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The Crystal Structure of Mono-*o*-phenylenebisdimethylarsine Tricarbonyl Iron(0)

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The structure of the five-coordinate iron complex mono-*o*-phenylenebisdimethylarsine tricarbonyl iron(0), $Fe(CO)_3(As(CH_3)_2)_2C_6H_4$, has been determined by conventional X-ray methods. The crystals are orthorhombic with four molecules of complex in a cell of dimensions $a=16{\cdot}73$, $b=10{\cdot}37$ and $c=9{\cdot}71$, all $\pm 0{\cdot}03$ Å. The space group is *Pnma*. It has been found that the arrangement of atoms round each iron atom forms a slightly distorted trigonal bipyramid.

Introduction

Iron with a coordination number of five has recently been shown (Hanson, 1962; Donohue & Caron, 1964) to have a trigonal bipyramid configuration in iron pentacarbonyl. However, this coordination number is still sufficiently unusual for the structure of mono-*o*-phenylenebisdimethylarsine tricarbonyl iron(0), $Fe(CO)_3(As(CH_3)_2)_2C_6H_4$, to be of interest.

Experimental

Specimens of the complex were supplied by Professor Nyholm of University College, London. The pale yellow crystals were unstable except in an atmosphere of carbon monoxide and for the purpose of X-ray analysis crystals, of maximum dimension 0·3 mm, were sealed in capillary tubes. Partial three-dimensional data were collected by the multiple-film Weissenberg technique, allowing the observation of 792 independent reflexions. Intensities were measured visually and converted to $|F|^2$ and $|F|$ by applying the usual corrections. No corrections were made for absorption or extinction.

Crystal data

$FeAs_2C_{13}H_{16}O_3$, $M=425{\cdot}6$,
Orthorhombic, $a=16{\cdot}73$, $b=10{\cdot}37$, $c=9{\cdot}71$, all $\pm 0{\cdot}03$ Å
$U=1684{\cdot}6$ Å^3, $Z=4$, $D_c=1{\cdot}68$ g.cm^{-3},
$F(000)=210$, Cu $K\alpha$, $\lambda=1{\cdot}542$ Å, $\mu=120$ cm^{-1}
Absent reflexions $hk0$ when h is odd,
$0kl$ when $k+l$ is odd.

Space group *Pnma* or $Pna2_1$. *Pnma* assumed after initially assuming lower symmetry.

Structure analysis

The structure was solved by the usual methods and refined by the method of least squares using Rollett's SLFS (ISO) program (Mills & Rollett, 1961). A weighting scheme,

$$\sqrt{w}=1 \quad \text{if} \quad |F_o|<F_A$$
$$\text{otherwise} \quad \sqrt{w}=F_A/|F_o|$$

was employed, and scattering factors of Thomas & Umeda (1957) for iron and arsenic, and of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for carbon and oxygen were used.

Convergence of the least-squares refinement was reached with a reliability index of $R=0{\cdot}161$. Final atomic parameters with their standard deviations are shown in Table 1 and the observed and calculated structure factors are set out in Table 2.

Description and discussion of the structure

For the space group *Pnma*, the four molecules of complex in each unit cell must occupy special positions.

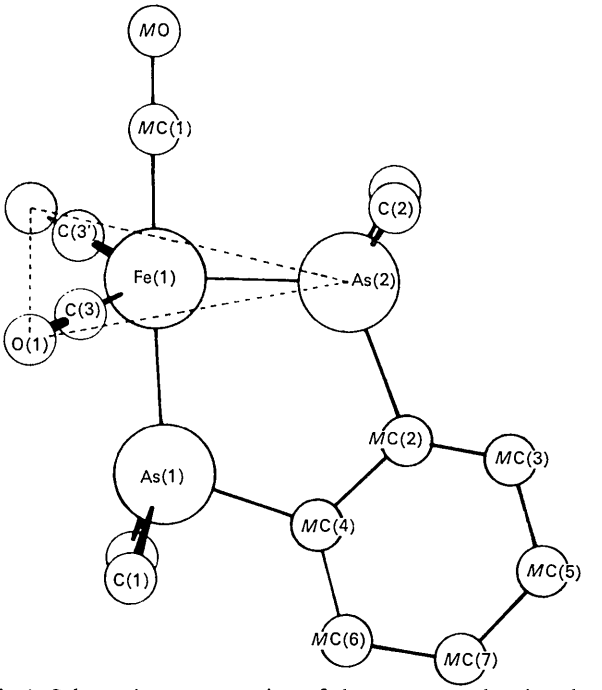

Fig. 1. Schematic representation of the structure, showing the environment of an iron atom.

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Table 1. *Observed and caculated structure factors*

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
2	0	0	192	182	12			9	1-	4			17	20	9			20	21-
4			219	212-	14			28	39	5			35	31	11			52	61-
6			74	81-	2	11	0	22	24	6			41	40	12			24	27
8			29	33	4			11	13	7			31	18-	13			52	56-
10			90	107	6			31	39-	10			31	32	14			24	26
12			9	6-	8			42	53-	14			46	54	0	4	2	59	61-
14			122	119-	12			18	24	16			41	49	1			29	19
16			105	113-	0	12	0	35	57	1	6	1	31	31	2			29	29-
2	1	0	142	146-	2			20	25	2			35	32	3			68	65
4			7	4-	4			13	20-	3			31	31-	4			42	41-
6			230	235	6			11	24-	6			94	91-	5			41	38
8			234	240	2	13	0	13	19-	8			70	73-	6			24	26-
10			63	58	1	0	1	39	48-	12			31	18	7			18	19
12			57	61-	2			85	118-	0	7	1	133	103	9			35	37
14			31	43-	3			42	37	1			94	20-	10			31	27
16			31	32	4			83	90	2			57	59	11			24	29
18			41	44	5			28	41	3			20	37-	12			61	62
0	2	0	470	401-	6			96	113	4			29	26-	13			33	34
2			311	249-	7			15	15-	5			22	14-	14			33	29
4			120	116	8			103	133	6			22	28-	1	5	2	24	16-
6			131	125	9			18	19-	14			41	42-	2			33	30-
8			68	65-	10			37	41	16			33	39-	3			44	42-
10			77	83-	11			33	35-	2	8	1	39	33-	4			63	66-
12			11	4	12			35	39-	6			46	48	5			52	58-
14			127	123	13			22	30-	8			50	61	6			33	34-
16			105	103	14			11	13-	12			31	22-	7			28	21-
2	3	0	79	71	15			11	11	0	9	1	50	63-	11			46	47
4			111	84	16			11	19	2			31	32-	12			24	27-
6			192	175-	17			22	15	8	10	1	35	40-	13			42	40
8			271	261-	18			9	18	0	11	1	48	38	14			24	19-
10			72	64-	19			9	11-	0	13	1	37	26-	0	6	2	20	11
12			79	81	20			18	23-	0	0	2	48	52-	1			33	31-
14			46	39	0	1	1	225	261-	1			4	1	2			39	38
16			31	35-	2			111	124-	2			22	20-	3			39	49-
18			28	34-	3			48	44	3			109	123	4			28	31
0	4	0	396	324	4			44	43	4			63	76-	5			41	43-
2			171	131	5			31	40	5			87	107	10			33	33-
4			50	51-	6			46	54	6			35	43-	11			33	35-
6			99	89-	7			29	27-	7			14	8-	12			33	35-
8			26	11	9			17	19-	8			24	18	13			24	34-
10			99	103	10			31	36-	9			24	16	4	7	2	37	34
12			24	17-	11			20	18	10			33	34	5			31	33
14			107	109-	13			31	32	11			42	52	6			33	26
16			76	79-	14			66	74	12			61	71	7			24	25
2	5	0	96	83-	16			59	70	13			52	51	11			33	37-
4			33	21-	19			31	35-	14			41	43	12			24	19.
6			155	133	1	2	1	79	67	15			11	8	13			22	24-
8			192	183	2			50	43	16			11	13	0	8	2	24	13-
10			42	42	3			48	49-	17			24	26-	3			33	35
12			63	57-	4			41	42	18			9	5	4			24	29-
14			24	32-	5			18	24-	19			26	34-	5			33	28
16			28	25	6			146	162-	20			22	15	0	10	2	26	5
0	6	0	263	239-	7			26	28-	1	1	2	70	66-	0	12	2	18	4-
2			138	119-	8			129	138-	2			42	47-	1	0	3	221	209-
4			94	88	10			31	30-	3			31	44-	2			15	9-
6			83	74	11			53	60	4			81	91-	3			39	32
8			42	37-	12			37	33	5			57	68-	4			72	84-
10			53	49-	13			31	26	6			42	47-	5			7	10
12			11	3-	0	3	1	142	138	7			41	39-	6			39	33-
14			68	76	1			52	33	8			24	27-	7			29	7-
16			66	76	2			114	115	9			24	27	8			71	5
2	7	0	68	68	4			13	6-	10			33	37-	9			31	30-
4			11	9	5			42	44-	11			53	63	10			13	14-
6			116	110-	6			52	54-	12			31	30-	11			24	18-
8			103	105-	9			26	22	13			46	50	12			50	59-
10			31	30-	10			33	36	18			29	30	13			46	43
12			31	34	11			29	17-	20			26	37	14			26	29-
14			24	29	12			31	22-	0	2	2	18	8-	15			52	59
16			15	19-	13			31	36-	1			81	70-	16			37	27
0	8	0	164	164	14			64	71-	2			87	80	17			35	30
2			61	61	15			22	12-	3			61	61-	18			31	39
4			53	50-	16			68	51-	4			42	45	19			7	11-
6			44	45-	17			31	25	5			42	48-	20			17	27·
8			11	11	18			28	7-	6			22	17	0	1	3	13	13-
10			44	46	1	4	1	55	39-	7			35	45-	1			57	70
12			11	2-	2			79	73-	8			24	20	2			15	6
14			52	55-	3			13	10	10			44	64-	3			46	59
16			39	52-	4			22	18	11			46	51-	4			63	73
2	9	0	41	42-	5			28	54	12			59	63-	5			66	85-
4			11	13-	6			48	89	13			41	42-	6			66	79
6			55	58	7			101	30	14			42	39-	7			107	136-
8			77	88	8			123	135	19			24	35	9			72	73-
10			11	21	9			20	19-	1	3	2	22	9-	10			66	70-
12			28	32-	10			29	28	2			42	40	12			61	62-
0	10	0	63	78-	11			48	53-	3			85	82	13			26	17
2			44	47-	12			44	44-	4			76	70	1	2	3	99	116
4			20	23	13			22	26-	5			79	82	2			76	78
6			31	40	0	5	1	147	152-	6			63	63	3			81	75
8			11	9-	2			85	73-	7			33	30	4			53	58
10			22	31-	3			31	30	8			26	22	5			31	43-

Table 1 (*cont.*)

h	k	l	F_o	F_c
6			42	37
9			29	36
12			50	52
13			46	38-
15			59	61-
18			39	45-
0	3	3	24	27
1			15	17-
2			39	30-
3			50	51-
4			63	74-
5			29	30
6			37	38-
7			112	138
9			81	87
10			48	47
12			52	49
1	4	3	88	102-
2			72	74-
3			68	33-
4			63	69-
9			33	32-
11			26	21-
12			37	42-
13			52	47
14			37	34-
15			44	45
18			28	40
0	5	3	18	16-
1			39	33
3			35	30
4			50	59
5			42	42-
6			44	44
7			83	94-
9			61	58-
10			46	43-
12			46	46-
13			26	16
1	6	3	79	89
2			39	37
3			22	16
4			41	40
5			33	37-
6			24	18
11			26	4
12			46	41
15			41	42-
0	7	3	24	23
2			24	3
3			24	31
4			35	40
5			44	39
6			44	47-
7			52	64
9			39	32
10			46	46
12			37	35
1	8	3	52	55-
4			37	35-
0	9	3	26	17-
7			37	45-
0	11	3	22	17
0	0	4	35	31-
1			70	104
2			18	81-
3			66	70
4			46	58
5			72	68-
6			53	55
7			140	161-
8			9	1
9			140	149-
10			31	38-
11			9	12
12			18	21
13			65	68
14			35	21
15			11	7
16			9	11
17			39	42-
1	1	4	160	225
2			15	7
3			20	18
4			18	22
5			94	100-
7			24	24-
9			66	69
11			39	39
13			64	56-
15			105	100-
17			53	47-
0	2	4	41	32
1			42	38-
2			17	12-
3			77	92-
4			41	48-
5			48	54
6			33	36-
7			157	190
8			20	12
9			112	113
13			64	64-
17			37	42
1	3	4	188	198-
2			41	51-
3			37	29-
4			22	25-
5			96	106
7			33	29
9			71	68-
11			41	35-
12			24	21-
13			37	53
15			83	84
16			33	7
17			41	42
0	4	4	28	27-
1			72	66
3			55	55
4			35	46
5			57	53-
7			127	140-
9			109	109-
11			24	25
13			48	50
17			28	31-
1	5	4	136	161
4			28	15
5			74	78-
7			31	35-
9			53	54
10			33	11
12			24	19
13			42	41-
15			70	74-
17			48	39-
0	6	4	33	24
1			35	34-
3			48	57-
5			46	36
7			105	112
9			70	75
12			24	11
13			41	46-
15			29	8-
17			26	33
1	7	4	83	105-
5			53	56
7			24	13
9			35	35-
15			55	61
0	8	4	26	14-
1			33	35
3			33	41
5			24	22-
7			70	80-
9			53	65-
13			26	36
1	9	4	48	71
5			33	38-
9			20	28
0	10	4	24	11
1			41	17-
7			42	57
9			33	35
0	12	4	17	9-
1	0	5	70	144
2			22	22-
3			7	7-
4			39	40-
5			37	36-
6			9	3
7			28	28-
8			42	47
			37	23
10			20	13
11			20	12
12			29	31-
13			57	57-
14			37	38-
15			79	77-
16			9	40-
17			37	34-
0	1	5	28	35-
1			29	43-
2			18	24-
3			31	45-
4			24	23
5			53	62
6			39	45
7			112	134
9			85	79
10			29	30-
11			29	20-
13			48	43-
16			20	18
17			26	20
1	2	5	105	135-
2			37	38
3			33	29-
4			13	16
5			70	78
6			14	5-
8			31	25-
9			33	26-
10			20	20-
12			29	28
13			53	47
14			29	32
15			76	77
17			29	29
0	3	5	59	58
1			22	20
2			21	17
3			29	30
4			41	44-
5			48	55-
6			35	34-
7			105	121-
8			20	7
9			29	61-
11			37	25
13			37	32
1	4	5	111	127
2			35	36-
3			17	4
4			30	23-
5			46	51-
7			33	34-
8			29	25
9			42	32
12			20	15-
13			53	48-
14			29	32-
15			59	61-
17			31	29-
0	5	5	29	31-
1			29	28-
2			18	10-
3			26	25-
4			26	23
5			39	41
6			29	24
7			83	92
9			61	57
10			20	17-
11			20	15-
13			29	28-
15			18	1-
17			20	15
1	6	5	72	84-
5			46	41
8			29	29-
13			28	30
14			17	26
15			48	55
0	7	5	26	18
3			37	30
5			37	30-
7			66	74-
9			44	45-
11			20	9
13			29	29
1	8	5	53	62
5			31	24-
8			20	20
13			15	23-
0	9	5	26	24-
7			44	50
9			26	28
1	10	5	35	45-
0	11	5	18	14
0	0	6	31	24
1			17	24-
2			15	14
3			22	13
4			28	36
5			53	64
6			48	59
7			50	61
8			17	21
9			24	30
10			26	22-
11			18	2
12			33	39-
13			11	14
14			28	15-
15			9	10
16			24	12
1	1	6	42	69-
2			20	25
3			15	13-
4			39	47
6			20	21
10			18	19
11			33	32
12			44	43
13			39	39
14			28	33
15			26	28
16			17	40
0	2	6	18	6
1			18	20-
2			18	28-
4			37	46-
5			33	47-
6			26	35-
7			50	59-
12			33	38
1	3	6	41	54
2			35	41-
3			31	33
4			29	40-
10			18	10-
11			18	15-
12			33	34-
13			42	40-
14			31	35-
15			29	29-
0	4	6	24	7
1			15	11
2			15	17
3			28	31
4			33	36
5			29	29
6			30	31
7			37	41
8			18	8
9			28	30
10			18	12-
12			28	30-
1	5	6	39	40-
2			24	30
3			18	17-
4			30	37
6			18	9
12			26	33
13			29	32
14			24	30
15			20	20
0	6	6	26	1
4			18	23-
5			33	34-
6			18	30-
7			33	37-
12			24	26
1	7	6	33	29
2			18	15-
3			28	10
0	8	6	26	9-
0	10	6	20	10
1	0	7	18	6-
2			53	49-
3			39	47-
4			20	1
5			61	73-
6			52	49
7			15	21-
8			55	64
9			24	34
10			29	32
11			39	54
12			9	16-
13			24	18
14			9	11-
15			7	11-
0	1	7	94	70-
0	3	7	101	72
0	5	7	90	55-
0	7	7	6	28
0	9	7	29	24-
0	0	8	122	111-
1			20	220
2			44	43-
3			48	42-
4			35	37
5			15	11-
6			24	36
7			11	15
8			11	5-
9			11	6
10			20	31-
11			9	15-
12			9	3
13			9	20-
14			37	46
0	2	8	118	97
0	4	8	122	89-
0	6	8	85	64
0	8	8	66	55-
0	10	8	31	37
1	0	9	15	14
2			50	50
3			11	6-
4			11	2-
5			18	24-
6			55	71-
7			9	19-
8			53	75-
9			9	2
10			9	16-
11			9	6
12			11	27
0	1	9	122	130
0	3	9	99	81-
0	5	9	92	69
0	7	9	72	58-
0	9	9	39	41
0	0	10	61	46
1			9	7-
2			26	29
3			15	16-
4			9	10
5			9	8-
6			9	5
7			9	9
8			9	4
0	2	10	57	38-
0	4	10	55	31
0	6	10	42	25-
0	8	10	22	18
1	0	11	18	15
2			22	36
3			9	1
4			15	33
5			7	5-
0	1	11	20	6
0	3	11	18	7-
0	5	11	15	7
0	0	12	15	11
0	2	12	15	13

Table 2. *Atomic parameters and their standard deviations*

Atom	x/a	y/b	z/c	B	σ_x	σ_y	σ_z
MC(1)	0·103	0·250	0·011	9·6 Å^2	0·05 Å	0·00 Å	0·09 Å
MC(2)	0·076	0·750	0·605	3·2	0·03	0·00	0·05
MC(3)	0·152	0·750	0·584	5·8	0·03	0·00	0·05
MC(4)	0·012	0·750	0·507	3·5	0·03	0·00	0·05
MC(5)	0·173	0·750	0·446	8·4	0·05	0·00	0·09
MC(6)	0·034	0·750	0·353	3·6	0·03	0·00	0·05
MC(7)	0·118	0·750	0·334	4·6	0·03	0·00	0·05
C(1)	0·140	0·392	0·530	4·7	0·03	0·04	0·04
C(2)	0·090	0·599	0·887	5·9	0·03	0·04	0·04
C(3)	0·156	0·403	0·192	5·1	0·03	0·04	0·04
MO(1)	0·101	0·250	0·887	4·7	0·02	0·00	0·04
O(1)	0·197	0·491	0·192	6·6	0·02	0·04	0·03
Fe(1)	0·1039	0·2500	0·1848	3·2	0·004	0·000	0·008
As(1)	0·0970	0·2500	0·4277	2·0	0·002	0·000	0·005
As(2)	0·0339	0·2500	0·8037	3·2	0·002	0·000	0·005

Of those available, positions (*c*) were chosen, implying a mirror plane of symmetry in the molecule. The iron and the two arsenic atoms, together with one carbonyl group and the benzenoid ring, were assumed to lie in this mirror plane.

The environment of each iron atom is shown diagrammatically in Fig. 1. The ligands form a slightly distorted trigonal bipyramid around the metal, the distortions from the ideal arrangement being only a few degrees. This is a similar stereochemical arrangement to that found for iron pentacarbonyl although in the latter distortions from a regular trigonal bipyramid are neglible.

Principal bond lengths and angles are given in Table 3. The two observed Fe–As bond lengths of 2·36 and 2·31 Å are of the expected order but the small difference between them is probably significant. The average Fe–C bond length of 1·75 Å is not significantly different from the value found for iron pentacarbonyl.

Table 3. *Principal bond lengths and angles*

	Length		Angle
Fe(1)–As(1)	2·36 Å	As(1)–Fe(1)–As(2)	84°
Fe(1)–As(2)	2·31	As(1)–Fe(1)–C(3)	89
Fe(1)–MC(1)	1·68	C(3)—Fe(1)–As(2)	119
Fe(1)–C(3)	1·81	C(3)—Fe(1)–C(3^1)	122
As(1)–C(1)	1·92	C(3)—Fe(1)–MC(1)	92
As(2)–C(2)	2·00	As(2)–Fe(1)–MC(1)	92
Average C–O	1·18	Fe(1)–As(1)–MC(4)	112
Average C–C	1·41	Fe(1)–As(2)–MC(2)	113

The relatively poor agreement between observed and calculated structure factors is partly a reflexion on the quality of the data obtained (a result of decomposition of samples during photography) but may also be partly due to the approximation of assuming a centrosymmetric space group. The high apparent temperature factors for the carbon atoms MC(1) and MC(5) suggest that these atoms could be slightly out of the mirror plane. However, such deviations from a centrosymmetric arrangement are probably small.

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