THE CRYSTAL STRUCTURE DETERMINATION OF 7-C5H5Fe(CO)2Mn(CO)5

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(Received January 17th, 1966)

INTRODUCTION

In 1960, Abel, Singh and Wilkinson¹ reported "the first carbonyl complex with a metal-metal bond between different transition metals". Numerous compounds of this type have since been reported; however, we believe this to be the first reported crystal structure determination of such a compound. The structure of π -C₅H₅Fe(CO)₂Mn(CO)₅ first became of interest owing to its relationship to two closely related compounds $[\pi$ -C₅H₅Fe(CO)₂]₂ and $[Mn(CO)_5]_2$. The structure of the former, reported by Mills², contains two bridging carbonyls and an Fe–Fe bond which appears to be a normal covalent bond of length 2.49 Å. On the other hand, the structure of the latter, reported by Dahl and Rundle³, contains no bridging carbonyls and a rather long Mn–Mn bond length of 2.92 Å. Thus the primary purpose of this investigation was to establish the skeletal geometry of the molecule and to determine the Fe–Mn bond length.

ENPERIMENTAL

The compound used in this X-ray investigation was prepared by King, Treichel and Stone⁴ from the reaction of NaMn(CO)₅ with π -C₅H₅Fe(CO)₂I. Single crystals were grown in this laboratory by vacuum sublimation at about 40°. Mounting of the crystals in thin-walled, Lindemann glass capillaries was necessary owing to the instability of the compound in air.

The red, platelike crystals were found, from systematic extinctions, to have space group symmetry $P 2_1/b$. The unit cell parameters obtained from precision measurements using a General Electric single crystal orienter are as follows:

a	=	7.220	± 0.006 Å	. b =	= 30.387	≟	0.008	Å
с	=	12.498	± 0.002 Å	, y =	= 90.21	÷	0.10°	

the calculated density of 1.80 g/cc, based on eight molecules per unit cell, compares favorably with the observed density of 1.78 g/cc, found by the flotation method using a $ZnCl_2$ solution.

Within a 2Θ sphere of approximately 145°, complete three-dimensional X-ray diffraction intensity data were taken with V-filtered Cr-radiation, utilizing a General Electric XRD-5 X-ray unit equipped with a goniostat and scintillation counter. The measurements were made using a one hundred second, $3^{1}/_{3}$ degree – 2Θ scan with a

 Θ -2 Θ coupling. Although about 1700 independent intensities were recorded, one hundred reflections, suspect of significant error due to non characteristic radiation, together with about four hundred "unobserved" reflections were not included in the subsequent computations. The intensities were corrected for Lorentz and polarization factors, crystal and capillary absorption, and crystal decomposition. The crystal from which the intensity data were obtained had a linear absorption coefficient of S3.9 cm⁻¹ and the general dimensions of 0.23 \times 0.10 \times 0.16 mm. An absorption correction program for polyhedral crystals, adapted from one originally written by Busing and Levy, was used to make this correction.

STRUCTURE DETERMINATION

The presence of eight molecules in a unit cell with space group symmetry of order four requires two crystallographically independent molecules. With each molecule containing one manganese, one iron, twelve carbon and seven oxygen atoms, the structure contains 126 independent positional parameters (neglecting hydrogen atoms) plus temperature factors.

The positions of two of the heavy atoms were obtained from an analysis of the Harker sections of a sharpened Patterson map. Using these two atoms to determine the signs, an electron-density map was computed which revealed the positions of the two remaining heavy atoms in the asymmetric unit. The positions of the twelve Harker and twenty-four non-Harker peaks corresponding to these four heavy atoms were subsequently verified in the sharpened Patterson map. The positions of the carbon and oxygen atoms were then obtained by employing conventional "heavy atom" techniques.

A full matrix least-squares refinement was initiated with the four heavy atoms being refined anisotropically and the thirty-eight lighter atoms being refined isotropically. The computations were performed on an IBM 7074 computer. Following several cycles of least-squares refinement a difference electron-density map was computed which revealed some maxima in positions consistent with the cyclopentadienyl ring hydrogens. The positions of the hydrogens were then calculated, assuming a C-H distance of 1.0 Å and included, although not varied, in the ensuing refinement. Also included at this point was an anomalous dispersion correction (real part only) of the iron and manganese scattering factors.

Following several additional cycles of full matrix least-squares refinement, a final agreement factor, $\mathbf{R} = \Sigma [| F_0 | - | F_c | | / \Sigma | F_0]$, of 0.064 was obtained.

DISCUSSION

The molecular structure of π -C₅H₅Fe(CO)₂Mn(CO)₅ is shown in Fig. 1. The crystal structure consists of discrete molecules which may be envisioned as the adducts of the monomeric forms of dimanganese decacarbonyl, [Mn(CO)₅]₂, and di- π -cyclopentadienyl-diiron tetracarbonyl, [π -C₅H₅Fe(CO)₂]₂, with the two moieties held together solely by an Fe-Mn bond of length 2.843 Å.

The structure unambiguously contains no bridging carbonyls, a finding which is entirely consistent with the absence of any carbonyl bands in the bridging C–O region of the infrared spectrum obtained by King, Treichel and Stone⁴ (using a $C_{*}Cl_{*}$

solution) or by the authors (using a CCl₄ solution). Any assumption that one or more of the carbonyls is a bridging carbonyl, would necessitate a metal-carbon bond length of at least 2.99 Å (the shortest metal to carbonyl carbon "nonbonded" distance) compared to the usual value of about 1.85 Å. Regarding the metal-metal linkage, the structure is therefore quite similar to the $Mn_2(CO)_{10}$ structure and quite unlike the $[\pi-C_5H_5Fe(CO)_2]_2$ structure.



Fig. 1. The molecular configuration of π -C₅H₅Fe(CO)₂Mn(CO)₅.

As would seem reasonable, the equatorial carbonyls in $Mn_2(CO)_{10}$ assume a highly symmetrical staggered conformation; however, as can be seen (Fig. 2), the equatorial carbonyls in π -C₅H₅Fe(CO)₂Mn(CO)₅ assume a conformation which is



Fig. 2. The conformations of the two crystallographically independent molecules of π -C₅H₅Fe(CO)₂-Mn(CO)₃.

neither perfectly staggered nor eclipsed. If the iron moiety were rotated about the Fe-Mn bond, such that the iron and manganese carbonyls assume a perfectly staggered conformation, atom C_s (the ring carbon atom which is in closest proximity to the manganese moiety and its associated hydrogen) would be eclipsed by one of the

manganese equatorial carbonyls. In like manner, a conformation in which atom C_8 is perfectly staggered, results in the eclipsing of the iron carbonyls. Surprisingly, the two crystallographically independent molecules do not assume identical conformations. The difference in the amount of the rotation about the metal-metal bond appears to be approximately seven degrees. Apparently the energy minimum is broad and the environmental differences are sufficient to produce significant differences in the intermolecular forces, thus leading to the conformational disparity.

The arrangement of the carbonyls about the manganese atom in this structure is virtually identical to that found in the $Mn_2(CO)_{10}$ structure. In both structures there are four equatorial carbonyls whose Mn-C distance is significantly longer than that of a lone axial (or apical) carbonyl. The values of the averages for these two distances in π -C₅H₅Fe(CO)₂Mn(CO)₅ are respectively 1.825 Å and 1.749 Å, while those reported for $Mn_2(CO)_{10}$ are 1.83 Å and 1.79 Å. Although the equatorial Mn-C distances compare very favorably, the axial Mn-C distances differ by approximately 0.04 Å. It is reasonable that these two distances would differ, since the species which are *trans* to the axial carbonyls, *i.e.* π -C₅H₅Fe(CO)₂- and Mn(CO)₅-, have not only a different chemical composition, but also occupy a slightly different position relative to the axial carbonyl. In this structure the Fe-Mn-C_{ax} angle has an average value of 168.9° whereas the corresponding Mn-Mn-C_{ax} angle in Mn₂(CO)₁₀ equals, within experimental error, 180°. Possibly this "bent" Fe-Mn bond (probably resulting from the repulsive forces between the two iron carbonyls and the two manganese carbonyls in closest proximity) produces a weaker Fe-Mn bond and consequently a stronger Mn-C bond.

It should also be noted that the average axial C-O bond in this structure is an extremely long 1.195 A, while the average equatorial C–O bond is a normal 1.156 A. Generally with metal carbonyls, one finds that as the metal-carbon bond order increases, the carbon-oxygen bond order decreases. This would lead one to expect a lengthened axial C-O distance to accompany the shortened axial Mn-C bond length. [Interestingly, Dahl and Rundle³ detected no such difference in Mn₂(CO)₁₀, but Bailey and Dahl⁵ recently reported an even greater disparity in the technetium analog $Tc_2(CO)_{10}$, in which the average equatorial C-O distance was 1.12 Å while the axial distance was 1.20_5 Å.] Since a carbonyl bond length of 1.195 Å approaches that expected for a bridging carbonyl group, one might expect that an infrared spectrum would show an absorption peak in or near the bridging carbonyl stretching frequency range of approximately 1750 to 1875 cm⁻¹. Examination of the previously mentioned infrared spectrum however, reveals the existence of no peaks with a frequency lower than 1944 cm^{-1} . But, it should be emphasized that such a bond length is not ruled out by this evidence, since the absorption frequency is certainly not a function of interatomic distance alone.

It is unlikely that the long C-O distance and the very short axial Mn-C distance are merely the result of random errors in the axial carbon positional parameters, since there are two crystallographically independent molecules in this structure, and the two values for each of these two distances differ by no more than 0.002 Å, as can be seen in Table 3. Admittedly a systematic error could be responsible for these atypical results. Dahl and Rundle³ noted that an anisotropic refinement resulted in a rather large shift of the axial carbon atom in $Mn_2(CO)_{10}$ from the position found by an isotropic refinement; however, most likely the anisotropy of the manganese atom rather than that of the carbon atom was responsible for this shift. And, although the light

Atom ^a	xja	yjb 	zjc	G _x	σ _y	σ.
Fe	0.4211	0.1361	0.3160	0.00041	0.0000\$	0.00021
Mn	0.3536	0.2253	0.3705	0.00043	0.0000\$	0.00022
Fe'	0.0749	0.0289	0.7534	0.00042	0.00008	0.00021
Mn'	0.1461	0.1162	0.8216	0.00042	0.0000S	0.00021

 β_{33}

0.0055

0.00023

0.00So

0.00028

0.0057

0.00021

0.0057

0.00023

 β_{12}

0.0005

-0.0007

--0.0008

--0.0005

0.00014

0.00014

0.00013

0.00013

 β_{13}

-0.0017

-0.0009

0.00037

0.00039

0.0006

0.00037

0.00039

-0.0008

FINAL HEAVY ATOM ATOMIC PARAMETERS AND STANDARD DEVIATIONS (A) POSITIONAL PARAMETERS AND STANDARD DEVIATIONS

β==

0.0013

0.00004

0.0010

0.0000.4

0.0010

0.00004

0.0010

0.00004

TABLE 1

Atom^a

Fe

σ Mn

σ Fe'

σ

σ

Mn'

β11

0.0289

0.00092

0.0260

0.00091

0.0309

0.00090

0.0246

0.00090

^a Unprimed atoms refer to molecule 1 and primed to molecule 2. ^b Anisotropic temperature
factors of the form: exp $(-\hbar^2\beta_{11} - \hbar^2\beta_{22} - l^2\beta_{33} - 2hk\beta_{12} - 2hl\beta_{13} - 2kl\beta_{23})$.

atoms in the π -C₅H₅Fe(CO)₂Mn(CO)₅ structure received only an isotropic refinement, the heavy atoms were refined anisotropically.

As in the structure of $Mn_2(CO)_{10}$, it was also found that the manganese equatorial carbonyls in this structure are bent inward towards the other half of the molecule such that the manganese atoms lie respectively 0.116 Å and 0.102 Å out of the leastsquares plane fitted to atoms C_4 , C_5 , C_6 and C_7 in each independent molecule. [Dahl and Rundle³ reported this distance to be 0.12 Å in $Mn_2(CO)_{10}$.] The average value of the eight $C_{ax}Mn-C_{eq}$ angles is 93.4². Since the equatorial carbonyls are all bent inward toward the iron moiety, one might expect all of the angles defined by two adjacent equatorial carbon atoms and a manganese atom (at the vertex), *i.e.* $C_{eq}-Mn-C_{eq}$, to be acute; however, one of these angles in each molecule, the C_7-Mn-C_4 angle, is obtuse. The two values of this angle are 92.3° and 93.7° versus an average 88.7°for the other six members of the set. This effect is apparently due to the close proximity of the cyclopentadienyl ring (see Figs. 1 and 2). It may be seen in Table 4 that angles Fe-Mn-C₄ and Fe-Mn-C₇ are significantly smaller than angles Fe-Mn-C₅ and Fe-Mn-C₆.

Although the Mn–C–O angles all appear to be within experimental error of 150° , the Fe–C–O angles range from 169.5° to 173.9° ; apparently this non-linearity tends to maximize certain critical intramolecular and intermolecular distances.

Concerning the equivalency of the C-C bond lengths and of the Fe- C_{ring} distances, early in the analysis of the results of this crystal structure determination, the authors noted a marked ordering of the deviations of the individual C-C and Fe- C_{ring} distances from their respective mean values. As may be seen in Table 3, in both molecules, the C_{s} - C_{s} distance is the longest, the C_{9} - C_{10} and C_{11} - C_{12} distances are respectively the second and third longest, while the C_{10} - C_{11} and C_{12} - C_{8} distances are

 β_{23}

-0.0002

0.00007

0.0003

0.00008

0.00007

0.00008

0.000 I

-0.0002

TABL	.E 2
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(A) FINAL LIGHT ATOM ATOMIC PARAMETERS

<i>x 2</i>	y/b	<i>z c</i>	B
; I			
0.2801	0.1433	0.2072	7.02
0.1758	0.1432	0.1351	S.85
0.2311	0.1258	0.1023	1.So
0.1213	0.1151	0.1591	6.61
0.3538	0.2822	0.3010	S.01
0.3503	0.3209	0.1078	10.23
0.5480	0.2166	0.4628	6.06
0.0004	0.2122	0.523.4	7.22
0 1000	0.2128	0.1505	6.02
0 1012	0.2061	0.5511	S.12
0 5576	0.2005	0.2821	6
0.1320	0.2287	0.20-4	0.77
0.0-3-	0.2207	0.2516	9.05
0.5075	0.2.90	0.4540	2-73
0.0032	0.231/	0.1705	9.01 6.05
0-,150	0.1410	0.3~39	6.05
0.0439	0.1133	0.4094	0.09
0.5550	0.0,03	0.3500	0.35
0.5094	0.0343	0.2437	7.15
0.0001	0.1235	0.2231	¥.00
2			
0.2279	0.0135	0.8520	0.0 <u>5</u>
0.3335	0.0003	0.9135	7.30
0.2430	0.0384	0.6599	6.33
0.3636	1110.0	0.5977	S.28
0.1457	0.1699	0.8751	5.90
0.1414	0.2066	0.9092	8.53
-0.0407	0.1269	0.7310	6.25
-0.1503	0.1345	0.6721	7.75
0.3103	0.1296	0.7190	6.16
0.1191	0.1353	0.6544	3.73
1011.0	0.0006	0.9197	5.14
0.4508	0.0010	0.0655	7.19
-0.0007	0.0057	0.0203	5.60
-0.1002	0.0827	0.00+7	6.88
	0.003-	0.9743	6.55
-0.2101	0 02 11	17 1911	
-0.2191	0.0344	0.5001	6.8=
0.2191 0.1576 0.6567	0.0344 0.0264 —0.0146	0.6524	6.85 7.07
0.2191 0.1576 0.0653	0.0344 0.0264 0.0146	0.6524 0.6515	6.85 7-02 6 -8
	x/2 0.2891 0.1758 0.2344 0.1213 0.3538 0.3503 0.5489 0.6664 0.1999 0.1612 0.1526 0.0252 0.5073 0.6032 0.7150 0.6489 0.5556 0.5556 0.5556 0.5556 0.5556 0.5661 0.22279 0.3335 0.2430 0.3636 0.1457 0.1414 -0.0407 -0.1603 0.3193 0.4191 0.3391 0.3191 0.3391	x/2 y/b 0.2891 0.1433 0.1758 0.1432 0.2344 0.1255 0.1213 0.1151 0.3503 0.2822 0.3503 0.2329 0.5489 0.2166 0.6664 0.2122 0.1909 0.2128 0.1750 0.2475 0.7526 0.2275 0.0252 0.2287 0.5073 0.2290 0.6032 0.2317 0.7150 0.1410 0.4489 0.1133 0.5556 0.0783 0.5556 0.0783 0.5556 0.0783 0.5556 0.0783 0.5556 0.0783 0.5556 0.0783 0.5556 0.0783 0.5556 0.0783 0.5556 0.0783 0.5430 0.0384 0.6661 0.1238 0.2279 0.0135 0.3335 -0.0003 0.1414	x/2 y/b z/c 0.2891 0.1433 0.2072 0.1758 0.1432 0.1351 0.2344 0.1258 0.4023 0.1213 0.1151 0.4591 0.3503 0.3209 0.4075 0.5489 0.2166 0.4628 0.4064 0.2122 0.5334 0.1090 0.2128 0.4808 0.1526 0.2275 0.2824 0.0252 0.2287 0.2271 0.5073 0.2290 0.2546 0.4052 0.2287 0.2271 0.5073 0.2290 0.2546 0.6032 0.2317 0.1785 0.7150 0.1410 0.3259 0.4489 0.1133 0.4094 0.5556 0.0783 0.3580 0.5694 0.0548 0.2487 0.6661 0.1238 0.2281

(B) AVERAGE STANDARD DEVIATIONS OF FINAL LIGHT ATOM ATOMIC PARAMETERS

Alom	zja	у/b	zje	B
C (carbonyl)	0.00279	0.00058	0.00152	0.90
0	0.00208	0.00043	0.00113	0.69
C (ring)	0.00278	0.00061	0.00156	0.92

J. Organometal. Chem., 6 (1966) 389-398

Atoms	Molecule 1	Molecule 2	Atoms	Molecule 1	Molecule 2
Mn–Fe	2.840	2.845	C,-O,	1.217	1.158
Fe-C,	1.676	1.726	с <u>-</u> О,	1.129	1.170
Fe-C,	1-754	1.709	$C_{3} - O_{3}$	1.194	1.195
Mn-C _a	1.748	1.750	CO_	1.146	1.159
Mn-C,	1.541	1.815	CO.	1.148	1.160
MnC5	1.509	1.819	C ₆ -O ₆	1.152	1.153
Mn-C	1.823	1.833	C,-O,	1.1ŜO	1.150
Mn-C-	1.827	1.833	C _a -C _a	1.421	1.439
Fe-C	2.130	2.131	CC10	1.413	1.410
Fe-C	2.133	2.101	C19~C11	1.384	1.388
Fe-Cin	2.077	2.096	$C_{11} - C_{12}$	1.398	1.407
Fe-C,	2.071	2.078	$C_{12} - C_8$	1.374	1.396
Fe-C,	2.110	2.102			

(A) INTERATOMIC DISTANCES (Å)

TABLE 3

(B) AVERAGE INDIVIDUAL STANDARD DEVIATIONS AND AVERAGE INTERATOMIC DISTANCES

Atoms	Average o	Average dist.
Mn-Fe	0.004	2.843
Fe-Cearbonyl	0.025	1.715
Mn-Cazial	0.025	1.749
Mn-Cegyatorial	0.026	1.825
Fe-Cring	0.024	2.104
C-OFe	0.023	1.169
C-OMR. ar	0.025	1.195
C-OMA. co	0.023	1.156
C-O _{all}	0.023	1.105
C-Cring	0.029	1.403

TABLE 4

BOND ANGLES AND AVERAGE STANDARD DEVIATIONS

Atoms	Mol. 1	Mol. 2	Std. dev.	Atoms	Mol. 1	Mol. 2	Std. dev.
Fe-C,-O,	169.5°	173.5°	2.0°	C ₃ -Mn-C ₄	93-0 ⁰	93.6°	1.00
Fe-CO.	173.10	173.9°	1.9°	$C_{3} - Mn - C_{5}$	95-4°	93.2°	1.0°
Mn-C,-O,	177.9°	178.62	2.2	C ₁ -Mn-C ₆	92.9°	92.8°	°0.1
Mn-C,-O,	177.10	178.6°	1.9°	C,-Mn-C,	93.3°	93.2°	1.0°
Mn-C ₅ -O ₅	177.8"	177.6°	2.1°	$C_1 - Mn - C_5$	\$7.8°	\$\$.7°	1.0°
Mn-C ₆ -O ₆	179.6°	177.2°	2.0°	C ₅ -Mn-C ₆	\$8.9°	89.5°	1.0°
Mn_CO_	178.5	179.1°	2.10	C ₆ -Mn-C ₇	90.1°	87.3°	1.0°
Mn_Fe_C,	\$\$.2°	Š5.0°	0.7°	C_Mn_C	92.3°	93-7°	1.0°
Mn-Fe-C	\$3.5°	86.0°	0.7°	C ₁ -Mn-C ₆	173.5°	173.5°	e.9°
Fe-Mn-C	168.6°	169.2°	0.8°	C ₅ -Mn-C ₇	171.2°	173.0°	1.0°
Fe-Mn-C,	δ3.0°	So.4°	0.7°	$C_{8} - C_{9} - C_{10}$	105.6°	107.6°	1.9°
Fe-Mn-C,	95.1*	95.6°	0.7	C ₀ -C ₁₀ -C ₁₁	107.S°	107.4°	2.0 [°]
Fe-Mn-C	91.7°	93.6°	0.7°	C10-C11-C1	109.S°	109.80	2.1 ^c
Fe-Mn-C-	76.23	78.3°	0.7°	C,,-C,,-C,	106.5°	107.6°	2.1°
C,-Fe-C.	94-9°	94-7°	1.12	$C_{12}^{11} - C_{5}^{12} - C_{9}^{12}$	110.20	107.5 ³	2.0 ^c

TABLE 5

OBSERVED AND CALCULATED STRUCTURE FACTORS

The three o	columns consis	t of <i>k</i> , 10F ₀ , an	d 10Fc.			
C # C	22 113 -111	15 427 -475	13 106 -109 14 446 -447	10 214 -178 17 428 -4CC	12 214 171 13 462 472	0 1122 8 737
E 3124 3270 12 2356 -2463	0 2 4	20 272 294	15 224 -244	2C 134 -77 21 354 355	14 331 337 18 242 272	16 533
14 754 733	6 282 223 1 141 744	21 194 131	1 5 9	• • •	19 184 -194	14 420
20 1245 -1214	2 547 -548	23 348 -311	3 254 350	2 - 3	21 243 -100	18 210
	4 1247 -1280	1 6 3	7 423 -573	3 208 -497	3 # 3	4 E
9 F 1	5 515 -514 # 735 75#	1 1004 -1037	10 122 -177 11 234 227	4 1148 1245 5 1232 124C	1 212 -100	1 100
7 312 30# # 15C# 1495	9 287 319 14 234 232	3 2145 2231 4 443 -418	12 225 247	4 458 448	2 418 -377	2 272
11 2253 2124	19 212 -222	4 642 638	1 # 10	4 222 -145	5 347 332	5 54C
13 234 244	18 177 155	8 1281 -1325	1 243 -242	12 472 488	8 239 214	20 235
15 253 -245	c x 7	10 350 -372	2 329 -239 3 272 246	13 214 25C 15 255 3C5	12 241 194 13 244 239	11 273 12 425
14 330 -267	1 259 -222	11 1C3C 957 12 285 -232	5 180 147	17 515 -512	14 24C 213 15 5CR -541	23 3Ce 14 734
18 298 -391 19 288 175	3 202 -155	13 544 521		19 193 121	14 324 382	17 190
20 484 425	4 389 -377	15 431 -400	7 876 - 676		14 ZAC 284	-
22 419 -411	8 1C47 -167C	18 136 -47	4 382 330		~	•••
24 477 -492	10 194 -177	20 245 845	£ 1761 -1649 £ 141 - 97	2 101 144	3 8 4	1 731
25 143 215	13 249 -232 15 277 284	21 439 425 22 175 224	10 683 -626	4 379 341 7 343 -395	1 289 -313 2 348 417	4 L97 5 345
C E 2	16 492 -449	23 453 -470	18 640 -643	8 520 511	3 827 939	4 442
C 2527 -2424		2 8 4	22 346 319	1 232 -23C	3 144 -219	12 279
2 1152 -1128		1 247 -195	2 # 1	14 315 494	1 112 -4CI 1 518 -517	
5 320 -245 4 570 -957	e 144 174 1 208 118	2 412 877 3 734 738	1 726 -725	17 315 233	9 27C -192 10 474 -493	10 137 17 317
7 1423 -1386 8 2049 -2014	Z 18C 145 3 301 322	8 370 -355	2 285 -508	2 K 7	11 445 560	12 154
10 1875 1754	4 1195 1247	12 872 -835	\$ 125 197	1 296 -292	23 245 253	4 E
12 590 1013	8 555 -554	15 325 325	12 632 -409	3 181 145	19 232 -292 15 653 -617	1 195
19 392 328	12 135 164	16 691 -676 76 462 -465	13 3CC 3C2 15 17C -159	4 1C25 -1C18 1C 493 -482	14 337 325 18 229 -230	2 152
17 146 -229	15 105 -07	23 253 252	14 215 -203	11 228 -188	19 424 432	A 217 ·
29 948 912		L K 5	19 121 -290	13 117 39	3 = 5	8 209 -
21 272 -246		1 250 224	21 371 344	34 427 433	2 451 405	10 244
24 334 283		2 254 -413 4 772 753	22 213 -228 23 137 -148	2 # 8	4 412 413 6 3 96 355	13 428 -
c # 3	▲ 22C 223 J 223 2CE	5 324 -295 6 734 7C5	2 # 2	1 149 212	7 43C -445 8 295 -363	14 155
1 474 535	8 848 822 4 AC1 - 74C	7 685 665 8 875 781	1 447 437	2 254 220	10 586 613	
4 786 -823	10 185 188	1¢ 1ee -117	3 413 312	7 247 245	12 255 -293	
8 911 -85e	12 148 128	12 458 441	5 638 -625	11 202 170	17 223 215	2 434 -
4 70C -078 1C 1C27 -1C29	a # 1c	14 347 338 15 ecz 337	7 638 637 9 262 -247	13 163 -125	18 156 -172	3 109 -
11 776752 17 101148	C 254 -258	17 184 151	11 141 202	2 8 9	3 5 6	4 177 -
13 825 819	2 299 -314	19 452 -439	13 1190 -1213	1 191 181	1 384 -386	4 J2C
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10 274 -355	7 311 315	1 2 6	10 232 -244	5 275 -272	4 275 284 5 582 -572	12 473 -
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22 433 405	4 1005 - 554	3 359 -344	20 143 192	4 245 344	# 171 -21C # 231 -329	4 E
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15 491 -727	4 SCJ -515	A 3C7 153	7 246 -281	4 372 355	2 236 224	5 x C
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26 318 -495	12 427 419 13 447 491	9 222 211 16 986 -946	11 250 -344 13 552 555	3 396 381 10 542 535	2 556 434	8 545 -5 IC 16C -1
21 240 -301	14 1021 995	11 134 -74	14 648 -615	II 664 -713	4 371 -374	12 204 -1

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287 -244	9 400 -401	14 192 147	11 454 414	10 245 -451		3 246 -262
300 -324	10 595 -572	15 175 -165	12 300 -255	11 294 377	2 210 21C	4 153 -131
	11 274 245		13 171 63	13 1e3 1Ce	5 254 -267	E (EZ -655
	12 734 -804	-1 # 4	14 2C4 2CE	14 645 615	E 762 76C	7 262 211
144 144	14 135 -41	1 784			7 145 143	10 256 -257
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	17 311 -351	3 152 172	19 345 316	19 121 50		13 100 -205
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245 277	C 1722 1218	-1 # 1C	4 201 -177	2 356 -362	A 155 184	A 242 365
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246 -367	7 611 622	2 531 942	15 592 -ECZ	14 166 -255		3 110 -70
2 284 11	11 640 -410	E 140 -126	16 415 354	15 462 462	C 265 -3C1	4 25t Z2t
234 351	13 ETC -836	12 1632 1644	18 636 660	17 223 -203	2 130 -118	5 151 141
246 240	14 241 -24E	14 246 -23E	20 205 -222	18 147 100	-4 K C	E 191 2C 8 165 374
3 172 -172	15 136 15e	16 652 -252		19 126 125	·	/C
115 57	18 365 -305	18 562 -561	-2 K E	20 230 288	C 1434 -1515	-5 # C
	11 220 242	20 657 690		21 295 -275	2 171 -156	
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	20 511 -514	-2 2 1	1 462 468	-3 4 3	C 1:54 -1284	225 225 9
3 259 -324	21 46C -484		3 228 146	1 840 844	e sel -315	1C 165 -1Se
291 -27e	23 130 192	C 351 -355	4 402 -342	2 712 577	12 223 727	14 159 179
-3. 307 -321		1 605 556	5 234 -183	3 565 -664	14 653 588	
-2. 143 -158	-1 # 5	4 147 -135	6 283 -235	4 ELC 797	16 161 -157	-5 × 1
	6 343 -344	5 eze -eje	8 411 -465	5 460 -385	18 386 -355	
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181 190	2 276 -287	9 1001 1130	11 111 116	11 361 -338	-4 4 1	• CSS -2C/
- 134 120	3 381 -391	10 204 -175	12 255 270	12 288 325	C 355 -3C5	8 254 263
225 -245	4 203 -171	11 122 -172	13 225 -185	13 615 -618	1 142 -175	9 157 -11C
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144 -147	7 625 196	13 927 -965	13 420 448	13 207 347	4 215	12 161 -145
1.1	4 524 509	15 482 -477	17 261 -246	17 175 412	6 444 -41P	14 91 -108
] 1 x c	9 23E 287	16 273 250	18 51 44	18 245 -243	7 210 -155	-5 * 2
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475 -441	14 547 411	22 ICI 125	1 234 247	1 873 947	14 194 171	7 111 - 114
1325 -1354	17 201 -244	23 221 241	2 442 -400	2 269 294	15 148 -177	E 426 -415
1084 -1084	14 122 136	-7 5 7	3 322 -327	3 252 -244	18 513 488	9 416 365
	-1 5 4		A 211 214	A 513 493	-4 8 3	10 200 -244
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15 / ECS 811	2 313 371	3 616 450	10 201 -525	11 427 -4 6 1	1 381 -404	
	4 181 -415	4 2046 -2084	15 114 75	12 344 336	3 245 -366	C 167 -SE
629 -367	6 811 -879	7 150 -175	10 342 -340	17 120 -107	5 750 -265	
S : 416 514	7 567 -465	8 244 -ZEE	-2 # 2	14 359 -325	A 71C -74C	3 343 344
5 1es ese	8 247 -181	5 581 542	-		7 657 63E	4 ZEE 284
220 221	1C e15 eec	1C 196 216	4 34C -314	-3 K 5	11 47c -452	5 535 -538
N 112 -115	12 410 454	12 178 -121	3 242 430		12 428 -415	E 135 150
- 155 J72	13 418 458	13 1092 1097	E 766 237	1 478 -504	14 538 -467	10 144 143
S. 211 179	14 383 -442	14 724 -7EC	9 186 -179	2 233 209	15 291 274	12 182 187
날 : 254 - 244	15 194 -212	15 214 204	11 124 -122	3 363 -37e	17 237 206	
	16 138 196	16 52C 523	14 221 -240	4 725 -744		-5 K 4
	10 214 -217	14 433 -424	-7 8 6	5 RCC 922	-4 K 3	
5 1118 -1114	19 237 244	21 294 407	-2 - 7	e 174 -275 E 337 -377	C 497 444	C 225 -366
R 15C4 -1524	20 359 393	22 123 131	2 130 146	9 368 -347	3 176 -254	5 1125 -135
182 222	. –	23 245 211	3 461 -424	10 736 711	4 382 385	6 180 213
E 1321 -13es	-1 ¥ 7		4 73C -49C	11 353 -332	6 145 41	e 208 -216
420 -404		-2 X 3	5 244 238	12 158 247	7 192 1ec	9 220 -200
A11 -425	4 271 -275	1 1865 -1774	7 311 315	13 328 530	8 18C -174	10 232 254
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A. 675 -664	4 355 -33e	3 873 -846	10 172 161	17 383 -400	13 296 -267	
E 684 676	\$ 3CE 2E7	4 626 -633	-	18 467 44C	14 225 205	1 271 -290
2 3CC 285	12 369 -255	7 1437 1431	-3 # C	-	15 168 -121	2 120 -50
F 711 741	19 347 -744	10 174 -111	6 257 25r	-3 K 6	16 343 -361	3 141 124
425 -425	15 156 -147	11 eTC -614	8 714 244	C #15 -#14	-4 7 4	5 LAL 151
E 451 421	17 36C 366	12 516 -467	10 1023 102e	1 1123 -1150		
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254 -242	-1 2 2	14 43C478 15 787 769	16 141 -176	5 18C 32C	2 316 -284	
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E 434 427	C 33C 333	19 415 -38C	22 322 281	1 152 -202	5 216 165	
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		22 127 -143	-1 5 1	11 125 -122	E 714 742	
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the shortest. A similar pattern also exists within the set of ten Fe– C_{ring} distances. (It should be noted that neither ring deviates significantly from perfect planarity. The maximum deviation of a carbon atom from the least-squares plane is 0.011 Å and the average deviation is only 0.006 Å.)

Since there have been reports of other structures of this type in which these distances were not equivalent, the existence of non-equivalent C-C and Fe-Cring distances in this structure would certainly not be surprising. Theoretical explanations which might account for these bonds being chemically non-equivalent have been given by Dahl and Wei^{\circ}, employing a simple valence bond approach and by Burnett *et al.*⁷, using a molecular orbital treatment.

Nevertheless, the authors feel that the magnitudes of the differences detected in this structure are not large enough for firm conclusions to be drawn. And it is conceivable that these results might merely be due to steric or packing effects or to some systematic error.

ACKNOWLEDGEMENTS

Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission (Contribution No. 1842) the use of whose facilities we gratefully acknowledge. We also wish to thank Mr. JAMES E. BENSON for his aid and assistance with the computations.

SUMMARY

The crystal structure of π -C₅H₅Fe(CO)_{*}Mn(CO)₅, has been determined by singlecrystal X-ray diffraction methods. Eight molecules crystallize in a monoclinic unit cell with dimensions $a = 7.220 \pm 0.006$, $b = 30.387 \pm 0.008$, $c = 12.498 \pm 0.002$ Å and $\gamma = 90.21 \pm 0.10^{\circ}$. The space group symmetry is P_{21}/b . Full matrix least-squares refinement with Fe and Mn atoms anisotropic, resulted in a final R value of 6.4% for 1201 "observed" reflections. The π -C₅H₅Fe(CO)-Mn(CO)₅ molecules contain a Mn-Fe bond of length 2.843 \pm 0.004 Å and no bridging carbonyls. Both metal atoms may be envisioned as having distorted octahedral coordination. The six sites about the iron atoms are occupied by two carbonyl groups, the manganese atom, and the cyclopentadienyl ring (which essentially occupies three sites); about the manganese atoms there are five carbonyl groups and the iron atom.

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