angle. It seems likely then that the 'double' bonds in the complex are intermediate in length to a normal single and a normal double bond.

We feel that we have obtained all of the information on the ring geometry which is possible with the present visual intensity data. We agree with Baenziger *et al.* (1961) that in this type of problem better data are probably required if significant information on ring geometry is to be obtained.

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The Crystal Structure of Iron Pentacarbonyl

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Iron pentacarbonyl at −80 °C. is monoclinic, probably *Cc*, with

$$a = 11{\cdot}71,\ b = 6{\cdot}80,\ c = 9{\cdot}28\ \text{Å};\ \beta = 107{\cdot}6^\circ;\ Z = 4\ .$$

Intensities were collected for the three zones [010], [001], and [110] at temperatures ranging from −70 to −110 °C. The crystal structure was determined by heavy-atom methods, and refined with the aid of two-dimensional Fourier syntheses. The molecule has the expected form of a trigonal bipyramid, but is slightly distorted in such a way as to allow closer packing.

Introduction

Ewens & Lister (1939) have shown by electron-diffraction studies of the gas that the molecule of iron pentacarbonyl ($Fe(CO)_5$) has the form of a trigonal bipyramid. However, recent investigations in the Division of Pure Chemistry have made it desirable to confirm this important result by crystal-structure analysis.

Experimental details

Iron pentacarbonyl is a straw-coloured liquid which freezes at −20 °C. The X-ray data were obtained from precession and Weissenberg photographs taken at temperatures ranging from −70 to −110 °C. Distilled material was sealed in a thin-walled glass capillary of about 0·4 mm. diameter, and single crystals were grown by alternate slow freezing and partial melting of the sample. Suitable crystals were easy to grow, but when cooled to the working temperature they invariably split into two or more fragments. Sometimes the damage to the crystal was comparatively slight, and the photographs were usable. All the X-ray data have been obtained from such photographs. Mo $K\alpha$ radiation was used throughout.

The crystal data at −80 °C. (obtained from precession photographs) are

Monoclinic, probably Cc

$a = 11{\cdot}71 \pm 0{\cdot}06$, $b = 6{\cdot}80 \pm 0{\cdot}04$, $c = 9{\cdot}28 \pm 0{\cdot}05$ Å; $\beta = 107{\cdot}6 \pm 0{\cdot}4°$.

D_x (calculated density) $= 1{\cdot}85 \pm 0{\cdot}03$ g.cm.$^{-3}$ ($Z = 4$).
D_o (observed density) not known; density of liquid 1·46 g.cm.$^{-3}$.
(Handbook of Chemistry & Physics, 1955).
$\mu = 22$ cm.$^{-1}$ (Mo $K\alpha$).

There seemed to be no preferred direction of crystal growth in the capillary, and much trial-and-error was needed to produce a crystal with a specific orientation. For some reason the most desirable orientation for Weissenberg photographs (with **b** approximately parallel to the capillary) was never found. The $h0l$ intensity data were therefore obtained from a set of precession photographs of the [010] zone. The low-temperature technique used for these photographs was essentially that described by Burbank & Bensey (1952) in which the crystal is maintained in a stream of cold nitrogen gas which is itself surrounded by an envelope of warm, scrupulously dry air. This technique was used also for a set of Weissenberg photographs of the [001] zone; the double-slit layer-line screen described by Hanson (1958) was used to allow access to the crystal and goniometer head. It was found, however, that confinement in the layer-line screen of the cold and warm gas streams led to some turbulence, with consequent frost formation and a higher working temperature. In order to obtain a set of Weissenberg photographs of the [110] zone, therefore, the warm air envelope was not used (except during preliminary adjustments), and the layer-line screen was provided with a heater, and partially sealed. The modified technique thus resembled that described by Kroeger (1955). The diversity of techniques resulted in somewhat different working temperatures for the three sets of photographs. These temperatures, measured by substituting a thermocouple for the capillary, were −80 °C. for [010] and lattice parameters, −70 °C. for [001], and −110 °C. for [110]. Because of the experimental difficulties encountered, it was not considered to be worthwhile to repeat the last set at a higher temperature.

The intensities were measured visually with the aid of a standard wedge. Corrections for absorption were considered to be unnecessary, and were not applied.

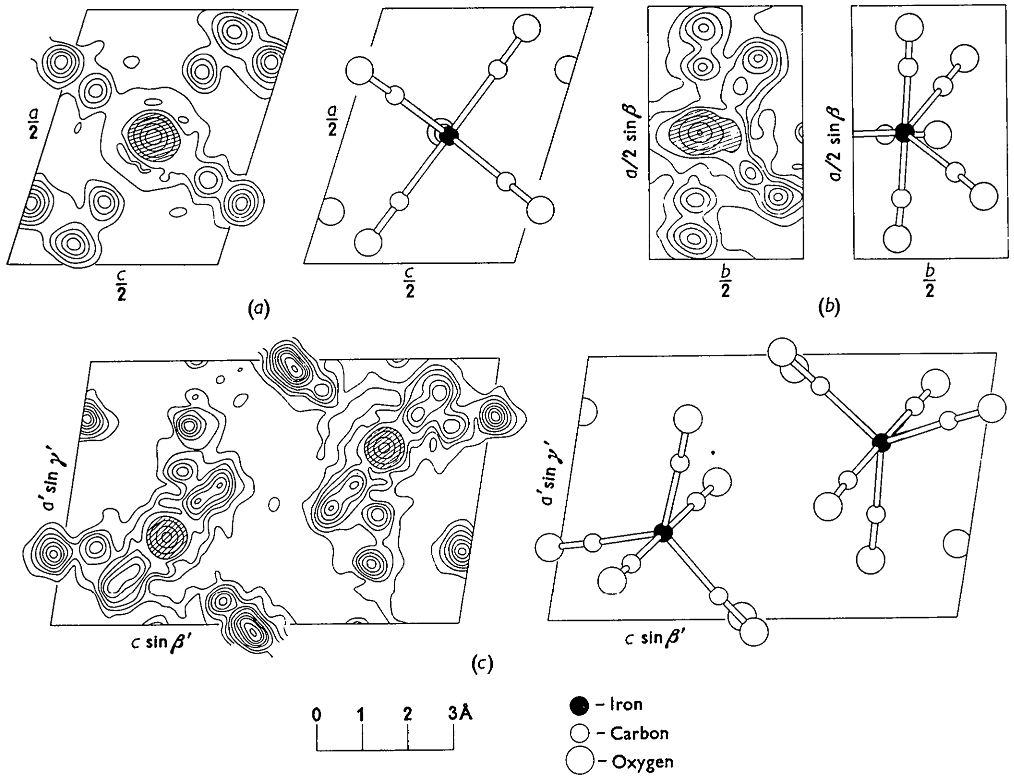

Fig. 1. Electron-density projections and interpretations. Contours are drawn at intervals of 2 e.Å^{-2} except in the neighbourhood of the iron atom (shaded areas) where the interval is 10 e.Å^{-2}. The lowest contour is at 2 e.Å^{-2}. (*a*) Projection along [010]. (*b*) Projection along [001]. (*c*) Projection along [110]. The primed quantities refer to a primitive unit cell.

Structure determination

The position of the iron atom was established by a rudimentary Patterson procedure, and the rest of the structure followed from standard heavy-atom methods. All but two of the light atoms were well resolved in the y- and z-axis electron-density projections, and these two were resolved in the projection along [110]. This projection showed the molecule in two orientations and thus provided all three coordinates of the atoms in question. [110] is of course the direction of one of the principal axes (in this case suitably short) of the primitive unit cell. Several cycles of structure-factor calculation and Fourier synthesis were used to refine the structure. The atomic positions at each stage were estimated by comparing F_o and F_c syntheses. The final electron-density maps are shown in Fig. 1, and the atomic positions are given in Table 1.

The scattering-factor curves used were those of McWeeny (1951) for carbon and oxygen, and that of Thomas & Umeda (1957) for iron. During refinement it was found that each zone required a different overall temperature factor; this was clearly a result of the difference in working temperatures mentioned above. In addition, comparison of observed and calculated peak heights suggested that individual atoms required different temperature factors, the inferences being reasonably consistent for the three zones. The values adopted are specified in Table 1: the temperature factor of the iron atom is given for each zone, and to each of the light atoms is assigned an increment to be added to the appropriate iron value.

Table 1. *Atomic positions*

$(0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, 0)+(x, y, z;\ x, \bar{y}, \tfrac{1}{2}+z)$

Atom	x	y	z	ΔB
Fe	0·0000	0·1663	0·0000	0·0
C_1	0·0800	0·3271	0·1572	0·0
C_2	0·1293	0·1530	−0·0675	0·3
C_3	−0·0899	0·2927	−0·1704	0·2
C_4	−0·1276	0·1769	0·0671	0·3
C_5	0·0037	−0·1020	0·0135	0·4
O_1	0·1283	0·4204	0·2607	0·1
O_2	0·2106	0·1367	−0·1082	0·8
O_3	−0·1462	0·3633	−0·2763	0·1
O_4	−0·2086	0·1832	0·1120	0·8
O_5	0·0055	−0·2705	0·0173	0·8

B for iron: [010]: $B=2·0$;
[001]: $B=2·3$;
[110]: $B=1·7$.

Reliability and accuracy

Observed and calculated structure amplitudes are compared in Table 2. Unobserved reflections are included only where F_c exceeds the estimated threshold value. The agreements residuals

$$(R=\Sigma||F_o|-|F_c||/\Sigma|F_o|)$$

Table 2. *Observed and calculated structure amplitudes*

hkℓ	F_o	F_c
000	-	384
	[010]	
002	102	101
004	75	78
006	39	38
008	40	46
0,0,10	19	23
0,0,12	18	21
$2,0,\overline{12}$	25	27
$2,0,\overline{10}$	17	18
$20\bar{8}$	60	58
$20\bar{6}$	70	74
$20\bar{4}$	85	88
$20\bar{2}$	90	98
200	111	101
202	133	143
204	109	124
206	77	80
208	14	16
2,0,10	24	23
$4,0,\overline{12}$	13	14
$4,0,\overline{10}$	37	43
$40\bar{8}$	50	49
$40\bar{6}$	71	68
$40\bar{4}$	55	46
$40\bar{2}$	206	213
400	60	49
402	75	69
404	44	48
406	58	61
408	32	38
4,0,10	24	26
$6,0,\overline{10}$	24	28
$60\bar{8}$	46	43
$60\bar{6}$	73	72
$60\bar{4}$	94	96
$60\bar{2}$	74	70
600	86	81
602	71	76
604	56	62
606	14	16
608	26	28
6,0,10	16	20
$8,0,\overline{12}$	24	28
$8,0,\overline{10}$	26	25
$80\bar{8}$	25	27
$80\bar{6}$	20	15
$80\bar{4}$	109	102
$80\bar{2}$	66	60
800	80	75
802	47	45
804	39	40
806	19	26
808	18	19
$10,0,\overline{12}$	20	22
$10,0,\overline{10}$	32	29
$10,0,\bar{8}$	42	36
$10,0,\bar{6}$	48	45
$10,0,\bar{4}$	29	23
$10,0,\bar{2}$	32	32
10,0,0	50	49
10,0,2	60	56
10,0,4	18	21
10,0,6	25	26
$12,0,\overline{10}$	16	19
$12,0,\bar{8}$	21	18
$12,0,\bar{6}$	61	55
$12,0,\bar{4}$	40	32
$12,0,\bar{2}$	38	35
12,0,0	20	20
12,0,2	19	19
12,0,4	19	21
$14,0,\bar{8}$	26	24
$14,0,\bar{6}$	21	18
$14,0,\bar{4}$	23	24
$14,0,\bar{2}$	37	32
14,0,0	35	33
14,0,2	9	11
$16,0,\bar{6}$	16	10
$16,0,\bar{4}$	18	19
$16,0,\bar{2}$	19	18
	[001]	
200	111	101
400	59	49
600	84	80
800	78	73
10,0,0	48	47
12,0,0	18	18
14,0,0	32	30
16,0,0	13	14
110	48	41
310	55	55
510	70	67
710	15	13
910	30	28
11,1,0	16	15
13,1,0	10	8
15,1,0	11	8
020	109	117
220	50	55
420	42	43
620	23	28
820	20	22
10,2,0	22	25
12,2,0	11	13
14,2,0	13	12
130	61	63
330	39	37
530	75	76
730	42	34
930	47	44
11,3,0	15	14
13,3,0	12	9
15,3,0	16	16
17,3,0	10	10
040	56	61
240	8	12
440	< 5	7
640	24	25
840	22	24
10,4,0	11	8
14,4,0	9	11
150	15	16
350	< 6	10
550	13	15
750	20	18
950	11	10
060	34	43
260	19	21
460	20	21
660	14	19
860	14	17
10,6,0	15	16
12,6,0	9	9
14,6,0	10	11
170	18	23
370	11	11
570	11	12
770	9	9
970	12	15
080	8	13
280	< 8	9
190	16	16
390	13	11
590	13	12
790	14	12
990	9	11
	[110]	
002	102	101
004	76	79
006	40	40
008	42	49
0,0,10	21	26
0,0,12	21	24
0,0,14	12	12
0,0,16	13	8
$1,1,\overline{15}$	12	10
$1,1,\overline{14}$	12	9
$1,1,\overline{13}$	16	15
$1,1,\overline{11}$	17	16
$1,1,\overline{10}$	23	23
$11\bar{9}$	17	16
$11\bar{8}$	14	14
$11\bar{7}$	49	44
$11\bar{6}$	47	43
$11\bar{5}$	26	27
$11\bar{4}$	< 6	10
$11\bar{3}$	40	53
$11\bar{2}$	56	62
$11\bar{1}$	102	90
110	48	41
111	89	80
112	121	122
113	85	85
114	40	39
115	27	19
116	14	14
117	22	24
118	16	16
1,1,10	10	13
1,1,11	20	22
1,1,12	11	9
1,1,13	12	10
$2,2,\overline{15}$	12	10
$2,2,\overline{14}$	12	9
$2,2,\overline{13}$	16	15
$2,2,\overline{12}$	13	12
$2,2,\overline{11}$	17	16
$2,2,\overline{10}$	9	9
$22\bar{9}$	17	16
$22\bar{8}$	20	24
$22\bar{7}$	49	44
$22\bar{6}$	35	39
$22\bar{5}$	26	27
$22\bar{4}$	24	32
$22\bar{3}$	40	53
$22\bar{2}$	40	48
$22\bar{1}$	102	90
220	51	56
221	101	101
222	38	48
223	67	70
224	59	62
225	66	65
226	29	34
227	20	19
229	16	17
2,2,10	10	9
2,2,11	10	8
2,2,12	11	9
2,2,13	12	9
$3,3,\overline{14}$	12	10
$3,3,\overline{12}$	21	21
$3,3,\overline{10}$	35	34
$33\bar{8}$	20	23
$33\bar{7}$	11	13
$33\bar{6}$	40	42
$33\bar{5}$	22	24
$33\bar{4}$	69	81
$33\bar{3}$	9	21
$33\bar{2}$	32	33
$33\bar{1}$	13	16
330	41	38
332	39	34
333	9	16
334	61	61
336	52	49
338	32	37
3,3,10	10	10
3,3,12	12	8
3,3,14	12	10
$4,4,\overline{13}$	12	9
$4,4,\overline{11}$	23	24
$4,4,\overline{10}$	17	18
$44\bar{9}$	26	26
$44\bar{8}$	12	11
$44\bar{7}$	31	32
$44\bar{6}$	25	26
$44\bar{5}$	51	48
$44\bar{3}$	47	48
$44\bar{2}$	44	41
$44\bar{1}$	50	55
441	53	48
442	21	25
443	20	24
444	< 8	11
445	26	30
446	22	23
447	36	40
448	14	15
449	21	21
4,4,11	12	9
4,4,13	12	8
$5,5,\overline{13}$	12	6
$5,5,\overline{11}$	11	10
$5,5,\overline{10}$	10	8
$55\bar{9}$	26	27
$55\bar{7}$	31	32
$55\bar{6}$	21	25
$55\bar{5}$	32	34
$55\bar{3}$	38	41
$55\bar{2}$	8	9
$55\bar{1}$	40	39
550	16	16
551	37	39
552	11	10
553	19	22
555	18	20
556	10	12
557	17	19
558	< 11	13
559	19	18
5,5,11	17	14
5,5,12	12	6
$6,6,\overline{10}$	11	10
$66\bar{8}$	17	19
$66\bar{6}$	23	24
$66\bar{4}$	28	30
$66\bar{2}$	24	24
660	18	22
661	9	11
662	24	25
663	< 8	11
664	14	18
666	15	8
668	11	11
6,6,10	17	14
$7,7,\overline{13}$	12	8
$7,7,\overline{11}$	12	10
$7,7,\overline{10}$	12	6
$77\bar{9}$	20	13
$77\bar{8}$	11	9
$77\bar{7}$	15	12
$77\bar{6}$	10	15
$77\bar{5}$	26	27
$77\bar{4}$	20	17
$77\bar{3}$	26	30
$77\bar{2}$	14	16
$77\bar{1}$	23	24
770	13	11
771	21	22
772	14	14
773	21	23
775	16	13
777	12	8
779	12	9
$8,8,\overline{11}$	12	8
$88\bar{9}$	12	11
$88\bar{7}$	11	9
$88\bar{5}$	15	12
$88\bar{4}$	11	9
$88\bar{3}$	19	17
$88\bar{1}$	21	17
881	19	18
882	11	8
883	16	12
885	12	10
887	12	8
$9,9,\overline{12}$	13	6
$9,9,\overline{10}$	13	9
$99\bar{8}$	18	9
$99\bar{6}$	12	8
$99\bar{4}$	12	8
$99\bar{2}$	16	13
990	18	14
992	17	11
994	12	10
996	13	8

for the zones [010], [001], and [110] are 0·08, 0·10, and 0·12 if unobserved reflections are not considered. The detailed agreement is reasonable, and there can be little doubt of the essential correctness of the structure. The accuracy is less satisfactory, however. The mean standard deviation of light-atom coordinates has been estimated by Cruickshank's method (Lipson & Cochran, 1953) to be about 0·04 Å. This value is rather high, but perhaps not unduly so considering that the positions of these atoms have been derived from non-centrosymmetrical projections, and that there is an iron atom present.

Discussion

Intramolecular distances are given in Table 3. Individual deviations from mean distances in no case exceed the estimated standard deviation of light-atom coordinates, and are therefore not significant. The results agree well with those found by Ewens & Lister but can hardly be said to be more accurate.

Table 3. *Interatomic distances*

Atoms	Range (Å)	Mean (Å)	Standard deviation* (Å)	Value from Ewens & Lister (Å)
Fe, C	1·79 – 1·84	1·82	0·02	1·84 ± 0·03
C, O	1·11 – 1·15	1·14	0·02	1·15 ± 0·04
Fe, O	2·92 – 2·98	2·95	0·03	—

* Standard deviation from experimental values of equivalent distances. The standard deviation of light-atom coordinates, estimated by Cruickshank's method, is 0·04 Å.

The molecule has the form of a trigonal bipyramid, as expected, but if an idealized molecule is so oriented as to coincide as nearly as possible with the observed molecule, some distortion is evident. The displacement of any atom from its ideal position does not exceed 0·13 Å, but for three of the oxygen atoms, the displacements lie in the range 0·12 to 0·13 Å. These distances are about three times the estimated standard deviation of light-atom coordinates, and therefore represent a significant distortion. A consideration of intermolecular distances suggests a reason for the distortion. For the observed structure the shortest intermolecular distance is 3·03 Å, while for the idealized structure it is 2·89 Å. It would appear that the distortion of the molecule allows a closer packing, or in other words, that the molecule is sufficiently non-rigid to be deformed by van der Waals forces.

The specimens of iron pentacarbonyl were prepared by Dr K. F. H. Spiesecke of the Division of Pure Chemistry. The computations were carried out by Dr F. R. Ahmed of this laboratory, using IBM 650 computers at No. 1 Army Pay Ledger Unit, and at the University of Ottawa. Their assistance, and the continued encouragement of Dr W. H. Barnes, are gratefully acknowledged.

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The Crystal and Molecular Structure of Monofluoroacetamide

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The structure of monofluoroactamide has been determined using three-dimensional intensities measured with a proportional counter. Atomic positions and anisotropic thermal-vibration parameters have been refined by the least-squares method and the atomic thermal-vibration parameters interpreted in terms of the rigid-body vibrations of the molecule. The principal interatomic distances (corrected for rotational vibrations) are

$$\text{C–C} = 1·533 \pm 0·006,\ \text{C–F} = 1·406 \pm 0·005,\ \text{C–N} = 1·319 \pm 0·005,\ \text{C–O} = 1·254 \pm 0·005\ \text{Å}\,.$$

The determination of the structure of monofluoroacetamide forms part of a series of investigations being carried out in this laboratory to examine the influence of different attached groups and environments upon one particular group, the amide group. It is of interest also in respect of any effect the