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THE CRYSTAL AND MOLECULAR STRUCTURE OF THE BIS(TRICARBONYLIRON) DERIVATIVE OF 3,3'-BIS(BICYCLO[4.2.0] OCTA-2,4-DIENE)

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Summary

The reaction of bicyclo[2.6.0] deca-2,4,6-triene containing about 5% impurities, mostly cyclooctatetraene, with diiron nonacarbonyl in ether at 22° gave a minor product, 3,3'-bis(bicyclo[4.2.0] octa-2,4-dienetricarbonyliron), [(C_8H_9)-$Fe(CO)_3$]$_2$, which is composed of two linked units of the previously reported compound. The origin of this new substance is at present unknown. Data were collected using the $\theta/2\theta$ scan technique and a total of 1788 reflections were measured. The structure was solved by Patterson and Fourier methods.

Non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically to give agreement factors of $R_1 = 0.030$, and $R_2 = 0.039$. The space group is $P\bar{1}$ with cell dimensions of a 8.178(2), b 6.800(3), c 9.729(3)Å, α 101.98(3)°, β 106.99(2)°, γ 95.83(3)°, and V 498.5(3)Å^3 with $Z = 1$.

The structure consists of two bicyclo[4.2.0]octa-2,4-dienetricarbonyliron moieties related by an inversion center. The molecule shows some distortion in the usual hexa-1,3-diene—tricarbonyliron bond distances and angles. This distortion is probably due to the carbon—carbon bond between the two halves of the molecule at the second carbon in the 1,3-diene group.

Introduction

The reaction of $Fe_2(CO)_9$ in ether at 22° with bicyclo[2.6.0] deca-2,4,6-triene containing about 5% impurities most of which is cyclooctatetraene produces several products, all of which have been characterized by single crystal X-ray structure techniques [1-7]. The major products are iron carbonyl derivatives of the bicyclo[2.6.0] deca-2,4,6-triene ligands. However, the impurities in the ligand also gave rise to several interesting products which were isolated in crystalline form and structurally characterized. The product reported here could possibly have originated from a cyclohexatriene impurity although there is no direct evidence that this is the case.

Experimental

Bicyclo[6.2.0]deca-2,4,6-triene, which contains at least a 5% impurity of cyclooctatetraene and possibly small quantities of other related impurities, was treated with diiron nonacarbonyl in ether at 20°C as described previously [1,2]. The products from the above reaction were separated by chromatography on Woelm activity 2 alumina by eluting with hexane. The second yellow band containing the previously identified product tricyclo[$6.2.0.0^{2,7}$]deca-3,5-dienetricarbonyliron $(C_{10}H_{12})Fe(CO)_3$ which has been fully characterized by an X-ray structure determination [7], was rechromatographed several times on Woelm activity 2 alumina until the yellow band separated into two distinct bands. The first band contained only $C_{10}H_{12}Fe(CO)_3$ as identified by NMR, and the second band showed a very complex NMR indicating a mixture of products. The second band was evaporated to dryness in vacuo and a few crystals of the title compoun were recovered by crystallization from (30-60°) petroleum ether at —5°.

A crystal measuring approximately 0.2 × 0.2 × 0.3 mm was selected for data collection and was mounted in a thin glass capillary to protect it from slow decomposition in air.

The crystal was found to be triclinic and space group $P\bar{1}$ was assumed. This choice was later confirmed by the successful solution and refinement of the struc ture. Preliminary examination of the crystal and data collection were performed on a Syntex $P\bar{1}$ diffractometer. Unit cell dimensions and the orientation matrix for data collection were determined using the Syntex software after automatically centering fifteen reflections. The width at half-height of 0.15° was obtained from ω scans of strong reflections. The cell dimensions and other important crystal data are given in Table 1.

The operation of the diffractometer has been described previously [3] and only deviations from this procedure are described here. Data were collected at 22° using the θ —2θ scan technique and a scan rate which varied from 2.0 to 24.0°/min depending on the intensity of the reflection. Unique data with 2θ-(Mo-$K\alpha$) values up to 50° were collected using a scan range of 0.8° before 2θ-(Mo-$K\alpha_1$) to 0.8° after 2θ(Mo-$K\alpha_2$). Three standard reflections checked during the data collection showed good electronic and crystal stability.

An absorption correction was not made in view of the small variation in transmission factors during data collection. Lorentz and polarization corrections were made. Only 1433 reflections of the 1788 reflections collected were found to have $F_o^2 > 3\sigma(F_o^2)$ and were used in the refinement of the structure.

*Solution and refinement of the structure**. The structure was solved using Patterson heavy atom methods. The iron atom was refined by two least-squares

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* The following computer programs written for the IBM360 were used: TRACER, a lattice transformation and cell reduction program by Lawton; DATARED, a data reduction program by Frenz; FOURIER, a Fourier summation program (based on Zalkin's FORDAP) by Dellaca and Robinson and modified by Hodgson; NUCLS, a full-matrix least-squares program (minimizing $\Sigma w(|F_o| - |F_c|)^2$) by Ibers and Doedens, similar to Busing and Levy's ORFLS; SADIAN, a distances and angles program by Baur, rewritten by Frenz and Brice; AGNOST, an absorption correction program by Cahen based on Coppens' DATAP and Tompa analytical subroutines of Cullen's program; PERFACT, a program for analysis of structure factors by Frenz; ORFFE, a function and error program by Busing, Martin, and Levy as modified by Brown, Johnson, and Theissen; ORTEP, a plotting program by Johnson; and LIST, a program for listing the data by Snyder.

TABLE 1

CRYSTAL DATA FOR $(C_8H_9)_2(Fe(CO)_3)_2$

a	8.178(2)Å	Triclinic
b	6.800(3)Å	Space group $P\bar{1}$
c	9.730(3)Å	Mo-K_α radiation
α	101.98(3)°	$Z = 1$
β	106.99(2)°	d_{calc} 1.47 g/cm^3
γ	95.83(3)°	
V	498.5(3)Å^3	

cycles to give the following agreement factors: $R_1 = (\Sigma ||F_o| - |F_c||)/\Sigma |F_o| = 0.398$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2} = 0.498$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes and w is the weighting factor given as $4|F_o|^2/\sigma^2$. Here σ is the e.s.d. of $|F_o|^2$. Scattering factors were taken from the International Tables [8]. Anomalous dispersion effects were included in the calculated structure factors for iron, using $\Delta f'$ and $\Delta f''$ values given by Cromer and Liberman [9]. All the non-hydrogen atoms were located on a difference Fourier map based on phases determined from the iron position.

Two full matrix least-squares cycles of isotropic refinement followed by two cycles of anisotropic refinement on all non-hydrogen atoms reduced the residuals to $R_1 = 0.046$ and $R_2 = 0.065$. A difference Fourier map calculated at this point in the refinement revealed the positions of all nine hydrogen atoms. The non-

TABLE 2

ATOMIC POSITIONAL PARAMETERS FOR $[(C_8H_9)Fe(CO)_3]_2$ [a]

Atom	x	y	z
Fe	−0.07700(6)	−0.10609(7)	0.21762(5)
O(1)	−0.3637(4)	−0.1386(4)	−0.0543(3)
O(2)	0.1091(4)	0.3069(4)	0.2652(3)
O(3)	0.1675(4)	−0.3045(4)	0.0931(3)
C(1)	−0.3971(4)	−0.1515(5)	0.3036(3)
C(2)	−0.2251(4)	−0.0082(5)	0.3557(3)
C(3)	−0.0703(4)	−0.0698(4)	0.4365(3)
C(4)	−0.0573(4)	−0.2724(5)	0.3734(3)
C(5)	−0.1953(4)	−0.3823(5)	0.2450(3)
C(6)	−0.3794(4)	−0.3688(5)	0.2369(4)
C(7)	−0.4402(6)	−0.4461(6)	0.3564(5)
C(8)	−0.4570(5)	−0.2294(6)	0.4238(4)
C(9)	−0.2502(5)	−0.1243(5)	0.0503(4)
C(10)	0.0379(4)	0.1451(5)	0.2467(3)
C(11)	0.0738(5)	−0.2257(5)	0.1421(4)
H(1)	−0.488(4)	−0.095(4)	0.236(3)
H(2)	−0.229(4)	0.129(5)	0.384(4)
H(3)	0.043(4)	−0.320(5)	0.409(4)
H(4)	−0.176(4)	−0.508(5)	0.187(3)
H(5)	−0.453(5)	−0.418(6)	0.138(4)
H(6)	−0.361(6)	−0.521(7)	0.412(5)
H(7)	−0.361(6)	−0.521(7)	0.313(5)
H(8)	−0.376(4)	−0.168(5)	0.525(4)
H(9)	−0.567(5)	−0.213(6)	0.422(4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits in this and all other tables.

TABLE 3

ATOMIC THERMAL PARAMETERS FOR $[(C_8H_9)Fe(CO)_3]_2$ [a]

Atom	β_{11} or β_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	125(1)	162(1)	63(1)	7(1)	38(1)	17(1)
O(1)	224(6)	379(10)	102(4)	16(6)	— 8(4)	61(5)
O(2)	212(6)	197(8)	178(5)	2(5)	73(4)	65(4)
O(3)	197(6)	329(9)	153(4)	44(6)	99(4)	0(5)
C(1)	114(6)	204(9)	86(4)	9(6)	31(4)	33(5)
C(2)	128(6)	150(8)	69(4)	17(5)	43(4)	12(4)
C(3)	113(5)	149(7)	62(3)	21(5)	42(3)	28(4)
C(4)	128(6)	143(7)	74(4)	21(5)	39(4)	25(4)
C(5)	162(6)	149(8)	81(4)	13(6)	53(4)	13(5)
C(6)	137(6)	218(9)	80(4)	—27(6)	34(4)	3(5)
C(7)	203(8)	228(10)	139(6)	—34(8)	94(6)	33(7)
C(8)	147(7)	227(11)	102(5)	1(7)	58(5)	32(6)
C(9)	172(7)	214(9)	92(5)	5(6)	53(5)	36(5)
C(10)	150(6)	217(10)	84(4)	36(6)	51(4)	45(5)
C(11)	158(7)	213(9)	80(4)	—10(6)	49(4)	13(5)
H(1)	2.9(6)					
H(2)	3.5(7)					
H(3)	2.2(8)					
H(4)	3.1(6)					
H(5)	4.5(9)					
H(6)	5.5(11)					
H(7)	5.4(10)					
H(8)	3.6(7)					
H(9)	4.7(9)					

[a] The anisotropic temperature parameters are of the form $10^{-4}\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

hydrogen atoms were refined anisotropically and hydrogen atoms isotropically by two full-matrix least-squares cycles to convergence giving final agreement factors of $R_1 = 0.030$, $R_2 = 0.039$. The e.s.d. in an observation of unit weight is 1.061.

No systematic trends were found in the data as a function of $\lambda^{-1}\sin\theta$, $|F_o|$, Miller indices, or reflection number. In the last difference Fourier the hydrogen atoms were observed as the highest peaks, indicating very little residual electron density. The atomic coordinates and thermal parameters with estimated standard deviations are given in Tables 2 and 3, respectively. Root-mean-square amplitudes of thermal vibration are available*.

Results

The structure of the complete molecule, in which the halves are related by a center of symmetry, is shown in Fig. 1. The numbering scheme used was chosen to be the same as the scheme used in the systematic name of the compound.

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* Supplementary material, which includes the r.m.s. amplitudes of thermal vibration and a list of F_o and F_c values has been deposited as NAPS Document No. 02388, with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 Third Avenue, New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting $2.00 for a microfiche or $5.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS-NAPS.

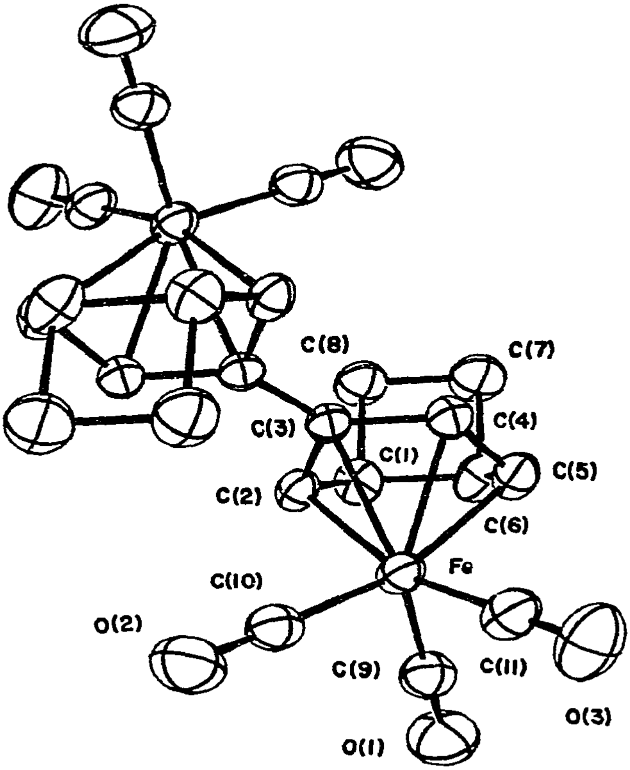

Fig. 1. An ORTEP drawing of $(C_8H_9Fe(CO)_3)_2$ showing 50% probability level ellipsoids of thermal vibration.

TABLE 4

BOND LENGTHS(Å)

Fe—C(2)	2.112(3)	C(1)—C(2)	1.512(4)
Fe—C(3)	2.076(3)	C(1)—C(6)	1.525(5)
Fe—C(4)	2.051(3)	C(1)—C(8)	1.558(4)
Fe—C(5)	2.128(3)	C(2)—C(3)	1.435(4)
Fe—C(9)	1.790(4)	C(3)—C(4)	1.415(4)
Fe—C(10)	1.789(4)	C(4)—C(5)	1.418(4)
Fe—C(11)	1.791(4)	C(5)—C(6)	1.497(5)
		C(6)—C(7)	1.555(5)
C(9)—O(1)	1.139(4)	C(7)—C(8)	1.521(6)
C(10)—O(2)	1.144(4)		
C(11)—O(3)	1.137(4)	C(1)—H(1)	1.01(3)
		C(2)—H(2)	0.93(3)
		C(4)—H(3)	0.90(3)
		C(5)—H(4)	0.98(3)
		C(6)—H(5)	0.93(4)
		C(7)—H(6)	0.93(4)
		C(7)—H(7)	0.98(4)
		C(8)—H(8)	0.98(4)
		C(8)—H(9)	0.91(4)

TABLE 5

BOND ANGLES (Deg.)

C(2)—Fe—C(3)	40.1(1)	Fe—C(9)—O(1)	177.9(3)
C(2)—Fe—C(4)	69.5(1)	Fe—C(10)—O(2)	179.0(3)
C(2)—Fe—C(5)	76.1(1)	Fe—C(11)—O(3)	178.9(3)
C(2)—Fe—C(9)	93.6(1)	C(2)—C(1)—C(6)	111.3(3)
C(2)—Fe—C(10)	93.9(1)	C(2)—C(1)—C(8)	117.2(3)
C(2)—Fe—C(11)	163.3(1)	C(6)—C(1)—C(8)	89.3(3)
C(3)—Fe—C(4)	40.1(1)	C(1)—C(2)—C(3)	119.8(3)
C(3)—Fe—C(5)	70.1(1)	C(2)—C(3)—C(4)	112.8(3)
C(3)—Fe—C(9)	132.1(1)	C(3)—C(4)—C(5)	117.0(3)
C(3)—Fe—C(10)	94.9(1)	C(4)—C(5)—C(6)	120.0(3)
C(3)—Fe—C(11)	124.1(1)	C(1)—C(6)—C(5)	111.2(3)
C(4)—Fe—C(5)	39.6(1)	C(1)—C(6)—C(7)	90.6(3)
C(4)—Fe—C(9)	129.9(1)	C(5)—C(6)—C(7)	115.5(3)
C(4)—Fe—C(10)	126.3(1)	C(6)—C(7)—C(8)	89.5(3)
C(4)—Fe—C(11)	94.2(1)	C(1)—C(8)—C(7)	90.6(3)
C(5)—Fe—C(9)	91.4(1)		
C(5)—Fe—C(10)	164.9(1)		
C(5)—Fe—C(11)	93.8(1)		
C(9)—Fe—C(10)	100.7(1)		
C(9)—Fe—C(11)	100.1(2)		
C(10)—Fe—C(11)	93.0(1)		

There are no intermolecular contacts closer than the sum of the Van der Waals radii. Selected bond distances and angles are given in Tables 4 and 5, respectively. Some mean planes and dihedral angles are given in Table 6.

TABLE 6

LEAST-SQUARES PLANES AND DIHEDRAL ANGLES

Plane	Atoms defining plane	Equation of mean plane [a]
I	C(1),C(6),C(7),C(8)	$6.565x - 0.409y + 3.037z = -1.621$
II	C(1),C(6),C(7)	$6.349x - 0.395y + 2.973z = -1.559$
III	C(1),C(7),C(8)	$6.385x - 0.410y + 2.920z = -1.587$

DISPLACEMENT OF ATOMS FROM MEAN PLANE (Å)

Plane I		Plane II		Plane III	
C(1)	−0.001	C(8)	0.008	C(6)	0.008
C(6)	0.001				
C(7)	−0.003				
C(8)	0.002				

DIHEDRAL ANGLES BETWEEN PLANES (Deg.)

I-II	0.19
I-III	0.22
II-III	0.40

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[a] Equation has the form $Ax + By + Cz = D$ where x, y, and z are fractional triclinic coordinates.

Discussion

The structure of the present compound was determined to be a dimer of [4.2.0] octa-2,4-dienetricarbonyliron. The halves of the molecule are joined by a carbon—carbon bond at C(3) in the hexa-1,3-diene ring. Wilkinson prepared the monomeric molecule $C_8H_{10}Fe(CO)_3$ by the reaction of dodecacarbonyltriiron with cyclohexatriene [10]. This reaction also produced a less stable product of the same stoichiometry but with an infrared band attributable to a free double bond. The dimer $[C_8H_9Fe(CO)_3]_2$ reported here has not been prepared previously.

The structure is essentially as expected with some asymmetry in the usually equivalent sets of iron—carbon and carbon—carbon bond distances of the 1,3-hexadienetricarbonyliron moiety. This asymmetry is attributed to the C(3)—C(3)′ bond between the symmetry-related halves of the molecule. The distortion can be seen by comparing the C(2)—C(3) bond distance of 1.435(4)Å to the C(4)—C(5) bond distance of 1.418(4)Å. Also, the Fe—C(3) bond distance of 2.076(3)Å and the Fe—C(4) bond distance of 2.051(3)Å differ by 0.025Å which is greater than eight estimated standard deviations. The bonding of tricarbonyliron to hexa-1,3-diene molecules is described in detail by Cotton and Troup [7].

The conformation of the six-membered ring fusion with the four-membered ring is *cis* as observed for similar molecules [7,11,12,14]. The four-membered ring was found to be planar as shown by the dihedral angle of 0.4° between carbon atoms C(1), C(6), C(7) and carbon atoms C(1), C(7), C(8). A planar four-membered ring was not unexpected in view of the recent structure of tricyclo-$[6.2.0.0^{2,7}]$deca-3,5-dienetricarboyliron [7] which exhibits two similar four-membered rings.

The organic precurser to the title compound could have been cyclohexa-1,3,5-triene. However, there is no direct evidence that the dimer we obtained is of this heritage.

Acknowledgements

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