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The Crystal Structure of a Tetrafluoroethyl–Iron Complex, $(HCF_2 \cdot CF_2)_2Fe(CO)_4$

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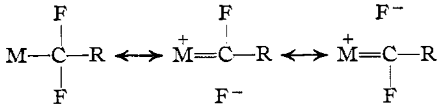
A full three-dimensional X-ray diffraction study of $(HCF_2 \cdot CF_2)_2Fe(CO)_4$ has been completed by the use of conventional Patterson, Fourier, and least-squares refinement techniques. All atoms other than hydrogen have been located. The final value for the discrepancy index, R_1, is 9.32% for 2090 independent nonzero reflections measured with a Buerger automated X-ray diffractometer. The molecule has the expected *cis*-octahedral stereochemistry with a mean Fe–CF_2 distance of 2.068 ± 0.014 A and an average Fe–C_α–C_β angle of 121.2 ± 1.3°.

Introduction

Although simple transition metal alkyls are unstable, it is often possible to isolate stable species provided that appropriate strong-field ligands are bonded to the metal.[1] Furthermore, fluoroalkyl complexes will, in general, be more stable than the corresponding nonfluorinated species.[2] In terms of the valence-bond approach, the relatively great thermal and aerobic stability of transition metal fluoroalkyls has been explained as the result of resonance between such canonical forms as



$$M{-}\overset{F}{\underset{F}{C}}{-}R \longleftrightarrow \overset{+}{M}{=}\overset{F}{\underset{F^-}{C}}{-}R \longleftrightarrow \overset{+}{M}{=}\overset{F^-}{\underset{F}{C}}{-}R$$

In more concrete terms, Cotton and McCleverty[3] suggest that the metal–fluoroalkyl linkage is strengthened as a result of d_π–σ^* back-donation from the metal to the ligand. The present structural analysis is one of a series being performed in order to obtain accurate molecular parameters for transition metal fluoroalkyls.[4,5]

Tetracarbonylbis(1,1,2,2-tetrafluoroethyl)iron(II), $(HCF_2 \cdot CF_2)_2Fe(CO)_4$, is prepared by the interaction of tetrafluoroethylene with iron carbonyl hydride, $H_2Fe(CO)_4$. The appearance of four carbonyl stretches in the infrared spectrum leads to the prediction that the molecule has a *cis* configuration.[6]

Experimental Section

Pale yellow monoclinic crystals of $(HCF_2 \cdot CF_2)_2Fe(CO)_4$ were grown over a period of 5 or 6 days by slow sublimation of the material onto the cold wall of a container at ~0° and atmospheric pressure. The compound is not air sensitive but *is* extremely volatile. Although there is a tendency for formation of platelike crystals, a number of approximately cubic crystals were also obtained. During the mounting of a crystal, sufficient sublimation took place to make the specimen lose all characteristic edges. The crystal used in the analysis was ellipsoidal in shape with a length of 0.16 mm and a diameter of 0.13 mm. It was mounted along its extended direction (c) and inserted into a 0.2-mm diameter thin-walled glass capillary tube. Unit-cell dimensions, obtained from zero-layer precession photographs and calibrated by means of a single crystal of sodium chloride ($a_{NaCl} = 5.6402$ A), were: $a = 20.588 \pm 0.015$, $b = 8.913 \pm 0.007$, $c = 13.241 \pm 0.009$ A, and $\beta = 92° 55' \pm 05'$. The unit-cell volume is 2427 A^3; the density obtained by flotation, $\rho_{obsd} = 1.99 \pm 0.05$ g cm^{-3}, is in satisfactory agreement with that calculated for $M = 370$ and $Z = 8$ ($\rho_{calcd} = 2.025$ g cm^{-3}). The absorption coefficient μ is 14.09 cm^{-1}. Since $\mu R_{max} = 0.112$ and the variation in absorption coefficient is small for the approximately spherical crystal,[7] no absorption correction was made.

The observed extinctions were: hkl for $h + l = 2n + 1$; $h0l$ for $h = 2n + 1$; $h0l$ for $l = 2n + 1$; $0k0$ for $k = 2n + 1$. The space group is therefore $B2_1/c$, which is a nonstandard setting of space group no. 14 (C_{2h}^5),[8] having the following equipoints: $x, y, z;\ -x, -y, -z;\ x, \frac{1}{2} - y, \frac{1}{2} + z;\ -x, \frac{1}{2} + y, \frac{1}{2} - z;\ \frac{1}{2} + x, y, \frac{1}{2} + z;\ \frac{1}{2} - x, -y, \frac{1}{2} - z;\ \frac{1}{2} + x, \frac{1}{2} - y, z;\ \frac{1}{2} - x, \frac{1}{2} + y, -z$.

The data-collecting system was composed of a fully stabilized Phillips X-ray generator (operated at 45 kv and 15 ma), a Phillips transistorized scintillation counter, a Phillips electronics panel, and a Buerger Automated X-Ray Diffractometer, which employed Weissenberg geometry. The over-all stability of the

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[1] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705 (1959).

[2] P. M. Triechel and F. G. A. Stone, *Advan. Organometal. Chem.*, **1**, 143 (1964).

[3] F. A. Cotton and J. A. McCleverty, *J. Organometal. Chem.* (Amsterdam), **4**, 490 (1965).

[4] M. R. Churchill, *Inorg. Chem.*, **4**, 1734 (1965).

[5] See ref 4 for the previous structural investigation in this series.

[6] E. Pitcher, Ph.D. Thesis, Radcliffe College, 1962.

[7] "International Tables for X-Ray Crystallography" Vol. 2, The Kynoch Press, Birmingham, England, 1959, Table 5.3.6B, p 302.

[8] "International Tables for X-Ray Crystallography" Vol. 1, The Kynoch Press, Birmingham, England, 1965, p 99.

system within a zone was monitored by remeasuring a check reflection after every 20 reflections had been collected.

The scintillation counter was adjusted to receive Mo Kα radiation (λ 0.7107 A), the Mo Kβ radiation being excluded by a 0.003-mm zirconium filter at the source. The base line of the pulse-height analyzer, the window voltage, and the counter-voltage were kept constant throughout the experiment. The diffractometer was programmed to scan all reflections up to sin $\theta = 0.45$ in a given Weissenberg zone.[9] The angle scanned is given by $\omega = (2.0 + 1.0L)$ degrees where L is the Lorentz factor. For a reflection hkl, having vertical and horizontal Weissenberg coordinates[10] Υhkl and Φhkl, the counting sequence consisted of five steps. (i) The counter was positioned to Υhkl where it remained throughout the cycle. (ii) The crystal was rotated about its spindle axis (c) until it reached the angle $\phi = (\Phi hkl - \omega/2)$. (iii) The first background count, B_1, was measured for t seconds. (iv) ϕ was increased ω degrees from $(\Phi hkl - \omega/2)$ to $(\Phi hkl + \omega/2)$ in time $2t$ at a constant rate of 2°/min, the total count being C. (v) The second background count, B_2, was measured for t seconds at $\phi = (\Phi hkl + \omega/2)$.

Reflections were omitted from the analysis if the net count, $C - (B_1 + B_2)$, was negative or if B_1 and B_2 were asymmetric by more than 20%. The 2090 acceptable reflections, obtained from the Weissenberg zones $hk0$ through $hk16$, were corrected for Lorentz and polarization effects. All zones were initially assumed to be on the same scale (an assumption later justified) and the absolute scale factor was determined from a Wilson plot, which also suggested an over-all isotropic thermal parameter, $\bar{B} = 2.9$ A^2. In the course of the subsequent analysis the computer programs OR-FLS,[11] ERFR-2,[12] and OR-FFE[13] were used on the Harvard IBM 7094 computer.

Determination of the Structure

The position of the iron atom ($X = -0.122$, $Y = +0.197$, $Z = +0.187$) was found from a three-dimensional Patterson synthesis which had been sharpened so that the average intensity was independent of sin θ and which had the origin peak reduced to the height of a single iron–iron interaction. A three-dimensional electron density map, phased by the iron atom alone ($R = 0.52$), revealed the positions of three carbonyl groups and seven of the fluorine atoms. A second electron density map, phased now by the iron and by 13 light atoms ($R = 0.38$), led to the unambiguous location of the remaining carbon, oxygen, and fluorine atoms. Structure factor calculations, phased by all atoms other than hydrogen, had an initial discrepancy index $R = 0.32$, which converged to a value of 0.17 after four cycles of least-square refinement of positional and isotropic thermal parameters. At this stage an attempted least-squares refinement of scale factors for the independent zones indicated that the zones were already, as expected, on a common scale (±2%). A difference Fourier now indicated that the thermal motions of the fluorine and oxygen atoms were not adequately described by isotropic parameters, and anisotropic thermal parameters (T) in the form

$$T = \exp(-b_{11}h^2 - b_{22}k^2 - b_{33}l^2 - 2b_{12}hk - 2b_{13}hl - 2b_{23}kl)$$

were used to continue the refinement. Owing to a limitation in the total number of parameters that could simultaneously be refined, the anisotropic refinement was performed in two parts. First, the iron atom and the tetrafluoroethyl groups and then the iron atom and the carbonyl groups were refined. This was repeated, and, finally, all positional parameters were refined while the anisotropic thermal parameters were held constant. The final discrepancy index was $R = 0.093$ for 2090 independent reflections.

TABLE I

FINAL ATOMIC COORDINATES FOR *cis*-$(HCF_2 \cdot CF_2)_2Fe(CO)_4$

Atom	x/a	y/b	z/c
Fe	0.12092	0.69875	0.31333
O_1	0.2369	0.8150	0.2166
O_2	0.0255	0.8161	0.1580
O_3	0.0067	0.6238	0.4293
O_4	0.1197	0.4132	0.1966
C_1	0.1936	0.7692	0.2520
C_2	0.0638	0.7777	0.2169
C_3	0.0521	0.6482	0.3882
C_4	0.1201	0.5187	0.2404
C_5	0.1252	0.8918	0.3998
C_6	0.0803	1.0173	0.3778
F_1	0.1151	0.8595	0.4994
F_2	0.1854	0.9582	0.4030
F_3	0.0913	1.0686	0.2818
F_4	0.0176	0.9712	0.3727
C_7	0.1883	0.5952	0.4115
C_8	0.1686	0.4739	0.4826
F_5	0.2332	0.5140	0.3549
F_6	0.2273	0.6892	0.4667
F_7	0.1296	0.3750	0.4335
F_8	0.1299	0.5396	0.5520

TABLE II

ANISOTROPIC THERMAL PARAMETERS FOR *cis*-$(HCF_2 \cdot CF_2)_2Fe(CO)_4$

Atom	10^4b_{11}	10^4b_{22}	10^4b_{33}	10^4b_{12}	10^4b_{13}	10^4b_{23}	B,[a] A^2
Fe	18.3	105.4	42.5	−3.7	−5.4	6.9	3.14
O_1	29.7	283	111	−18	16	40	7.25
O_2	31.3	203	74	7	−11	39	5.64
O_3	26.2	201	76	−13	7	16	5.37
O_4	35.6	175	94	4	−7	−40	6.06
C_1	26.5	143	70	−3	−1	−3	4.64
C_2	23.1	110	51	−5	−2	8	3.66
C_3	25.1	127	40	−2	−6	−1	3.71
C_4	23.2	137	53	3	−5	13	3.98
C_5	22.7	124	76	−21	−4	−9	4.38
C_6	40.4	130	100	4	−19	−21	5.98
F_1	54.1	194	61	−25	−1	−18	6.52
F_2	30.2	141	119	−13	−19	−9	5.96
F_3	74.5	144	116	−6	−22	30	8.43
F_4	29.1	229	166	15	−6	−49	7.93
C_7	23.8	159	65	−5	−5	6	4.54
C_8	30.2	175	81	7	−15	10	5.45
F_5	29.7	296	93	35	9	4	6.98
F_6	30.6	152	116	−17	−31	23	6.03
F_7	46.1	138	108	−21	−16	20	6.58
F_8	42.2	310	75	16	7	9	7.40

[a] B is an approximate "equivalent isotropic temperature factor" obtained by averaging $4b_{11}/a^{*2}$, $4b_{22}/b^{*2}$, and $4b_{33}/c^{*2}$.

The least-squares refinement was based upon a unit weighting scheme; the residual minimized was $\Sigma w \cdot$

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[9] Diffractometer settings were calculated using the program PREPAR by G. N. Reeke.

[10] C. T. Prewitt, *Z. Krist.*, **13**, 355 (1960).

[11] OR-FLS, by W. R. Busing, K. O. Martin, and H. A. Levy, is a Fortran program for structure-factor calculations and full-matrix least-squares refinement of positional and thermal parameters.

[12] ERFR-2, by W. G. Sly, D. P. Shoemaker, and J. H. van der Hende, is a two- and three-dimensional Fourier program.

[13] OR-FFE, by W. R. Busing, K. O. Martin, and H. A. Levy, is a Fortran crystallographic function and error program.

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR *cis*-$(HCF_2 \cdot CF_2)_2Fe(CO)_4$

H	K	FO	FC

$||F_o| - |F_c||^2$. Throughout the analysis, the scattering factors for the neutral atoms as compiled by Ibers[14] were used. Dispersion corrections are small[15] and were ignored.

Final atomic coordinates are collected in Table I, anisotropic thermal parameters in Table II; observed and calculated structure factors are shown in Table III.

The Molecular Structure

Table IV shows the important bond lengths and intramolecular contacts; bond angles are listed in Table V. The essential geometry of the molecule and the numbering system are shown in Figure 1.

Table IV

Interatomic Distances[a] for *cis*-$(HCF_2 \cdot CF_2)_2Fe(CO)_4$

Atoms	Distance, A	Atoms	Distance, A
	(a) Bond Lengths		
Fe–C_1	1.848	C_5–C_6	1.471
Fe–C_2	1.832	C_7–C_8	1.503
Fe–C_3	1.826	C_5–F_1	1.377
Fe–C_4	1.873	C_5–F_2	1.374
Fe–C_5	2.066	C_7–F_5	1.418
Fe–C_7	2.070	C_7–F_6	1.349
C_1–O_1	1.107	C_6–F_3	1.382
C_2–O_2	1.134	C_6–F_4	1.352
C_3–O_3	1.126	C_8–F_7	1.339
C_4–O_4	1.104	C_8–F_8	1.377
	(b) Distances from Iron Atom		
Fe–O_1	2.955	Fe–F_1	2.857
Fe–O_2	2.962	Fe–F_2	2.892
Fe–O_3	2.949	Fe–F_5	2.869
Fe–O_4	2.977	Fe–F_6	2.911
	(c) Contacts between Carbonyl Groups		
C_1–C_2	2.689	O_1–O_2	4.382
C_1–C_4	2.698	O_1–O_4	4.319
C_2–C_3	2.567	O_2–O_3	4.017
C_2–C_4	2.595	O_2–O_4	4.101
C_3–C_4	2.719	O_3–O_4	4.377
	(d) Contacts within Tetrafluoroethyl Groups		
F_1–F_2	2.166	F_5–F_6	2.160
F_1–F_3	3.446	F_5–F_8	3.457
F_1–F_4	2.737	F_5–F_7	2.720
F_2–F_3	2.643	F_6–F_8	2.702
F_2–F_4	3.461	F_6–F_7	3.463
F_3–F_4	2.167	F_7–F_8	2.148
	(e) Miscellaneous Intramolecular Contacts <3 A		
C_1–C_5	2.699	C_1–F_2	2.627
C_1–C_7	2.626	C_1–F_5	2.753
C_2–C_5	2.860	C_1–F_6	2.978
C_3–C_5	2.641	C_2–F_3	2.781
C_3–C_7	2.844	C_2–F_4	2.888
C_4–C_7	2.692	C_3–F_1	2.684
C_5–C_7	2.946	C_3–F_4	2.970
F_1–F_6	2.816	C_3–F_8	2.802
F_1–F_8	2.948	C_4–F_5	2.714
F_2–F_6	2.670	C_4–F_7	2.858

[a] The average estimated standard deviations are: σ(Fe–C) = 0.014, σ(Fe–O) = 0.010, σ(Fe–F) = 0.009, σ(C–O) = 0.017, σ(C–F) = 0.016, σ(C–C) = 0.020, σ(F–F) = 0.013, σ(O–O) = 0.014, σ(O–F) = 0.013 A. These values do not include any contribution from errors in the unit-cell constants. Also, since it proved impossible to refine all parameters simultaneously, the estimated standard deviations given here are derived from blocks of the true full matrix and are probably underestimated by an uncertain amount.

Table V

Interatomic Angles[a] for *cis*-$(HCF_2 \cdot CF_2)_2Fe(CO)_4$

Atoms	Angle, deg	Atoms	Angle, deg
Fe–C_1–O_1	178.1	C_4–Fe–C_5	176.8
Fe–C_2–O_2	174.3	C_4–Fe–C_7	86.0
Fe–C_3–O_3	174.5	C_5–Fe–C_7	90.9
Fe–C_4–O_4	179.1		
		Fe–C_5–C_6	121.0
C_1–Fe–C_2	93.9	Fe–C_5–F_1	110.7
O_1–Fe–O_2	95.6	Fe–C_5–F_2	112.9
C_1–Fe–C_3	171.9	F_1–C_5–F_2	103.9
O_1–Fe–O_3	171.3	F_1–C_5–C_6	102.9
C_1–Fe–C_4	92.9	F_2–C_5–C_6	103.7
O_1–Fe–O_4	93.5	C_5–C_6–F_3	107.6
C_1–Fe–C_5	87.0	C_5–C_6–F_4	111.6
C_1–Fe–C_7	84.0	F_3–C_6–F_4	104.8
C_2–Fe–C_3	89.2		
O_2–Fe–O_3	85.6	Fe–C_7–C_8	121.4
C_2–Fe–C_4	88.9	Fe–C_7–F_5	109.2
O_2–Fe–O_4	87.3	Fe–C_7–F_6	115.1
C_2–Fe–C_5	94.2	F_5–C_7–F_6	102.6
C_2–Fe–C_7	174.4	F_5–C_7–C_8	99.7
C_3–Fe–C_4	94.6	F_6–C_7–C_8	106.2
O_3–Fe–O_4	95.2	C_7–C_8–F_7	110.1
C_3–Fe–C_5	85.3	C_7–C_8–F_8	107.2
C_3–Fe–C_7	93.6	F_7–C_8–F_8	104.5

[a] Average estimated standard deviations are: σ(Fe–C–O) = 1.2°, σ(C–Fe–C) = 0.6°, σ(O–Fe–O) = 0.5°, σ(F–C–F) = 1.1°, σ(Fe–C–C) = 1.3°, σ(C–C–F) = 1.4°.

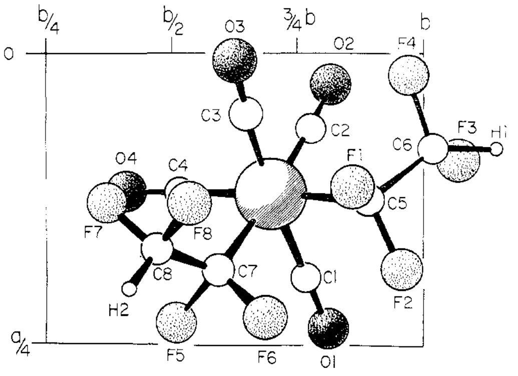

Figure 1.—The numbering of atoms in the molecule *cis*-$(HCF_2 \cdot CF_2)_2Fe(CO)_4$.

The molecule is a typical octahedral complex of a d^6 Fe(II) ion. All angles between adjacent ligands are approximately 90° although, *vide infra*, there are some statistically significant deviations from this value. The tetrafluoroethyl groups are arranged so as to give the molecule the expected *cis* configuration. However, in the solid state the iron atom does not appear to maintain accurate local C_{2v} symmetry. The carbon–carbon contacts between adjacent carbonyl groups vary in the range 2.57–2.72 A (0.15 A = 7.5σ), the variations not always being consistent with ideal C_{2v} symmetry, where the expected relationships are

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(14) "International Tables for X-Ray Crystallography," Vol. 3, The Kynoch Press, Birmingham, England, 1962. Values for iron are taken from p 211; those for carbon, oxygen, and fluorine, from p 202.

(15) The corrected scattering factor for iron would be $f_\theta = f_{o,\theta} + \Delta f' + i\Delta f''$ where $\Delta f'$ = 0.4 electron and $\Delta f''$ = 1.0 electron; see ref 14, p 215.

$$\left.\begin{matrix}C_5\\C_1\\C_2\end{matrix}\right\} \equiv \left\{\begin{matrix}C_7\\C_3\\C_4\end{matrix}\right.$$

For example, the angles C_5–Fe–C_2 (94.2°) and C_7–Fe–C_4 (86.0°) vary by approximately 13σ, and the distances C_2–C_5 (2.86 A) and C_4–C_7 (2.69 A) vary by 8.5σ. These variations are believed to be caused by a combination of (i) nonbonded interactions between fluorine atoms and the carbon atoms of the carbonyl ligands and (ii) intermolecular repulsions involving the oxygen atoms of the carbonyl groups.

The metal–carbonyl linkages are approximately linear, but the variations of Fe–C_2–O_2 (174.3°) and Fe–C_3–O_3 (174.5°) from linearity are statistically significant (5.4° = 4.5σ). Since the pattern of these distortions from linearity is not consistent with maintaining C_{2v} symmetry, it is believed that these distortions also are the result of crystal forces rather than orbital overlap criteria.[16]

The Tetrafluoroethyl Groups.—This analysis, as in the case of that involving the $[Co(CN)_5C_2F_4H]^{3-}$ ion,[17] confirms that the reaction of a transition metal hydride with tetrafluoroethylene leads to the formation of a tetrafluoroethyl ligand with the hydrogen attached to the β-carbon atom. Figure 1 shows each of the tetrafluoroethyl groups to be in the expected staggered conformation; the exact correspondence between the two groups can very clearly be seen by means of the intramolecular contacts in Table IV(d). The average fluorine–fluorine distance within a CF_2 group is 2.16 A; the mean F–C–F angle of 104° shows an angular contraction from the regular tetrahedral value in the same sense, but magnified, as that observed in fluorinated methanes and ethanes.[18,19] Table VI gives a summary of the average bond angles and bond lengths. The average Fe–C_α–C_β angle is seen to be 121.2°. The increase in the metal–carbon–carbon bond angle from the formal sp^3 angle of 109° 28′ appears to be a general phenomenon in transition metal fluoroalkyls. In each of the complexes which has previously been studied, a significant increase of the angle M–C_α–C_β has been noted, the observed values being: 116.4° in π-$C_5H_5Rh(CO)(C_2F_5)I$,[5] 119.7° in $K_3[Co(CN)_5CF_2CF_2H]$,[17] and 123.3° in π-$C_5H_5Mo(CO)_3C_3F_7$.[20] It must be realized, however, that *non*fluorinated transition metal alkyls also show M–C_α–C_β angles greater than the regular tetrahedral value.[21,22]

TABLE VI

AVERAGE BOND DISTANCES AND ANGLES WITHIN *cis*-$(HFC_2 \cdot CF_2)_2Fe(CO)_4$

No. of observations	Atoms	Bond Length, A: Largest	Smallest	Av
4	Fe–CO	1.873	1.826	1.845
2	Fe–CF_2	2.070	2.066	2.068
4	C–O	1.134	1.107	1.118
2	C_α–C_β	1.503	1.471	1.487
4	C_α–F	1.418	1.349	1.379
4	C_β–F	1.382	1.339	1.363
		Angle, deg: Largest	Smallest	Av
2	Fe–C_α–C_β	121.4	121.0	121.2
4	Fe–C_α–F	115.1	109.2	112.0
2	F–C_α–F	103.9	102.9	103.4
4	F–C_α–C_β	106.2	99.7	103.1
4	C_α–C_β–F	111.6	107.2	109.1
2	F–C_β–F	104.8	104.5	104.7

TABLE VII

INTERMOLECULAR CONTACTS TO 3.5 A FOR *cis*-$(HCF_2 \cdot CF_2)_2Fe(CO)_4$

Atom	Atom in neighboring molecule	Distance, A
O_1	$F_5\ ({}^1/_2 - x, 1 - y, {}^1/_2 - z)$	3.15
	$F_8\ (x, 1{}^1/_2 - y, -{}^1/_2 + z)$	3.29
	$F_6\ (x, 1{}^1/_2 - y, -{}^1/_2 + z)$	3.30
O_2	$F_8\ (x, 1{}^1/_2 - y, -{}^1/_2 + z)$	2.92
	$O_3\ (-x, {}^1/_2 + y, {}^1/_2 - z)$	3.04
	$O_3\ (x, 1{}^1/_2 - y, -{}^1/_2 + z)$	3.08
	$F_4\ (-x, -{}^1/_2 + y, {}^1/_2 - z)$	3.22
	$F_1\ (x, 1{}^1/_2 - y, -{}^1/_2 + z)$	3.26
	$F_3\ (-x, -{}^1/_2 + y, {}^1/_2 - z)$	3.39
	$F_7\ (-x, {}^1/_2 + y, {}^1/_2 - z)$	3.40
	$C_3\ (-x, {}^1/_2 + y, {}^1/_2 - z)$	3.40
	$C_6\ (-x, -{}^1/_2 + y, {}^1/_2 - z)$	3.46
O_3	$O_2\ (-x, -{}^1/_2 + y, {}^1/_2 - z)$	3.04
	$O_2\ (x, 1{}^1/_2 - y, {}^1/_2 + z)$	3.08
	$F_3\ (-x, -{}^1/_2 + y, {}^1/_2 - z)$	3.40
O_4	$F_4\ (-x, -{}^1/_2 + y, {}^1/_2 - z)$	2.97
	$F_5\ ({}^1/_2 - x, 1 - y, {}^1/_2 - z)$	3.20
	$F_1\ (x, 1{}^1/_2 - y, -{}^1/_2 + z)$	3.30
	$F_3\ (x, -1 + y, z)$	3.33
C_1	$F_5\ ({}^1/_2 - x, 1 - y, {}^1/_2 - z)$	3.30
	$F_8\ (x\ 1{}^1/_2 - y, -{}^1/_2 + z)$	3.36
C_2	$F_8\ (x\ 1{}^1/_2 - y, -{}^1/_2 + z)$	3.09
	$F_1\ (x, 1{}^1/_2 - y, -{}^1/_2 + z)$	3.35
	$F_4\ (-x, -{}^1/_2 + y, {}^1/_2 - z)$	3.39
C_3	$O_2\ (-x, -{}^1/_2 + y, {}^1/_2 - z)$	3.40
C_4	$F_4\ (-x, -{}^1/_2 + y, {}^1/_2 - z)$	3.17
	$F_5\ ({}^1/_2 - x, 1 - y, {}^1/_2 - z)$	3.35
	$F_1\ (x, 1{}^1/_2 - y, -{}^1/_2 + z)$	3.37
C_6	$F_7\ (x, 1 + y, z)$	3.42
	$O_2\ (-x, {}^1/_2 + y, {}^1/_2 - z)$	3.46
F_1	$O_2\ (x, 1{}^1/_2 - y, {}^1/_2 + z)$	3.26
	$O_4\ (x, 1{}^1/_2 - y, {}^1/_2 + z)$	3.30
	$C_2\ (x, 1{}^1/_2 - y, {}^1/_2 + z)$	3.35
	$C_4\ (x, 1{}^1/_2 - y, {}^1/_2 + z)$	3.37
F_3	$F_8\ (x, 1{}^1/_2 - y, -{}^1/_2 + z)$	3.33
	$O_4\ (x, 1 + y, z)$	3.33
	$O_2\ (-x, {}^1/_2 + y, {}^1/_2 - z)$	3.39
	$O_3\ (-x, {}^1/_2 + y, {}^1/_2 - z)$	3.40
	$F_7\ (x, 1 + y, z)$	3.46
F_4	$O_4\ (-x, {}^1/_2 + y, {}^1/_2 - z)$	2.97
	$C_4\ (-x, {}^1/_2 + y, {}^1/_2 - z)$	3.17
	$O_2\ (-x, {}^1/_2 + y, {}^1/_2 - z)$	3.22
	$C_2\ (-x, {}^1/_2 + y, {}^1/_2 - z)$	3.39
F_5	$F_5\ ({}^1/_2 - x, 1 - y, {}^1/_2 - z)$	2.91
	$O_1\ ({}^1/_2 - x, 1 - y, {}^1/_2 - z)$	3.15
	$O_4\ ({}^1/_2 - x, 1 - y, {}^1/_2 - z)$	3.20
	$C_1\ ({}^1/_2 - x, 1 - y, {}^1/_2 - z)$	3.30
	$C_4\ ({}^1/_2 - x, 1 - y, {}^1/_2 - z)$	3.35
F_6	$O_1\ (x, 1{}^1/_2 - y, {}^1/_2 + z)$	3.30
F_7	$O_2\ (-x, -{}^1/_2 + y, {}^1/_2 - z)$	3.40
	$C_6\ (x, -1 + y, z)$	3.42
	$F_3\ (x, -1 + y, z)$	3.46
F_8	$O_2\ (x, 1{}^1/_2 - y, {}^1/_2 + z)$	2.92
	$C_2\ (x, 1{}^1/_2 - y, {}^1/_2 + z)$	3.09
	$O_1\ (x, 1{}^1/_2 - y, {}^1/_2 + z)$	3.29
	$F_3\ (x, 1{}^1/_2 - y, {}^1/_2 + z)$	3.33
	$C_1\ (x, 1{}^1/_2 - y, {}^1/_2 + z)$	3.36

The mean Fe–CF_2 bond length of 2.068 A in the present complex is some 0.223 A longer than the average Fe–CO distance of 1.845 A. After making the appropriate correction of 0.07 A (which allows for the difference in covalent radii of sp and sp^3 hybridized

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carbon atoms), the "effective contraction" of the Fe–CO bond length, relative to the Fe–CF_2 distance, is ~0.15 A.[23]

Since such species as $(C_nH_{2n+1})_2Fe(CO)_4$ are not known, no comparison of analogous alkyl and fluoroalkyl complexes is possible. There are, however, a number of polynuclear iron–carbonyl species which, formally at least, contain simple iron–carbon σ bonds, but a wide variety of bond lengths have been observed. For example, the ferracyclopentadiene species $(CH_3C_2OH)_2Fe_2(CO)_6$,[24] $C_6H_5C_2C_6H_5Fe_2(CO)_6$,[25] and black $(C_6H_5C_2C_6H_5)_2Fe_3(CO)_8$[26] have iron–carbon σ bonds ranging from 1.948 to 2.063 A in length. The acetylene complex violet $(C_6H_5C_2C_6H_5)_2Fe_3(CO)_8$[26] has eight iron–carbon σ bonds varying from 1.954 to 2.057 A. The heterocyclic $(C_6H_5C_2H)_3CoFe_2(CO)_5$[27] has iron–carbon σ bonds of 2.006, 2.088, and 2.097 A, and the σ-vinyl complex, $(C_6H_5C_2CO_2CH_3)_3COFe(CO)_2$, has an iron–carbon distance of 1.99 A.[28] In each of the above molecules there is a considerable likelihood that the iron–carbon linkage is part of a large delocalized system, rather than being an isolated σ bond.

However, the complex $(OC)_2FeC_5H_4$–$CH_2Fe(CO)_4$ *does* have a distinct Fe–CH_2 bond of length 2.123 A,[29] but, since the iron atom is in a formal +1 oxidation state and the over-all configuration may well involve some strain in the Fe–CH_2 linkage, a direct comparison of this bond length with the Fe–CF_2 distance in *cis*-$(HCF_2 \cdot CF_2)_2Fe(CO)_4$ is not strictly valid. The crystal structure of π-$C_5H_5Fe(CO)_2(\sigma$-$C_5H_5)$ has recently been determined;[30] the Fe^{II}–CH< distance is found to be 2.11 ± 0.02 A, but the structure is of limited accuracy. Thus, although further substantiation would be welcome, it seems that the contraction in iron–carbon bond length caused by fluorinating the α-carbon atom is probably about 0.05 A in Fe(II) complexes.

The Crystal Structure

All intermolecular contacts less than 3.5 A are collected in Table VII. The shortest F···F contact is 2.91 A between F_5 and F_5 ($^1/_2 - x, 1 - y, ^1/_2 - z$). There are several F···O contacts below 3.0 A, and it is possible that these participate in distorting the iron atom coordination sphere from strict C_{2v} symmetry.

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(23) The "effective contraction" defined here is one of the few possible measures of the relative amounts of π bonding in metal–carbon linkages. A comparison with values for other molecules may be made by consulting Table V of ref 4.

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The Crystal and Molecular Structure of Azulene Diiron Pentacarbonyl

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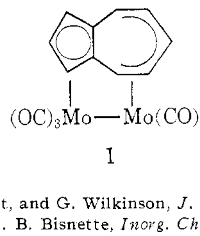
Azulene diiron pentacarbonyl, $C_{10}H_8Fe_2(CO)_5$, crystallizes in the triclinic space group $C\bar{1}$ (no. 2) with $a = 7.32 \pm 0.01$ A, $b = 14.48 \pm 0.02$ A, $c = 14.76 \pm 0.02$ A, $\alpha = 116.2 \pm 0.2°$, $\beta = 92.3 \pm 0.2°$, $\gamma = 93.0 \pm 0.2°$, $Z = 4$. A three-dimensional single-crystal X-ray analysis, based on 2579 independent nonzero reflections collected with an automated diffractometer, has been completed ($R_F = 10.75\%$). The carbon atoms from the five-membered ring of the azulene form a π-cyclopentadienyl system which is bonded to an $Fe(CO)_2$ group, while three atoms of the seven-membered ring participate in a π-allyl linkage to an $Fe(CO)_3$ group. Unequal Fe–C(allyl) bond lengths, a distortion of the azulene ligand from planarity, and a rather long iron–iron bond of 2.782 A indicate that the molecule may be rather strained.

Introduction

The preparation of molybdenum- and iron–azulene complexes such as $C_{10}H_8Mo_2(CO)_6$[1] and $C_{10}H_8Fe_2(CO)_5$[2] was reported in 1958. An investigation of their proton magnetic resonance spectra led to the suggestion of a number of structures, each involving metal–diene or metal–triene bonding, but no unique formulation was possible.[3] King and Bisnette[4] have pointed out that recent developments make it likely that $C_{10}H_8Mo_2(CO)_6$ is represented as in I, with a π-cyclopentadienyl–metal



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