ anions within a dimer: (a) intradimer separation (3.22 Å); (b) interdimer overlap (3.675 Å).

Solid-State Structure. The solid is comprised of segregated chains of $S = {}^1/_2$ cations and $S = {}^1/_2$ anions. This motif is frequently observed for numerous simple and complex salts of TCNQ.[31,32] We previously reported a similar solid-state arrangement for $[Fe(C_5H_4Me)_2][TCNQ]_2$,[34] which unlike this

---

(27) Metzger, R. M.; Heimer, N. E.; Gundel, D.; Sixl, H.; Harms, R. H.; Keller, H. J.; Nothe, D.; Wehe, D. *J. Chem. Phys.* **1982**, *77*, 6203–6214.

(28) Soos, Z. G.; Keller, H. J.; Ludolf, K.; Queckborner, J.; Wehe, D.; Flandrois, S. *J. Chem. Phys.* **1981**, *76*, 5287–5294.

(29) Emge, T. J.; Maxfield, M.; Cowan, D. O.; Kistenmacher, T. J. *Mol. Cryst. Liq. Cryst.* **1981**, *65*, 161–178.

(30) Flandrois, S.; Chasseau, D. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 2744–2750.

(31) Herbstein, F. H. *Perspect. Struct. Chem.* **1971**, *4*, 166–395.

(32) Shibaeva, R. P.; Atovmyan, L. O. *J. Struct. Chem.* (*Engl. Transl.*) **1972**, *13*, 514–531.

(33) Molecular orbital calculations on (TCNQ)F$_4$, $[(TCNQ)F_4]^{\bullet-}$, and $[TCNQF_4]^{2-}$: Dixon, D. A.; Miller, J. S., manuscript in preparation.

Table IV. Bond Angles (deg) for $[Fe(C_5H_5)_2][(TCNQ)F_4]$

C13–Fe–C14	39.7 (6)	C18–Fe–C21	57 (2)	C1–C7–C9	121 (1)	C22–C21–C27	44 (3)
C13–Fe–C15	67.4 (7)	C18–Fe–C22	36 (1)	C8–C7–C9	115 (1)	C23–C21–C27	139 (8)
C13–Fe–C16	67.2 (7)	C18–Fe–C23	73 (1)	N2–C8–C7	174 (2)	Fe–C22–C18	69 (2)
C13–Fe–C17	39.8 (6)	C18–Fe–C24	58 (2)	N1–C9–C7	172 (2)	Fe–C22–C21	68 (2)
C13–Fe–C18	174 (1)	C18–Fe–C25	22 (1)	C4–C10–C11	126 (2)	Fe–C22–C26	78 (3)
C13–Fe–C19	145 (1)	C18–Fe–C26	23 (1)	C4–C10–C12	121 (2)	Fe–C22–C27	83 (3)
C13–Fe–C20	119 (1)	C18–Fe–C27	58 (2)	C11–C10–C12	112 (2)	C18–C22–C21	97 (4)
C13–Fe–C21	117 (1)	C19–Fe–C20	36 (1)	N4–C11–C10	176 (2)	C18–C22–C26	40 (3)
C13–Fe–C22	138 (1)	C19–Fe–C21	59 (2)	N3–C12–C10	175 (2)	C18–C22–C27	142 (4)
C13–Fe–C23	101.8 (9)	C19–Fe–C22	62 (1)	Fe–C13–C14	69 (1)	C21–C22–C26	134 (5)
C13–Fe–C24	121 (1)	C19–Fe–C23	62 (1)	Fe–C13–C17	68 (1)	C21–C22–C27	47 (3)
C13–Fe–C25	162 (1)	C19–Fe–C24	25 (1)	C14–C13–C17	107 (2)	C26–C22–C27	156 (5)
C13–Fe–C26	153 (1)	C19–Fe–C25	22 (1)	Fe–C14–C13	72 (1)	Fe–C23–C20	69 (2)
C13–Fe–C27	115 (1)	C19–Fe–C26	58 (1)	Fe–C14–C15	71 (1)	Fe–C23–C21	66 (3)
C14–Fe–C15	40.0 (7)	C19–Fe–C27	76 (1)	C13–C14–C15	110 (2)	Fe–C23–C24	67 (2)
C14–Fe–C16	67.8 (7)	C20–Fe–C21	34 (1)	Fe–C15–C14	69 (1)	Fe–C23–C27	68 (1)
C14–Fe–C17	67.0 (7)	C20–Fe–C22	60 (1)	Fe–C15–C16	69.4 (8)	C20–C23–C21	80 (5)
C14–Fe–C18	140 (2)	C20–Fe–C23	27 (1)	C14–C15–C16	106 (2)	C20–C23–C24	11 (3)
C14–Fe–C19	175 (1)	C20–Fe–C24	20 (1)	Fe–C16–C15	69 (1)	C20–C23–C27	101 (3)
C14–Fe–C20	147 (1)	C20–Fe–C25	55 (1)	Fe–C16–C17	69.1 (9)	C21–C23–C24	89 (5)
C14–Fe–C21	121 (2)	C20–Fe–C26	72 (1)	C15–C16–C17	107 (2)	C21–C23–C27	22 (5)
C14–Fe–C22	115 (1)	C20–Fe–C27	58 (1)	Fe–C17–C13	72 (1)	C24–C23–C27	109 (2)
C14–Fe–C23	120 (1)	C21–Fe–C22	36 (1)	Fe–C17–C16	71.2 (9)	Fe–C24–C19	70 (3)
C14–Fe–C24	159 (1)	C21–Fe–C23	21 (1)	C13–C17–C16	110 (2)	Fe–C24–C20	70 (4)
C14–Fe–C25	154 (1)	C21–Fe–C24	53 (2)	Fe–C18–C19	74 (2)	Fe–C24–C23	67 (2)
C14–Fe–C26	117 (1)	C21–Fe–C25	69 (2)	Fe–C18–C22	75 (2)	Fe–C24–C25	66 (2)
C14–Fe–C27	103 (1)	C21–Fe–C26	57 (2)	Fe–C18–C25	89 (4)	C19–C24–C20	96 (5)
C15–Fe–C16	41.4 (7)	C21–Fe–C27	25 (1)	Fe–C18–C26	33 (4)	C19–C24–C23	108 (4)
C15–Fe–C17	67.9 (7)	C22–Fe–C23	57 (1)	C19–C18–C22	116 (4)	C19–C24–C25	5 (3)
C15–Fe–C18	116.0 (1)	C22–Fe–C24	73 (1)	C19–C18–C25	40 (4)	C20–C24–C23	15 (4)
C15–Fe–C19	137 (1)	C22–Fe–C25	58 (1)	C19–C18–C26	153 (6)	C20–C24–C25	96 (5)
C15–Fe–C20	173 (1)	C22–Fe–C26	24 (1)	C22–C18–C25	155 (7)	C23–C24–C25	106 (3)
C15–Fe–C21	148 (2)	C22–Fe–C27	23.8 (9)	C22–C18–C26	41 (4)	Fe–C25–C18	69 (4)
C15–Fe–C22	118 (1)	C23–Fe–C24	46 (1)	C25–C18–C26	158 (8)	Fe–C25–C19	72 (4)
C15–Fe–C23	158 (1)	C23–Fe–C25	79 (1)	Fe–C19–C18	70 (2)	Fe–C25–C24	67 (2)
C15–Fe–C24	156 (1)	C23–Fe–C26	78 (1)	Fe–C19–C20	72 (2)	Fe–C25–C26	65 (2)
C15–Fe–C25	118 (1)	C23–Fe–C27	43 (1)	Fe–C19–C24	84 (3)	C18–C25–C19	100 (7)
C15–Fe–C26	103 (1)	C24–Fe–C25	47 (1)	Fe–C19–C25	86 (4)	C18–C25–C24	99 (5)
C15–Fe–C27	122 (1)	C24–Fe–C26	78 (1)	C18–C19–C20	102 (4)	C18–C25–C26	11 (4)
C16–Fe–C17	39.8 (6)	C24–Fe–C27	77 (1)	C18–C19–C24	137 (5)	C19–C25–C24	5 (3)
C16–Fe–C18	119 (1)	C25–Fe–C26	45 (1)	C18–C19–C25	40 (4)	C19–C25–C26	108 (5)
C16–Fe–C19	112.7 (9)	C25–Fe–C27	78 (1)	C20–C19–C24	36 (3)	C24–C25–C26	106 (3)
C16–Fe–C20	137 (1)	C26–Fe–C27	47 (1)	C20–C19–C25	141 (6)	Fe–C26–C18	73 (3)
C16–Fe–C21	170 (2)	C2–C1–C6	112 (2)	C24–C19–C25	170 (6)	Fe–C26–C22	78 (3)
C16–Fe–C22	146 (1)	C2–C1–C7	125 (1)	Fe–C20–C19	73 (2)	Fe–C26–C25	70 (2)
C16–Fe–C23	154 (1)	C6–C1–C7	123 (2)	Fe–C20–C21	71 (2)	Fe–C26–C27	69 (1)
C16–Fe–C24	117 (1)	F1–C2–C1	118 (1)	Fe–C20–C23	84 (2)	C18–C26–C22	99 (5)
C16–Fe–C25	104 (1)	F1–C2–C3	118 (1)	Fe–C20–C24	90 (4)	C18–C26–C25	11 (4)
C16–Fe–C26	123 (1)	C1–C2–C3	123 (1)	C19–C20–C21	109 (3)	C18–C26–C27	103 (5)
C16–Fe–C27	163 (1)	F2–C3–C2	119 (1)	C19–C20–C23	149 (4)	C22–C26–C25	108 (4)
C17–Fe–C18	146 (2)	F2–C3–C4	115 (2)	C19–C20–C24	48 (4)	C22–C26–C27	12 (3)
C17–Fe–C19	116 (1)	C2–C3–C4	126 (2)	C21–C20–C23	42 (3)	C25–C26–C27	110 (2)
C17–Fe–C20	115.1 (9)	C3–C4–C5	111 (2)	C21–C20–C24	155 (6)	Fe–C27–C21	68 (3)
C17–Fe–C21	138 (1)	C3–C4–C10	124 (2)	C23–C20–C24	155 (6)	Fe–C27–C22	73 (3)
C17–Fe–C22	174 (1)	C5–C4–C10	125 (2)	Fe–C21–C20	75 (2)	Fe–C27–C23	69 (1)
C17–Fe–C23	116.6 (9)	F3–C5–C4	121 (2)	Fe–C21–C22	76 (2)	Fe–C27–C26	64 (1)
C17–Fe–C24	103 (1)	F3–C5–C6	116 (2)	Fe–C21–C23	92 (4)	C21–C27–C22	89 (5)
C17–Fe–C25	124 (1)	C4–C5–C6	123 (1)	Fe–C21–C27	87 (3)	C21–C27–C23	19 (4)
C17–Fe–C26	162 (1)	F4–C6–C1	118 (2)	C20–C21–C22	116 (5)	C21–C27–C26	92 (4)
C17–Fe–C27	151 (1)	F4–C6–C5	117 (1)	C20–C21–C23	58 (4)	C22–C27–C23	107 (4)
C18–Fe–C19	36 (2)	C1–C6–C5	125 (2)	C20–C21–C27	157 (6)	C22–C27–C26	12 (3)
C18–Fe–C20	57 (2)	C1–C7–C8	124 (1)	C22–C21–C23	168 (6)	C23–C27–C26	108 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

material is a 1:2 salt. Except for the 3.225-Å interdimer interactions, there are no significant interion separations less than the sum of the van der Waals radii. A view of the unit cell based on ordered anions can be seen in Figure 5.

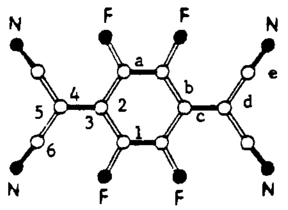
$[Fe(C_5H_5)_2]_2[(TCNQ)F_4]_3$. This *C*-centered monoclinic unit cell is comprised of a cation with one ordered and one disordered C_5H_5 ring and a $(TCNQ)F_4$ as well as half of a $[(TCNQ)F_4]_2^{2-}$ dimer. The fractional atomic coordinates and interatomic distances and angles are located in Tables VI–VIII, respectively. Atom labeling for the cation and anion can be found in Figures 6 and 7, respectively.

$[Fe(C_5H_5)_2]^{\bullet+}$. As noted above for the 1:1 salt, the cation possesses one ordered and one disordered C_5H_5 ring. The average Fe–C and C–C distances for the ordered ring range from 2.087 (7) to 2.097 (7) Å and from 1.371 (12) to 1.436 (12) Å and average 2.091 and 1.414 Å, respectively. These are in excellent agreement with values previously reported.[9] The disordered ring is modeled by equal occupancy of rings C6–C10 and C11–C15 (Figure 6). Each refined ring average Fe–C and C–C distance deviates from that of the ordered ring, i.e., Fe–C ~ 2.05 and 2.127

---

(34) Wilson, S. R.; Corvan, P. J.; Seiders, R.; Hodgson, D. J.; Brookhart, M.; Hatfield, W. E.; Miller, J. S.; Reis, A. H.; Rogan, P. K.; Gebert, E.; Epstein, A. J. *NATO Conf. Ser.*, *6* **1978**, 407–414.

Table V. Structural Parameters for $(TCNQ)F_4$ and $[(TCNQ)F_4]^{-a}$



	$(TCNQ)F_4$	$[Me_2Phen][(TCNQ)F_4]$	$[N\text{-BuPhen}][(TCNQ)F_4]$	$[Fe(C_5H_5)_2][(TCNQ)F_4]$	$[Fe(C_5H_5)_2]_2[(TCNQ)F_4]_3$	
form	$(TCNQ)F_4^0$	$[(TCNQ)F_4]^{\bullet-}$	$[(TCNQ)F_4]_2^{2-}$	$[(TCNQ)F_4]_2^{2-}$	$(TCNQ)F_4^0$	$[(TCNQ)F_4]_2^{2-}$
a	1.334	1.353	1.350	1.36	1.331	1.345
b	1.437	1.415	1.410	1.42	1.439	1.419
c	1.372	1.415	1.413	1.42	1.373	1.419
d	1.437	1.429	1.417	1.435	1.438	1.423
e	1.140	1.144	1.144	1.14	1.149	1.148
1	123.2	123.7	123.6	123	122.8	123.9
2	113.5	112.5	112.7	111	114.5	112.2
3	123.2	123.8	123.5	124	127.7	123.7
4	123.8	124.1	123.5	123	123.8	123.8
5	112.6	111.9	113.2	113.5	112.2	112.2
6	175.2	174	176.3	174	174.4	174.9
T,C	RT[b]	RT	RT	RT	–97 C	–97 C
R, %	3.6	7.2	6.9	6.8	6.8	6.8
interdimer sepn			3.150	3.225	3.155	3.155
ref	29	28	27			

[a] Distances in Å; angles in deg. [b] Room temperature.

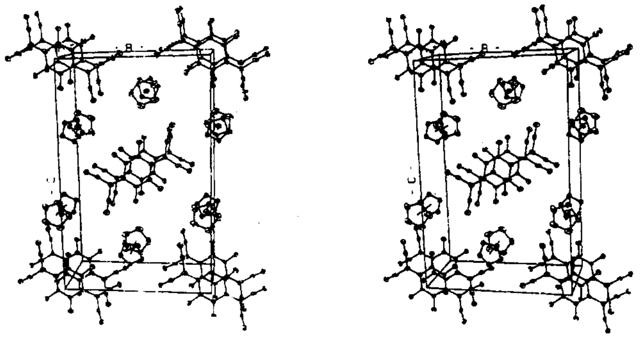


Figure 5. Stereoview of the unit cell of $[Fe(C_5H_5)_2][(TCNQ)F_4]$ along the *a* axis.

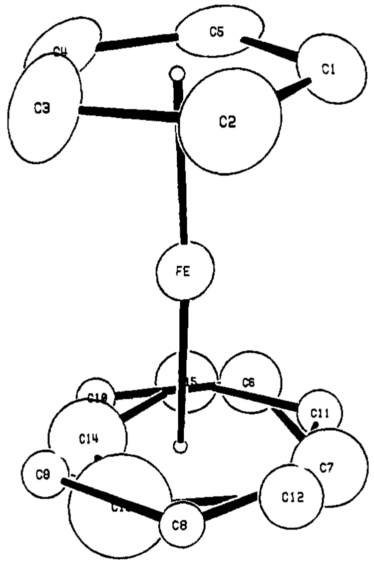


Figure 6. Atom labeling for the $[Fe(C_5H_5)_2]^{\bullet+}$ cation in $[Fe(C_5H_5)_2]_2[(TCNQ)F_4]_3$.

Å and C–C ~ 1.324 and 1.582 Å. The cations are located in columns with an intrachain separation of 6.993 Å, and the shortest intrachain Fe^{III}–Fe^{III} separations are 7.414 and 8.057 Å.

$[(TCNQ)F_4]^{\bullet-}$'s structure is summarized in Table V. This planar anion possesses local crystallographic C_{2v} symmetry, and the bond distances and angles are summarized in Figure 7. On the basis of the bond lengths, the 2:3 salt is a complex mixture

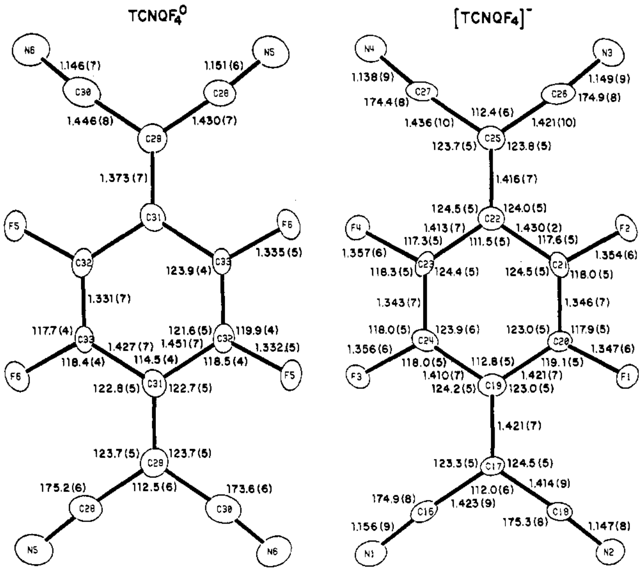


Figure 7. Atom labeling for $[(TCNQ)F_4]^0$ and the $[(TCNQ)F_4]^{\bullet-}$ anion in $[Fe(C_5H_5)_2]_2[(TCNQ)F_4]_3$.

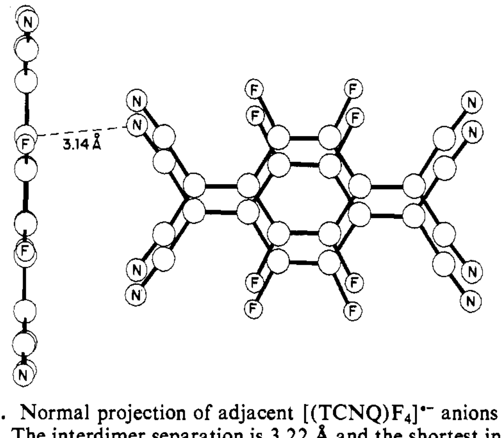


Figure 8. Normal projection of adjacent $[(TCNQ)F_4]^{\bullet-}$ anions within a dimer. The interdimer separation is 3.22 Å and the shortest intermolecular N···C distance between the dimer and $(TCNQ)F_4{}^0$ is 3.14 Å.

Table VI. Fractional Positional Parameters and Their Estimated Standard Deviations[a,b] for $[Fe(C_5H_5)_2]_2[(TCNQ)F_4]_3$

atom	*x*	*y*	*z*
Fe	0.24900 (4)	0.2658 (7)	0.12611 (7)
F1	−0.4041 (1)	0.1589 (2)	0.4898 (3)
F2	0.4053 (1)	0.3378 (2)	0.4880 (3)
F3	−0.5965 (1)	0.1560 (2)	0.2391 (3)
F4	−0.5971 (1)	0.3357 (2)	0.2378 (3)
F5	0.0770 (1)	0.2472 (2)	0.1736 (2)
F6	−0.0291 (1)	0.2476 (2)	0.0363 (2)
N1	−0.5859 (2)	−0.0546 (4)	0.2689 (4)
N2	−0.4156 (2)	−0.0529 (4)	0.4740 (4)
N3	−0.4185 (2)	0.5491 (4)	0.4729 (4)
N4	−0.5879 (2)	0.5478 (4)	0.2636 (4)
N5	0.1539 (2)	0.2458 (4)	0.6065 (4)
N6	0.1975 (2)	0.2503 (4)	0.3543 (4)
C1	0.2981 (3)	0.0237 (6)	0.0453 (5)
C2	0.2771 (3)	0.1138 (6)	0.0414 (6)
C3	0.2177 (3)	0.1087 (6)	−0.0128 (6)
C4	0.2037 (3)	0.0152 (6)	−0.0412 (5)
C5	0.2514 (3)	−0.0360 (6)	−0.0071 (5)
C6	0.2590 (6)	−0.0749 (10)	0.2434 (11)
C7	0.2998 (7)	0.0130 (11)	0.2951 (12)
C8	0.2586 (4)	0.0937 (8)	0.2662 (8)
C9	0.2025 (4)	0.0600 (8)	0.2113 (8)
C10	0.2018 (4)	−0.0375 (8)	0.1993 (8)
C11	0.2901 (4)	−0.0430 (8)	0.2749 (8)
C12	0.2906 (5)	0.0524 (9)	0.2898 (9)
C13	0.2334 (8)	0.0749 (16)	0.2466 (17)
C14	0.2073 (7)	0.0060 (12)	0.2142 (14)
C15	0.2345 (6)	−0.0647 (10)	0.2215 (11)
C16	−0.5486 (2)	−0.0051 (4)	0.3096 (5)
C17	−0.5000 (2)	0.0495 (4)	0.3664 (4)
C18	−0.4525 (2)	−0.0044 (4)	0.4285 (5)
C19	−0.5009 (2)	0.1469 (4)	0.3660 (4)
C20	−0.4527 (2)	0.2010 (4)	0.4263 (4)
C21	−0.4534 (2)	0.2932 (4)	0.4257 (4)
C22	−0.5018 (2)	0.3476 (4)	0.3638 (4)
C23	−0.5489 (2)	0.2923 (4)	0.3033 (4)
C24	−0.5485 (2)	0.2003 (4)	0.3043 (4)
C25	−0.5021 (2)	0.4446 (4)	0.3631 (4)
C26	−0.4544 (3)	0.4933 (4)	0.4252 (5)
C27	−0.5514 (3)	0.4988 (4)	0.3058 (5)
C28	0.1341 (2)	0.2468 (4)	0.5137 (5)
C29	0.1140 (2)	0.2476 (4)	0.3992 (4)
C30	0.1587 (3)	0.2502 (5)	0.3686 (5)
C31	0.0585 (2)	0.2473 (4)	0.3264 (4)
C32	0.0392 (2)	0.2469 (4)	0.2105 (4)
C33	−0.0150 (2)	0.2472 (4)	0.1416 (4)

[a] Estimated standard deviations in the least significant digits are shown in parentheses. [b] Atoms C6–C15 were refined at half-occupancy.

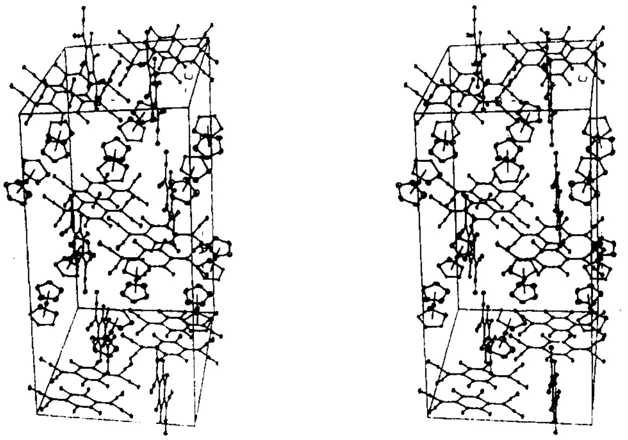


Figure 9. Stereoview of the unit cell of $[Fe(C_5H_5)_2]_2[(TCNQ)F_4]_3$.

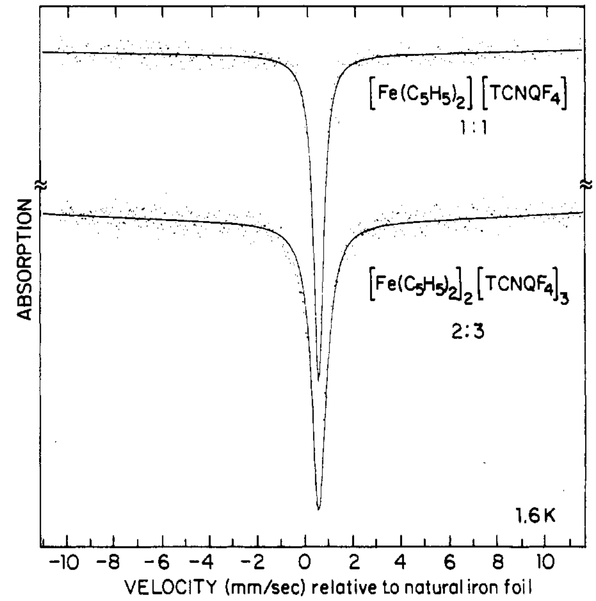


Figure 10. ^{57}Fe Mössbauer spectra of $[Fe(C_5H_5)_2][(TCNQ)F_4]$ (top) and $[Fe(C_5H_5)_2]_2[(TCNQ)F_4]_3$ (bottom) at 1.6 K.

of $(TCNQ)F_4{}^0$ and $[(TCNQ)F_4]_2{}^{2-}$ dimers (Figure 9). The dimer $[(TCNQ)F_4]^{-}$'s are separated by 3.155 Å, which is comparable to that reported for the *N*-butylphenazenium salt (i.e., 3.15 Å).[27] The metric parameters listed in Table V are consistent with the anionic formulation; likewise, the third $(TCNQ)F_4$'s parameters are in excellent agreement with the previously reported structure of $(TCNQ)F_4{}^0$. Thus, the 2:3 salt is best formulated as $[Fe(C_5H_5)_2]_2{}^{\bullet+}[(TCNQ)F_4]_2{}^{2-}\cdot(TCNQ)F_4{}^0$. This formulation is consistent with the vibrational spectrum which possesses ab-

Table VII. Bond Distances (Å) for $[Fe(C_5H_5)_2]_2[(TCNQ)F_4]_3$[a]

Fe–C1	2.087 (7)	C4–C5	1.371 (12)	C10–C15	0.88 (2)	C19–C24	1.410 (7)
Fe–C2	2.093 (7)	C6–C7	1.63 (3)	C11–C12	1.41 (2)	C20–C21	1.346 (7)
Fe–C3	2.097 (7)	C6–C10	1.48 (2)	C11–C15	1.37 (2)	C21–C22	1.430 (7)
Fe–C4	2.086 (9)	C6–C11	0.88 (2)	C12–C13	1.41 (3)	C22–C23	1.413 (7)
Fe–C5	2.093 (7)	C6–C14	1.73 (3)	C13–C14	1.19 (3)	C22–C25	1.416 (7)
Fe–C6	2.13 (2)	C6–C15	0.61 (2)	C14–C15	1.24 (3)	C23–C24	1.343 (7)
Fe–C7	2.12 (3)	C7–C8	1.54 (3)	F1–C20	1.347 (6)	C25–C26	1.421 (10)
Fe–C8	2.089 (11)	C7–C11	0.87 (2)	F2–C21	1.354 (6)	C25–C27	1.436 (10)
Fe–C9	2.133 (12)	C7–C12	0.62 (3)	F3–C24	1.356 (6)	F5–C32	1.332 (5)
Fe–C10	2.165 (11)	C7–C13	1.83 (4)	F4–C23	1.357 (6)	F6–C33	1.335 (5)
Fe–C11	2.111 (12)	C8–C9	1.43 (2)	N1–C16	1.156 (9)	N5–C28	1.151 (6)
Fe–C12	2.06 (2)	C8–C12	0.98 (2)	N2–C18	1.147 (8)	N6–C30	1.146 (7)
Fe–C13	2.03 (2)	C8–C13	0.66 (3)	N3–C26	1.149 (9)	C28–C29	1.430 (7)
Fe–C14	2.02 (2)	C8–C14	1.78 (3)	N4–C27	1.138 (9)	C29–C30	1.446 (8)
Fe–C15	2.04 (2)	C9–C10	1.43 (2)	C16–C17	1.423 (9)	C29–C31	1.373 (7)
C1–C2	1.423 (11)	C9–C13	0.78 (3)	C17–C18	1.414 (9)	C31–C32	1.451 (7)
C1–C5	1.426 (12)	C9–C14	0.80 (2)	C17–C19	1.421 (7)	C31–C33	1.427 (7)
C2–C3	1.426 (10)	C10–C13	1.83 (3)	C19–C20	1.421 (7)	C32–C33	1.331 (7)
C3–C4	1.423 (11)	C10–C14	0.66 (3)				

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table VIII. Bond Angles (deg) for $[Fe(C_5H_5)_2]_2[(TCNQ)F_4]_3$[a]

C1–Fe–C2	39.8 (3)	C7–Fe–C15	55.7 (8)	Fe–C8–C12	75 (1)	C10–C13–C12	101 (2)
C1–Fe–C3	66.7 (4)	C8–Fe–C9	39.7 (5)	Fe–C8–C13	76 (3)	C10–C13–C14	7 (2)
C1–Fe–C4	65.8 (3)	C8–Fe–C10	67.4 (5)	Fe–C8–C14	62.5 (8)	C12–C13–C14	108 (3)
C1–Fe–C5	39.9 (3)	C8–Fe–C11	61.6 (5)	C7–C8–C9	110 (1)	Fe–C14–C6	69 (1)
C1–Fe–C6	120.5 (6)	C8–Fe–C12	27.2 (5)	C7–C8–C12	12 (2)	Fe–C14–C8	66.3 (8)
C1–Fe–C7	110.3 (7)	C8–Fe–C13	18.5 (8)	C7–C8–C13	106 (3)	Fe–C14–C9	87 (2)
C1–Fe–C8	132.1 (5)	C8–Fe–C14	51.2 (8)	C7–C8–C14	84 (1)	Fe–C14–C10	93 (3)
C1–Fe–C9	167.8 (5)	C8–Fe–C15	71.3 (6)	C9–C8–C12	121 (1)	Fe–C14–C13	73 (2)
C1–Fe–C10	153.2 (5)	C9–Fe–C10	38.9 (6)	C9–C8–C13	8 (3)	Fe–C14–C15	73 (1)
C1–Fe–C11	109.9 (4)	C9–Fe–C11	75.2 (5)	C9–C8–C14	26.0 (9)	C6–C14–C8	90 (2)
C1–Fe–C12	116.0 (6)	C9–Fe–C12	60.5 (6)	C12–C8–C13	117 (3)	C6–C14–C9	142 (3)
C1–Fe–C13	150 (1)	C9–Fe–C13	21.5 (8)	C12–C8–C14	95 (2)	C6–C14–C10	57 (3)
C1–Fe–C14	169.4 (8)	C9–Fe–C14	21.9 (7)	C13–C8–C14	22 (3)	C6–C14–C13	102 (3)
C1–Fe–C15	133.8 (7)	C9–Fe–C15	57.0 (7)	Fe–C9–C8	68.5 (6)	C6–C14–C15	14 (1)
C2–Fe–C3	39.8 (3)	C10–Fe–C11	59.3 (4)	Fe–C9–C10	71.7 (6)	C8–C14–C9	52 (2)
C2–Fe–C4	66.3 (3)	C10–Fe–C12	72.6 (5)	Fe–C9–C13	72 (2)	C8–C14–C10	147 (3)
C2–Fe–C5	66.6 (3)	C10–Fe–C13	51.5 (8)	Fe–C9–C14	71 (2)	C8–C14–C13	12 (2)
C2–Fe–C6	154.4 (7)	C10–Fe–C14	17.8 (7)	C8–C9–C10	111 (1)	C8–C14–C15	104 (2)
C2–Fe–C7	117.6 (7)	C10–Fe–C15	24.0 (6)	C8–C9–C13	6 (2)	C9–C14–C10	157 (5)
C2–Fe–C8	108.4 (4)	C11–Fe–C12	39.4 (6)	C8–C9–C14	102 (3)	C9–C14–C13	41 (2)
C2–Fe–C9	128.7 (5)	C11–Fe–C13	64.6 (8)	C10–C9–C13	108 (3)	C9–C14–C15	154 (4)
C2–Fe–C10	164.6 (5)	C11–Fe–C14	61.5 (8)	C10–C9–C14	10 (2)	C10–C14–C13	159 (4)
C2–Fe–C11	133.0 (5)	C11–Fe–C15	38.6 (6)	C13–C9–C14	98 (3)	C10–C14–C15	43 (2)
C2–Fe–C12	110.8 (5)	C12–Fe–C13	40.4 (8)	Fe–C10–C6	68.5 (7)	C13–C14–C15	116 (3)
C2–Fe–C13	121.0 (9)	C12–Fe–C14	62.1 (9)	Fe–C10–C9	69.4 (6)	Fe–C15–C6	90 (3)
C2–Fe–C14	150.6 (8)	C12–Fe–C15	64.6 (6)	Fe–C10–C13	60.4 (8)	Fe–C15–C10	86 (2)
C2–Fe–C15	171.0 (8)	C13–Fe–C14	34.2 (9)	Fe–C10–C14	69 (2)	Fe–C15–C11	73.6 (9)
C3–Fe–C4	39.8 (3)	C13–Fe–C15	61 (1)	Fe–C10–C15	70 (1)	Fe–C15–C14	72 (1)
C3–Fe–C5	66.1 (4)	C14–Fe–C15	35.6 (8)	C6–C10–C9	111 (1)	C6–C15–C10	166 (4)
C3–Fe–C6	164.1 (7)	Fe–C1–C2	70.3 (4)	C6–C10–C13	87 (1)	C6–C15–C11	28 (2)
C3–Fe–C7	149.3 (8)	Fe–C1–C5	70.3 (4)	C6–C10–C14	101 (3)	C6–C15–C14	135 (4)
C3–Fe–C8	114.7 (4)	C2–C1–C5	107.6 (8)	C6–C10–C15	6 (2)	C10–C15–C11	139 (2)
C3–Fe–C9	106.8 (4)	Fe–C2–C1	69.9 (4)	C9–C10–C13	24.1 (9)	C10–C15–C14	31 (2)
C3–Fe–C10	127.1 (4)	Fe–C2–C3	70.2 (4)	C9–C10–C14	12 (3)	C11–C15–C14	108 (2)
C3–Fe–C11	171.9 (5)	C1–C2–C3	107.6 (8)	C9–C10–C15	117 (2)	N1–C16–C17	174.9 (8)
C3–Fe–C12	134.5 (6)	Fe–C3–C2	70.0 (4)	C13–C10–C14	13 (3)	C16–C17–C18	112.0 (6)
C3–Fe–C13	114.5 (8)	Fe–C3–C4	69.7 (5)	C13–C10–C15	93 (2)	C16–C17–C19	123.3 (5)
C3–Fe–C14	122.7 (8)	C2–C3–C4	106.8 (8)	C14–C10–C15	106 (3)	C18–C17–C19	124.5 (5)
C3–Fe–C15	148.9 (7)	Fe–C4–C3	70.5 (5)	Fe–C11–C6	79 (2)	N2–C18–C17	175.3 (8)
C4–Fe–C5	38.3 (3)	Fe–C4–C5	71.1 (5)	Fe–C11–C7	79 (2)	C17–C19–C20	123.0 (5)
C4–Fe–C6	127.3 (6)	C3–C4–C5	109.8 (8)	Fe–C11–C12	68.5 (7)	C17–C19–C24	124.2 (5)
C4–Fe–C7	169.4 (7)	Fe–C5–C1	69.8 (4)	Fe–C11–C15	67.9 (8)	C20–C19–C24	112.8 (5)
C4–Fe–C8	147.1 (5)	Fe–C5–C4	70.6 (5)	C6–C11–C7	138 (3)	F1–C20–C19	119.1 (5)
C4–Fe–C9	116.4 (4)	C1–C5–C4	108.2 (7)	C6–C11–C12	123 (2)	F1–C20–C21	117.9 (5)
C4–Fe–C10	108.6 (4)	Fe–C6–C7	67 (1)	C6–C11–C15	19 (2)	C19–C20–C21	123.0 (5)
C4–Fe–C11	146.6 (5)	Fe–C6–C10	71.2 (8)	C7–C11–C12	15 (2)	F2–C21–C20	118.0 (5)
C4–Fe–C12	173.7 (7)	Fe–C6–C11	77 (1)	C7–C11–C15	119 (2)	F2–C21–C22	117.6 (5)
C4–Fe–C13	135.5 (9)	Fe–C6–C14	62.3 (9)	C12–C11–C15	104 (1)	C20–C21–C22	124.5 (5)
C4–Fe–C14	117.4 (9)	Fe–C6–C15	73 (3)	Fe–C12–C7	87 (3)	C21–C22–C23	111.5 (5)
C4–Fe–C15	119.0 (6)	C7–C6–C10	105 (1)	Fe–C12–C8	78 (1)	C21–C22–C25	124.0 (5)
C5–Fe–C6	109.3 (5)	C7–C6–C11	21 (1)	Fe–C12–C11	72.1 (7)	C23–C22–C25	124.5 (5)
C5–Fe–C7	132.5 (7)	C7–C6–C14	83 (1)	Fe–C12–C13	68 (1)	F4–C23–C22	117.3 (5)
C5–Fe–C8	171.8 (5)	C7–C6–C15	113 (3)	C7–C12–C8	149 (4)	F4–C23–C24	118.3 (5)
C5–Fe–C9	148.5 (5)	C10–C6–C11	126 (2)	C7–C12–C11	22 (3)	C22–C23–C24	124.4 (5)
C5–Fe–C10	119.2 (4)	C10–C6–C14	22 (1)	C7–C12–C13	124 (4)	F3–C24–C19	118.0 (5)
C5–Fe–C11	116.4 (4)	C10–C6–C15	9 (3)	C8–C12–C11	128 (2)	F3–C24–C23	118.0 (5)
C5–Fe–C12	146.7 (6)	C11–C6–C14	104 (2)	C8–C12–C13	25 (2)	C19–C24–C23	123.9 (6)
C5–Fe–C13	169.6 (9)	C11–C6–C15	134 (4)	C11–C12–C13	103 (2)	C22–C25–C26	123.8 (5)
C5–Fe–C14	136.0 (8)	C14–C6–C15	31 (3)	Fe–C13–C7	67 (1)	C22–C25–C27	123.7 (5)
C5–Fe–C15	112.5 (6)	Fe–C7–C6	68 (1)	Fe–C13–C8	86 (3)	C26–C25–C27	112.4 (6)
C6–Fe–C7	45.0 (7)	Fe–C7–C8	67 (1)	Fe–C13–C9	87 (2)	N3–C26–C25	174.9 (8)
C6–Fe–C8	72.1 (6)	Fe–C7–C11	77 (2)	Fe–C13–C10	68.1 (9)	N4–C27–C25	174.4 (8)
C6–Fe–C9	68.6 (6)	Fe–C7–C12	76 (3)	Fe–C13–C12	71 (1)	N5–C28–C29	175.2 (6)
C6–Fe–C10	40.2 (6)	Fe–C7–C13	61 (1)	Fe–C13–C14	73 (2)	C28–C29–C30	112.5 (5)
C6–Fe–C11	24.0 (5)	C6–C7–C8	103 (2)	C7–C13–C8	54 (3)	C28–C29–C31	123.7 (5)
C6–Fe–C12	57.7 (7)	C6–C7–C11	21 (1)	C7–C13–C9	133 (3)	C30–C29–C31	123.7 (5)
C6–Fe–C13	67.1 (8)	C6–C7–C12	122 (4)	C7–C13–C10	85 (1)	N6–C30–C29	173.6 (6)
C6–Fe–C14	49.1 (9)	C6–C7–C13	83 (2)	C7–C13–C12	16 (1)	C29–C31–C32	122.7 (5)
C6–Fe–C15	16.6 (6)	C8–C7–C11	124 (3)	C7–C13–C14	92 (2)	C29–C31–C33	122.8 (5)
C7–Fe–C8	42.9 (7)	C8–C7–C12	19 (3)	C8–C13–C9	166 (5)	C32–C31–C33	114.5 (4)
C7–Fe–C9	69.7 (7)	C8–C7–C13	20 (1)	C8–C13–C10	138 (4)	F5–C32–C31	118.5 (4)
C7–Fe–C10	70.1 (7)	C11–C7–C12	143 (5)	C8–C13–C12	38 (2)	F5–C32–C33	119.9 (4)
C7–Fe–C11	23.6 (6)	C11–C7–C13	104 (3)	C8–C13–C14	145 (5)	C31–C32–C33	121.6 (5)
C7–Fe–C12	16.8 (7)	C12–C7–C13	39 (3)	C9–C13–C10	48 (2)	F6–C33–C31	118.4 (4)
C7–Fe–C13	52 (1)	Fe–C8–C7	70 (1)	C9–C13–C12	148 (4)	F6–C33–C32	117.7 (4)
C7–Fe–C14	64.6 (9)	Fe–C8–C9	71.8 (7)	C9–C13–C14	41 (2)	C31–C33–C32	123.9 (4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IX. ^{57}Fe Mössbauer Parameters for $[Fe(C_5H_5)_2][(TCNQ)F_4]$ and $[Fe(C_5Me_5)_2]_2[(TCNQ)F_4]_3$

compd	temp (T), K	isomer shift (δ), mm/s	line width (Γ), mm/s
$[Fe(C_5Me_5)_2][(TCNQ)F_4]$	300	0.411	0.374
	4.23	0.528	0.395
	1.60	0.530	0.512
$[Fe(C_5Me_5)_2]_2[(TCNQ)F_4]_3$	300	0.439	0.360
	4.23	0.544	0.878
	1.60	0.539	0.734

sorptions at 2225 cm^{-1} ($(TCNQ)F_4{}^0$) and at 2179 and 2195 cm^{-1} ($[(TCNQ)F_4]^{\bullet-}$).

Solid-State Structure. The solid possesses a complex structure that is comprised of segregated chains of $S = {}^1/_2$ cations and anions. The anions reside as $[(TCNQ)F_4)]_2{}^{2-}$ dimers perpendicular to $(TCNQ)F_4{}^0$ and are best seen in Figures 8 and 9. This motif has not been reported for any simple or complex salts of TCNQ.

The $[(TCNQ)F_4]_2{}^{2-}$ dimers lie perpendicular to $(TCNQ)F_4{}^0$. Neutral $(TCNQ)F_4$, unlike TCNQ, possesses a similar motif[29] but exhibits short intermolecular C···N distances of 2.97 and 3.18 Å. As noted in Figure 8, there is a similar intermolecular N···C of 3.14 Å between the dimer and $(TCNQ)F_4{}^0$.

Electron Spin Resonance. At 100, 273, and 343 K, the 1:1 and 2:3 salts do not exhibit ESR spectra. $[(TCNQ)F_4]_2{}^{2-}$ dimers with similar interplanar separations were reported to exhibit triplet behavior.[27,28] However, such behavior was not observed. This presumably arises from fast relaxation, which is characteristic of $S = {}^1/_2$ $[Fe(C_5H_5)_2]^{\bullet+}$.[35] The ferrocenium cation couples with the $[TCNQ]_2{}^{2-}$ triplets and broadens the signal.

^{57}Fe Mössbauer Spectroscopy. The ^{57}Fe Mössbauer spectra were collected at 1.6, 4.2, and 300 K. Singlets characteristic of Fe^{III} ferrocenium were observed (Figure 10, Table IX). At low temperature there was no evidence for zero-field Zeeman-split Mössbauer spectra. This contrasts strongly with what we have reported for the $[DDQ]^{\bullet-}$,[8] $[TCNE]^{\bullet-}$,[9] $[TCNQ]^{\bullet-}$,[36] $[C_4(CN)_6]^{\bullet-}$,[11] and $[C_6(CN)_6]^{\bullet-}$ [12] salts, respectively. Decamethylferrocenium salts of these $S = {}^1/_2$ anions exhibit resolved magnetic hyperfine splitting. Our present observations are consistent with a $S_{total} = 0$ ground state of $[(TCNQ)F_4]_2{}^{2-}$ dimers and $S = 0$ for $(TCNQ)F_4{}^0$.

It was our observation that zero-field Zeeman-split ^{57}Fe Mössbauer spectra are a necessary, but not sufficient, condition to anticipate cooperative magnetic properties.[6b,37] Since the 1:1 and the 2:3 salts do not possess the structural motif we have identified to support meta/ferromagnetism, i.e., $\cdots D^+{\cdot}A^-{\cdot}D^+{\cdot}A^-\cdots$ (D = donor; A = acceptor), and these salts do not exhibit Zeeman-split ^{57}Fe Mössbauer spectra, we elected to not pursue the study of the magnetic properties.

Acknowledgment. We thank C. Vazquez (Du Pont) for synthetic assistance and M. Extine (Molecular Structure Corp.) for helpful discussions regarding the refinement of the structures.

Supplementary Material Available: Tables of the thermal parameters, general temperature factors, and weighted least-squares planes for both the 1:1 and 2:3 salts (13 pages); listings of structure factors for both compounds (29 pages). Ordering information is given on any current masthead page.

---

[35] Prins, R.; Kortbeek, A. G. T. G. *J. Organomet. Chem.* **1971**, *33*, C33–C34. Anderson, S. E.; Rai, R. *Chem. Phys.* **1973**, *2*, 216–225. Prins, R. *Mol. Phys.* **1970**, *19*, 603–620.

[36] Miller, J. S.; Zhang, J. H.; Reiff, W. M.; Dixon, D. A.; Preston, L. D.; Reis, A. H., Jr.; Gerbert, E.; Extine, M.; Troup, J.; Epstein, A. J., submitted for publication.

[37] Miller, J. S.; Epstein, A. J.; Reiff, W. M., submitted for publication.

Contribution from the Departments of Chemistry, University of Missouri—Rolla, Rolla, Missouri 65401, and Abilene Christian University, Abilene, Texas 79699, Nuclear Physics Division, Atomic Energy Research Establishment, Harwell, Didcot OX11 0RA, England, and Department of Physics, University of Liverpool, Liverpool L69 3BX, England

Spin Equilibrium in Iron(II) Poly(1-pyrazolyl)borate Complexes: Low-Temperature and High-Pressure Mössbauer Spectral Studies

Gary J. Long* and Bennett B. Hutchinson

Received July 22, 1986

A high-pressure and low-temperature applied field Mössbauer effect study has revealed that $Fe[HB(pz)_3]_2$, which contains low-spin iron(II) from room temperature down to 4.2 K, may be converted in part to high-spin iron(II) at pressures above ca. 40 kbar. In contrast, $Fe[HB(3,4,5\text{-}(CH_3)_3pz)_3]_2$, which our studies reveal remains high-spin down to 1.7 K, may be converted to the low-spin state at high pressure. Because of the weaker crystal field potential of the substituted ligand in this compound, a pressure of ca. 55 kbar is required to make the high-spin $^5T_{2g}$ state and low-spin $^1A_{1g}$ state equivalent in energy at room temperature. In $Fe[HB(3,5\text{-}(CH_3)_2pz)_3]_2$ the intermediate crystal field potential yields a spin crossover at low temperature (ca. 195 K), and in this case only 4 kbar is required to make the two spin states equivalent in energy at room temperature. All three compounds show a linear dependence of the isomer shift and quadrupole interaction upon the applied pressure, and the spin-state transitions are completely reversible.

Introduction

The preparation of the poly(1-pyrazolyl)borate ions[1] led to the immediate investigation of their chelating ability with divalent transition-metal ions.[2,3] Perhaps most interesting were the iron(II) complexes formed with the hydrotris(1-pyrazolyl)borate ligand and its dimethyl and trimethyl derivatives.[4-6] These ligands formed complexes of stoichiometry $Fe[B(pz)_4]_2$, $Fe[HB(pz)_3]_2$, $Fe[HB(3,5\text{-}(CH_3)_2pz)_3]_2$, and $Fe[HB(3,4,5\text{-}(CH_3)_3pz)_3]_2$ (pz is 1-pyrazolyl), in which the crystal field potential of the different ligands spanned the range needed to produce iron(II) in its high- and low-spin states. Hence in the solid state $Fe[HB(pz)_3]_2$ is low spin, $Fe[HB(3,4,5\text{-}(CH_3)_3pz)_3]_2$ is high spin, and $Fe[HB(3,5\text{-}(CH_3)_2pz)_3]_2$ is high spin at room temperature and low spin at 78 K and below.[6] This set of complexes thus provides a range

---

*To whom correspondence should be addressed at the University of Missouri—Rolla.

[1] Trofimenko, S. *J. Am. Chem. Soc.* **1966**, *88*, 1842, **1967**, *89*, 3165–3170.

[2] Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3170–3177. Jesson, J. P.; Trofimenko, S.; Eaton, D. R. *J. Am. Chem. Soc.* **1967**, *89*, 3148–3158.

[3] Trofimenko, S. *Acc. Chem. Res.* **1971**, *4*, 17–22.

[4] Jesson, J. P.; Weiher, J. F. *J. Chem. Phys.* **1967**, *46*, 1995–1996.

[5] Jesson, J. P.; Trofimenko, S.; Eaton, D. R. *J. Am. Chem. Soc.* **1967**, *89*, 3158–3164.

[6] Jesson, J. P.; Weiher, J. F.; Trofimenko, S. *J. Chem. Phys.* **1968**, *48*, 2058–2066.

0020-1669/87/1326-0608$01.50/0