Studies of Some Carbon Compounds of the Transition Metals.
Part II: The Structure of $MeC \colon CMe \,.\, H_2Fe_2(CO)_8$

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The structure of the complex $MeC \colon CMe \,.\, H_2Fe_2(CO)_8$, isolated from the reaction of but-2-yne with alkaline solutions of iron hydrocarbonyl, has been determined by three-dimensional Fourier methods and refined by least-squares methods. The compound crystallizes in the monoclinic system, space group $P2_1/c$, with four molecules in a unit cell of dimensions

$$a = 12 \cdot 26, \quad b = 7 \cdot 47, \quad c = 15 \cdot 7 \text{ Å}, \quad \beta = 97 \cdot 5°.$$

The structure exhibits a number of novel features which include (i) a four-carbon chain chelated on to one of the iron atoms with which it forms single metal–carbon bonds, (ii) π-bonds between this four-carbon chain and the second iron atom, (iii) the probability that one of the six Fe–C≡O linkages is non-linear (168°). The metal–carbon separations can be classified into three groups of average length 2·13, 1·95 and 1·78 Å. The latter is significantly shorter than the single-bond distance (1·95 Å) and provides confirmation for the shortening of the metal–CO distance as a result of partial double-bond character. Carbon–oxygen separations correspond either to normal triple-bond carbonyl links (1·14 Å) or to phenolic C–OH lengths (1·37 Å) in agreement with chemical and spectroscopic evidence. The metal atoms are bonded together with a normal covalent Fe–Fe separation of 2·49 Å.

Introduction

The reaction of metal carbonyls with unsaturated organic molecules can lead to substitution of some or all of the CO groups by the organic ligand, to addition o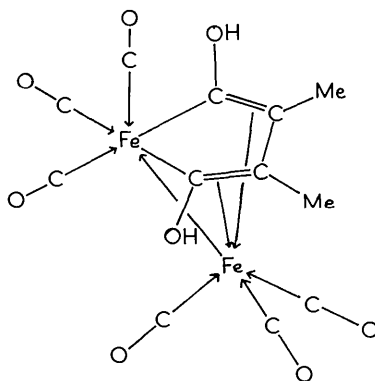f the organic molecule with incorporation of one or more CO groups into the organic skeleton, or to synthesis of larger organic molecules by a catalytic mechanism; in the last case, synthesis may often be improved by the use of the corresponding hydrocarbonyl.
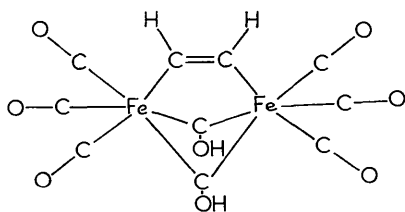
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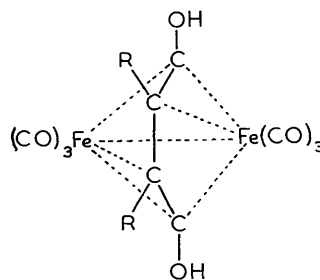
II

III

Although many of these complexes have been prepared, relatively few structures have been unambiguously determined experimentally. These include ferrocene (Dunitz, Orgel & Rich, 1956) and ruthenocene (Hardgrove & Templeton, 1959) and, in the mixed hydrocarbon–carbonyl class, $(C_5H_5)_2Mo_2(CO)_6$ (Wilson & Shoemaker, 1957) and $(C_5H_5)_2Fe_2(CO)_4$ (Mills, 1958). Both of these pairs of closely related compounds nevertheless exhibit significantly different structures. The structures of two cobalt acetylene carbonyls have been reported (Sly, 1959) (Mills & Robinson, 1959) both of which involve novel molecular arrangements as does the reported structure for $(C_5H_5)_3Ni_3(CO)_2$ (Mills, Hock & Robinson, 1959). In the present paper we present the evidence for another molecular configuration which contains hitherto unsuspected types of chemical binding.

In their study of the catalytic reaction of alkaline solutions of iron pentacarbonyl, Reppe & Vetter (1953) isolated a binuclear complex $Fe_2C_{10}O_8H_4\,H_2O$ (and from it the anhydrous complex), together with hydroquinone, when acetylene was the organic reactant. This reaction was later studied by Sternberg, Markby & Wender (1956) and by Clarkson, Jones, Wailes & Whiting (1956). The former workers proposed structure (I) $(R=R'=H)$ for the general complex, $RCCR'H_2Fe_2(CO)_8$, but this formulation was criticized by the latter workers who demonstrated the presence of a four-carbon chain in the complex for which they proposed structure (II). Other structures have been proposed (e.g. Sternberg, Markby & Wender, 1958), and as it has been found that infra-red spectroscopic analysis in these compounds is not unambiguous it became clear that perhaps the only solution of the structure would be through a complete three-dimensional X-ray analysis which, as well as yielding the overall molecular geometry, might give information about the types of bonding involved in this novel compound. (All three postulated structures involve features which were novel at the time of publication.)

The complex formed with but-2-yne was chosen for analysis on account of its greater stability and absence of solvent of crystallization. A preliminary report of the structure has been published (Hock & Mills, 1958).

Experimental

The sample of $Fe_2C_{12}O_8H_8$ was kindly supplied by Dr M. C. Whiting, and suitably small crystals were used without absorption correction (the crystal used was of dimensions $0.29 \times 0.20 \times 0.16$ mm.; for Co $K\alpha$ radiation $\mu = 47.8$ cm.$^{-1}$). Oscillation and Weissenberg photographs showed that the system was monoclinic with cell parameters:

$$a = 12.26,\ b = 7.47,\ c = 15.70\ \text{Å},\ \beta = 97.5°.$$

Systematic absences are $0k0$ when $k = 2n+1$ (observed up to $k = 8$), and $h0l$ when $l = 2n+1$ (observed up to

$h = 13$, $l = 17$). These absences are consistent with the space group $P2_1/c$. From the density, $\varrho_o = 1.79$ g.cm.$^{-1}$, $Z = 4$ (the calculated density is 1.83 g.cm.$^{-3}$) and thus the space group affords no information about the molecular symmetry.

Three-dimensional intensity data accessible to Co $K\alpha$ radiation were collected from equi-inclination Weissenberg photographs by the multiple-film technique and were estimated visually. In this way a total of 1923 reflexions were included of which 272 were too weak to be measured.

Solution of the structure

Attempts to solve the structure by two-dimensional methods failed to determine even the positions of the Fe atoms uniquely. Projections down [010] and [100] yielded Patterson maps with numerous solutions whilst that down [001] gave a single set of related peaks which suggested that both Fe atoms had x and y co-ordinates in common. The electron-density projections for these principal zones completely failed to reveal any recognizable fragments of the molecule, although we later found that in one of the trial projections down [010] the Fe atoms had been correctly placed. This failure to find the signs of the reflexions correctly on the basis of the heavy atoms alone was due to the considerable overlap of light atoms in projection; the later inclusion of these reversed the signs of a number of strong reflexions including that of the strongest observed $30\bar{4}$.

That the x and y co-ordinates were common to both heavy atoms was unambiguously confirmed by a three-dimensional Patterson synthesis based upon some 1400 terms. Figs. 1 and 2 show the presence of non-Harker peaks of double weight in the Harker sections at $V = 0$ and $V = \frac{1}{2}$. Fig. 3 shows the corresponding [010] Patterson projection; the Fe–Fe vector peaks here are much smaller than the superimposed light-atom peaks.

Calculations of electron density in three dimensions were based initially on the two Fe atoms; successive projections were calculated from signs with 8, 12 and 20 additional light atoms; at this stage no distinction was made between carbon and oxygen atoms. The combined structure-factor and electron-density calculations were performed on the Manchester University Mark I electronic Computer; with the programme used, reflexions were calculated, in the early stages, only if $|F_c|$ was greater than one eighth of the maximum iron contribution, otherwise they were rejected. When all the light atoms had been located by this method and the oxygens distinguished by peaks of greater weight, an initial calculation of structure factors with B_{Fe} of 2.0 and B_C and B_O of 3.5 Å^2, gave an agreement index $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ of 39% for the 1400 terms.

The structure was then refined by least-squares methods. The scattering curves used were those of Berghuis et al. (1955) for carbon and oxygen and that
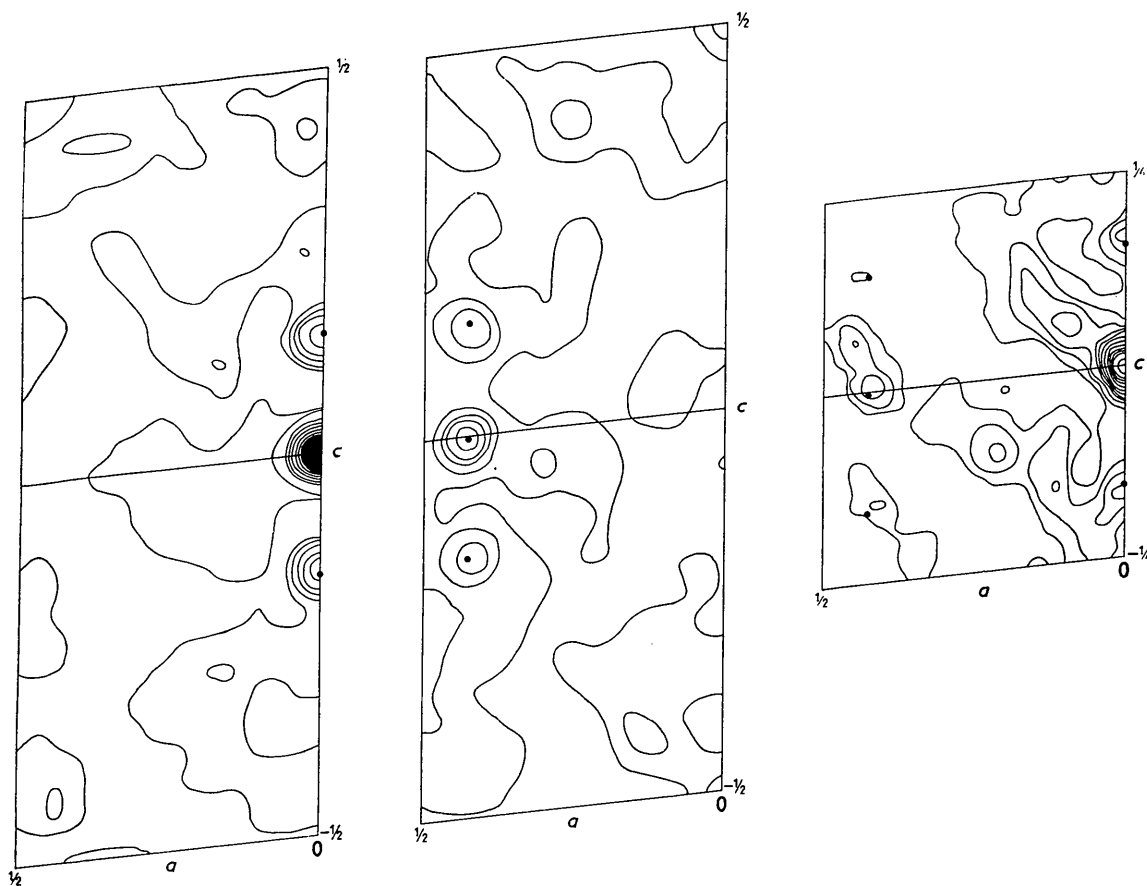
Fig. 1   Fig. 2   Fig. 3

Figs. 1 and 2. Three-dimensional Patterson sections, P(UVW), at V = 0 and V = ½.
Fig. 3. Patterson projection down [010]. The heavy-atom vector peaks are marked by dots. The contours are at equal, though arbitrary, intervals.

of Freeman & Wood (1959) for iron. An allowance was made for the anomalous scattering by iron, due to the proximity of an absorption edge, by subtracting 3·8 electrons over the whole range of the curve before application of the thermal factor.

Throughout the whole of the isotropic refinement we used a programme, written for the Manchester University Mercury Computer, which utilised the diagonal terms of the least-squares matrix only. The programme solved for shifts in positional and individual isotropic thermal parameters and the overall scale-factor. In spite of the neglect of off-diagonal terms, full shifts were able to be applied and no instability in the solution was observed, probably because of the fairly uniform selection of the data from reciprocal space. An allowance for their interaction with the overall scale-factor shift was made to the individual thermal shifts by applying a 'back-shift' correction*; this was obtained from evaluation of the overall thermal shift

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* This method of allowance for the most important off-diagonal interaction was suggested to us by Dr D. W. J. Cruickshank.

both with and without allowance for interaction with the scale-factor. Thus if ΔB_1 and ΔB_2 are the overall thermal shifts found from 1×1 and 2×2 matrices respectively (the latter incorporating the scale-factor interaction) then the thermal shift applied to the individual atoms were

$$\Delta B_i = \Delta B_i + \Delta B_2 - \Delta B_1$$
applied   diagonal   overall   overall

Throughout the refinement, the weighting factor used was

$$w = 1/[1 + F_o^2/8F^2(\text{min.})] .$$

For unobserved reflexions, a contribution to the least-squares totals was made only if $|F_c| > F_{\text{min.}}$ in which case ΔF was put equal to $\pm |F_{\text{min.}}| - F_c$, and an arbitrary weight of 0·9 applied. Reflexions 002, 100, 110, 200, 2C$\bar{2}$ and 30$\bar{4}$ always calculated greater than observed; these terms were omitted from the refinement as they were probably subject to extinction.

When the isotropic refinement gave negligible shifts, the R factors, for non-zero and all reflexions respectively, were 13·8% and 15·6%. The estimated standard

Table 1. *Final positional parameters and estimated standard deviations*

	x/a	y/b	z/c	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Fe(O)	0·2178	0·1697	0·3273	0·0013 Å	0·0014 Å	0·0013 Å
Fe(II)	0·2129	0·1432	0·1685	0·0013	0·0014	0·0013
O_5	0·2334	0·5301	0·2231	0·0050	0·0049	0·0052
O_6	0·3546	−0·1456	0·2558	0·0056	0·0049	0·0057
O_7	0·1208	−0·2037	0·1013	0·0069	0·0061	0·0062
O_8	0·0322	0·3392	0·0685	0·0072	0·0072	0·0070
O_9	0·3726	0·1995	0·0528	0·0056	0·0075	0·0058
O_{10}	−0·0012	0·0471	0·2632	0·0059	0·0083	0·0061
O_{11}	0·1351	0·4597	0·4248	0·0071	0·0076	0·0065
O_{12}	0·2471	−0·0925	0·4647	0·0088	0·0089	0·0079
C_1	0·4124	0·4795	0·3522	0·0079	0·0077	0·0076
C_2	0·3558	0·3282	0·3004	0·0066	0·0067	0·0069
C_3	0·3870	0·1439	0·3084	0·0068	0·0075	0·0072
C_4	0·4819	0·0770	0·3701	0·0069	0·0081	0·0078
C_5	0·2639	0·3528	0·2360	0·0068	0·0069	0·0070
C_6	0·3210	0·0277	0·2524	0·0069	0·0069	0·0066
C_7	0·1580	−0·0680	0·1279	0·0075	0·0078	0·0070
C_8	0·1014	0·2667	0·1084	0·0073	0·0080	0·0071
C_9	0·3083	0·1782	0·0969	0·0069	0·0073	0·0072
C_{10}	0·0898	0·0958	0·2802	0·0079	0·0090	0·0078
C_{11}	0·1679	0·3466	0·3873	0·0080	0·0083	0·0073
C_{12}	0·2354	0·0060	0·4106	0·0081	0·0093	0·0085

Average values for positional standard deviations

Fe 0·0013, O 0·0066, C 0·0075 Å .

Standard deviations of bond lengths and angles

Fe–Fe	0·0018 Å	Fe–C–O	(180°)	0·7°
Fe–C	0·0075	C–C–C	(120)	0·7
C–O	0·0098	C–Fe–C	(90)	0·4
C–C	0·0104			

Table 2. *Allowance was made for anisotropic thermal motion by the expression*

$$\exp\ -10^{-5}(b_{11}h^2 + b_{12}hk + b_{13}hl + b_{22}k^2 + b_{23}kl + b_{33}l^2)$$

for the thermal exponent

	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}	Root mean square amplitudes of vibration		
Fe(O)	365	−169	59	1275	25	224	0·194 Å	0·166 Å	0·161 Å
Fe(II)	359	−74	8	1215	9	220	0·187	0·173	0·155
O_5	515	163	−116	1053	221	372	0·236	0·192	0·155
O_6	662	370	6	1029	113	428	0·243	0·220	0·159
O_7	1044	−122	−173	1493	−257	465	0·301	0·233	0·193
O_8	918	1065	−367	2767	50	527	0·330	0·271	0·190
O_9	559	−265	168	3211	382	390	0·307	0·217	0·196
O_{10}	516	−1222	126	3955	−262	410	0·349	0·224	0·170
O_{11}	1071	500	262	2781	−568	433	0·307	0·274	0·203
O_{12}	1384	−315	338	3547	1792	600	0·378	0·322	0·173
C_1	650	−673	−223	1296	−130	312	0·259	0·203	0·139
C_2	377	−173	71	1037	173	280	0·197	0·173	0·153
C_3	336	−34	87	1637	45	287	0·216	0·187	0·158
C_4	375	288	−234	1548	388	402	0·252	0·213	0·130
C_5	374	71	−57	1150	129	275	0·200	0·181	0·152
C_6	470	−65	104	1039	187	237	0·190	0·185	0·152
C_7	581	41	−101	1436	149	259	0·225	0·204	0·162
C_8	510	3	18	1546	−88	288	0·212	0·202	0·181
C_9	402	−16	40	1381	183	300	0·210	0·182	0·171
C_{10}	574	−781	265	2073	−188	335	0·268	0·200	0·171
C_{11}	584	54	−60	2026	−83	222	0·241	0·217	0·158
C_{12}	546	−299	116	2145	391	403	0·264	0·211	0·191

deviations from the diagonal approximations gave average positional standard deviations of 0·0018 Å for Fe; 0·0091 Å for O and 0·0099 Å for C.

Finally, eight rounds of anisotropic refinement were applied. At this stage the intensity data were re-scaled; each Weissenberg level was separately scaled to the refined structure and observed reflexions averaged. In the anisotropic treatment, a 10×10

Table 3. *Observed and calculated structure factors*

The three columns in each group contain the values of l, $10F_o$, $10F_c$, reading from left to right. Each group is headed by the common values of h and k for that group printed after an *. The value of $F_{min.}$ used was 24 on this scale

THE STRUCTURE OF $MeC\colon CMe . H_2Fe_2(CO)_8$

Table 3 (cont.)

This page consists of a dense crystallographic structure-factor listing arranged in multiple columns, each block headed by k,l index values followed by rows of h, F_o, F_c values.

Table 3 (cont.)

h	k	l	Fo	Fc

(structure factor table — multiple column groups)

```
•  9   4
0        -50
1   95   61
2        -18
3        -10
4  230   212
5 -224  -224
-1 -126  -116
-2  159   150
-3 -114   -98
-4    0    -6
-5  335   320
•  9   5
0        -43
1  -63   -64
2  118    23
3   47    28
4  -72   -78
-1 -135  -142
-2    0   -24
-3  145   150
-4  107   131
-5  -56   -63
•  9   6
0  219   206
1         -8
2 -105  -105
-1    0   -46
-2 -132  -146
-3  -59   -59
• 10   0
0  262   280
2 -283  -259
4 -183  -160
6  334   327
8    0    24
10  -82   -94
-2 -176  -155
-4 -300  -288
-6  282   245
-8 -271  -246
-10 119   102
-12 210   226

• 10   1
0 -223  -208
1 -122   -89
2   63    39
3   51    45
4  169   153
5  146   114
6 -198  -186
7  -83   -77
8  182   183
9    0   -24
10   92    98
-1  201   172
-2  268   249
-3    0   -17
-4  186   174
-5 -187  -168
-6 -465  -464
-7  192   170
-8  192   172
-9 -141  -125
-10   0    42
-11  -65   -79
-12 -205  -196
-13  318   281
• 10   2
0 -125  -120
1 -484  -473
2    0   -34
3  175   162
4  260   278
5    0    37
6 -127  -141
7 -130  -139
8    0    -2
9    0   -43
-1  489   514
-2 -112  -108
-3    0    -3
-4   58    54
-5 -118  -133
-6   59    43
-7  133   125
-8  170   164
-9  -92   -87
-10  -77   -84
-11    0   -28
-12  -85   -96

• 10   3
0  -66   -56
1  310   316
2    0   -45
3  -40   -47
4   96    95
5 -256  -259
6    0   -14
7  149   163
8    0   -28
-1 -366  -356
-2    0   -30
-3    0   -15
-4    0     9
-5  379   408
-6 -289   -70
-7 -257  -227
-8  169   163
-9   86    89
-10 -29   -48
-11 117   128
• 10   4
0  -77   -60
1    0   -23
2  170   157
3   85    80
4   63    55
5  -83   -79
-1 -315  -312
-2 -105   -98
-3  193   182
-4   96   102
-5    0    75
• 10   5
0  193   159
1 -124  -111
2    0   -46
3    0    22
4 -112  -137
-1  117   109
-2 -110  -108
-3    0    -0
-4    0   -37

• 11   0
0 -309  -293
2  -76   -64
4  127   126
6 -230  -241
8  166   168
-2  197   179
-4   43   415
-6 -311  -300
-8  206   193
-10   0   -14
-12 -208  -239
• 11   1
0 -379  -385
1 -233  -209
2    0    46
3   79    48
4  144   143
5  179   163
6 -201  -205
7 -175  -163
8  112   110
-1  240   241
-2  184   162
-3    0   -26
-4  133   137
-5 -175  -171
-6 -230  -212
-7  161   155
-8  246   244
-9  -98   -89
-10  34    20
-11   0     8
-12 -104  -147
• 11   2
0  -81   -75
1  350   331
2   77    65
3  -83   -84
4    0    26
5 -172  -177
6   86    68
7   53    51
-1 -274  -290
-2 -116  -133
-3   31    80
-4 -168   -94
-5  196   213
-6  208   200

-7 -167  -176
-8    0     3
-9   99    94
-10 -49   -63
-11 102   117
• 11   3
0 -121  -104
1  248   236
2   96    84
3   94    87
4   47    52
5 -225  -251
6  -70   -57
-1 -313  -336
-2    0   -23
-3    0    22
-4   93    79
-5  163   145
-6 -103  -101
-7 -237  -236
-8    0    -5
-9  215   232
-10   0    18
• 11   4
0    0    13
1 -230  -215
2  113    88
3   80    98
4 -164  -188
-1  189   182
-2    0     6
-3    0    23
• 11   5
0 -224  -220
2  -90   -87
4  139   131
6 -228  -243
-2  150   146
-4  207   194
-6 -380  -374
-8  401   417
-10   0   -62

• 12   0
0  154   141
1  125   119
2    0   -21
3   80    68
4    0   -30
5 -162  -154
6  110   101
-1 -187  -193
-2 -155  -145
-3    0   -42
-4 -116  -116
-5   48    58
-6  158   148
-7    0    27
-8 -104   -93
-9    0    17
-10 -49   -66
• 12   1
0  277   269
1  210   217
2  -75   -79
3   48   135
4  -69   -65
5 -354  -296
-1 -148  -269
-2 -147  -126
-3   62    61
-4   70    55
-5  168   161
-6    0    18
-7 -266  -283
-8  -61   -59
-9   54    85
• 12   2
0    3     3
1   77    83
2 -205  -204
3  105   104
-1  211   249
-2 -135  -117
-3  -34   -35
-4   86    75
-5 -115  -122
-6    0    30
-7  155   201

• 12   4
-1  158   179
-2  -35   -66
-3  -69  -119
• 13   0
0  198   207
1    0    -1
2 -158  -142
4    0   -45
6   54    66
• 13   1
0  175   188
1   92    82
2  -55   -55
3  -70    61
-1 -133  -118
-2 -147  -145
-3   86    88
-4   47    48
-5   28    41
-6  217   226
-7  -63   -84
• 13   2
0   65    73
1 -140  -170
-1  250   287
-2 -132  -133
-3 -150  -160
-4  144   147
-5   72    82
-6  -24  -100
```

Table 3 (cont.)

Discussion of the structure

least-squares matrix was formed for each atom, which allowed for positional (Δx), thermal (Δb_{ij}) and overall scale-factor interactions. Each 10×10 matrix was reduced to 9×9 at the end of a cycle by applying the overall scale-factor shift, obtained from the 2×2 matrix involving overall thermal shift, to form a modified set of right-hand sides. Each 9×9 matrix was then inverted, shifts were obtained and estimates of standard deviations were obtained from the diagonal elements. This procedure gives a better, though larger, value of σ than does the diagonal approximation. The final positional parameters, together with the estimated standard deviations, are given in Table 1. The magnitudes of the principal axes defining the anisotropic motion are given in Table 2 together with the final values of the individual thermal parameters. The final values of the R factors, defined above, were 8·75% and 10·47%.

Discussion of the structure

The relevant bond lengths and bond angles (calculated by the Mercury programme of R. A. Sparks) are shown in Figs. 4 and 5. The standard deviations of some bond lengths and bond angles, based on the usual formula (Cruickshank & Robertson, 1953) with the approximation that σ is independent of direction are given in Table 1. Fig. 6 shows the Fourier projection down [010] based upon the final analysis.

The structure is clearly different from any which have been proposed and contains a number of features which, though postulated in other compounds, have not, as yet, been found by structural analysis. The structure is in agreement with spectroscopic and chemical evidence. The molecule is built up from a four-carbon chain and two trigonal $Fe(CO)_3$ groups, but the latter, contrary to general expectation, are not arranged with respect to one another as in $Fe_2(CO)_9$ (Powell & Ewens, 1939). In the latter compound, the trigonal axes of the $Fe(CO)_3$ groups coincide to give an eclipsed arrangement of the terminal carbonyl groups (a similar arrangement holds for some acetylene substituted cobalt carbonyls e.g. $Co_2(CO)_6C_2H_2$ (Sly, 1959), $Co_2(CO)_9C_2H_2$ (Mills & Robinson, 1959)); here, however, whilst the Fe atom of one $Fe(CO)_3$ group lies on the 3-fold axis of the other, the two axes make an angle of 113° with one another. The two Fe atoms have different co-ordination polyhedra and different valency states. They are labelled Fe(0) and Fe(II) on this basis.

The Fe–Fe distance of 2·49 Å indicates a covalent bond similar to those found in $Fe_2(CO)_9$ (2·46 Å) and $(C_5H_5)_2Fe_2(CO)_4$ (2·49 Å) (Mills, 1958). This distance is therefore of 'normal' length in contrast to the long bonds found in $(C_5H_5)_2Mo_2(CO)_6$ (Wilson & Shoemaker, 1957) $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ (Dahl & Rundle, 1957).

Atoms C_1–C_4 are clearly those of the original butyne. The central carbons, together with the reduced carbonyl group carbons C_5 and C_6, form the four-carbon chain which acts as a bidentate ligand to Fe(II). At the same time these four carbons are nearly equidistant from Fe(0) whilst the 3-fold axis of the carbonyl groups attached to Fe(0) is roughly perpendicular to the plane of these four carbons. The geometrical arrangement of this fraction of the molecule is very similar to that envisaged for Reihlen's compound, butadiene iron tricarbonyl, $C_4H_6Fe(CO)_3$ (Hallam &
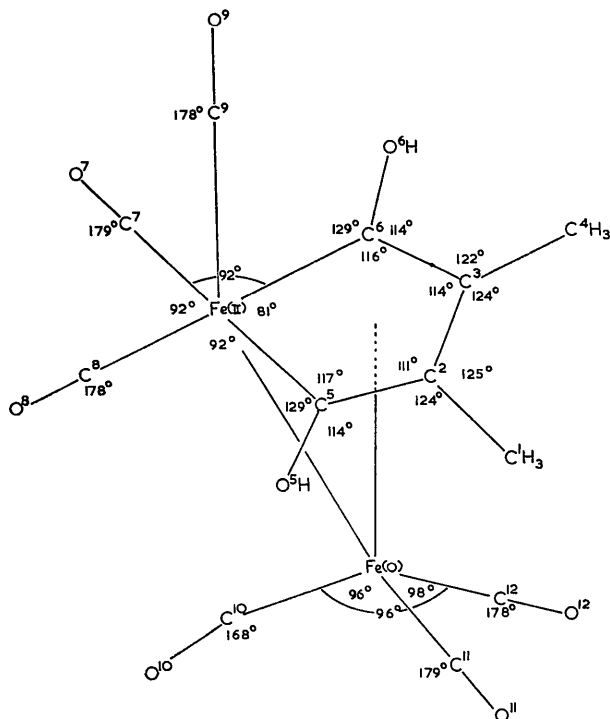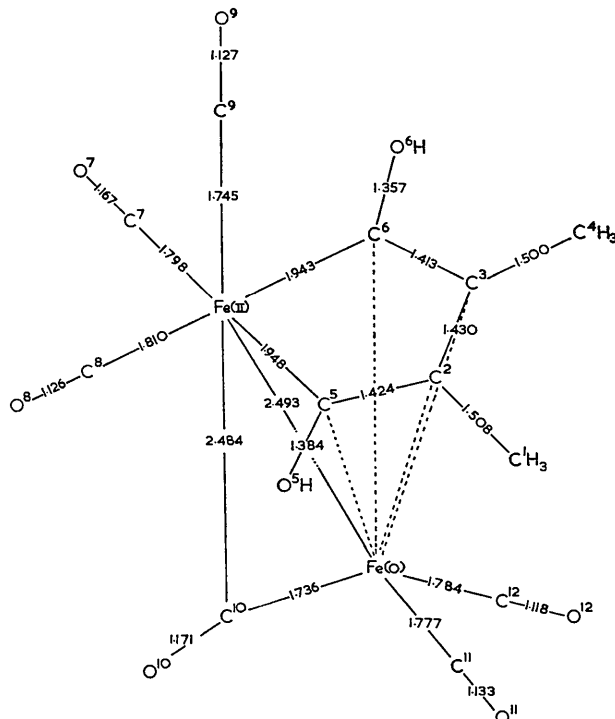
Fig. 4

Fig. 5

Figs. 4 and 5. Bond angles and bond lengths. Standard deviations of these molecular parameters
are listed in Table 1. The following angles and distances are also important:

C_8–Fe(II)–C_9	96°	Fe(II)–C_2 2·884 Å	C_7–C_8	2·602 Å
C_7–Fe(II)–C_9	99	Fe(II)–C_3 2·855	C_{10}–C_{11}	2·613
C_5–Fe(II)–C_9	92	C_8–C_9 2·650	C_{10}–C_{12}	2·622
C_6–Fe(II)–C_9	93	C_7–C_9 2·692	C_{11}–C_{12}	2·686
		Fe(O)–C_2 2·150	Fe(O)–C_5	2·111
		Fe(O)–C_3 2·142	Fe(O)–C_6	2·121
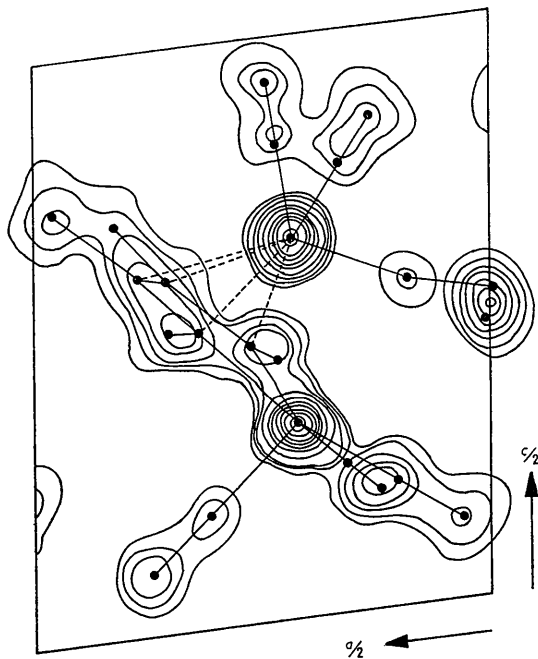
Fig. 6. Electron-density projection down [010]. The contours
are at equal interval except around each heavy atom where
the intervals are 1·5 times the remainder.

Pauson, 1958), the structure of which is being deter-
mined in these laboratories. The conventional valence
bond structure for the molecule implies a diene system
which could account for two π-bonds formed with
Fe(0) (structure III). However, conjugation results in
the three C–C distances of the chain becoming vir-
tually identical. (3σ for C–C 0·03 Å is greater than
the maximum variation). The C–OH distances (aver-
age 1·37 Å) are very close to values found in phenolic
compounds; the phenolic character of the hydroxyl
groups had been previously demonstrated by $_pK_A$
measurements (Sternberg, Markby & Wender, 1956),
and by the formation of mono- and di-acetates
(Clarkson, Jones, Wailes & Whiting, 1956). These
properties agree with the view that electrons are
withdrawn from the system by the π-bonds formed
with Fe(0). The C–methyl distance (1·51 Å) is in ex-
cellent agreement with the value expected for a single
bond formed between tetrahedrally and trigonally
hybridised carbon atoms.

The co-ordination polyhedra of the two metal atoms
Fe(0) and Fe(II) may be regarded as a distorted
trigonal prism and a distorted octahedron respectively.
In the former, the three CO groups, the second iron
atom and the two double bonds form the co-ordination

framework; in the latter only five of the sites are occupied by carbon atoms. Alternatively these five carbons can be imagined as occupying the corners of a distorted square pyramid. The Fe(II) atom lies 0·18 Å out of the least-squares plane containing atoms C_5, C_6, C_7 and C_8. Three distinct types of Fe–C separations occur in the molecule namely (i) Fe–CO (terminal), (ii) Fe(II)–C (chain and (iii) Fe(O)–C(chain). The latter, 2·13 Å, is, as would be expected, very similar to that exhibited in $(C_5H_5)_2Fe$ (2·05 Å) and in $(C_5H_5)_2Fe_2(CO)_4$ (2·12 Å). The other two distances are of particular interest as they afford a test in one molecule of the postulated shortening of the Fe–C distance in carbonyls as a result of the partial double-bond character acquired through back donation of electrons from the filled d-orbitals of the metal atom into empty p-orbitals on the carbon atom. We should thus be able to compare the lengths of these bonds with those of the σ-bonds formed between Fe(II) and the terminal atoms of the four-carbon chain. The predicted covalent single-bond length for a tetrahedrally hybridized C atom is $1·24 + 0·77 = 2·01$ Å. Reduced radii for trigonal and digonal hybridization (0·74 and 0·70 Å respectively) lead to single-bond lengths respectively of 1·98 and 1·94 Å. The observed values of 1·95 Å for Fe(II)–C_5 and Fe(II)–C_6 (compared to 1·98 Å) show that no appreciable shortening of this bond has occurred and this value is thus the first example for what is effectively an Fe–C (alkyl) bond length. All the Fe–C (carbonyl) lengths are appreciably shorter than the sum of covalent radii; the average is 1·78 Å compared with 1·94 Å. The observed shortening between the observed single bond and these carbonyl bonds, after allowance for differences in hybridization of the carbon atoms, is seventeen times the estimated standard deviation of an Fe–C length and hence is significant.

Of the six Fe–C≡O groups, five are linear (the maximum deviation is 2·5°) but the sixth deviates by as much as 12°. The molecule, as a whole, contains a plane of symmetry (see Fig. 7) which contains both Fe atoms, atoms C_9, C_{10}, O_9 and O_{10} and which bisects the bond C_2–C_3. This 'bent' group thus lies in this plane of symmetry but with the oxygen atom forced away from the other $Fe(CO)_3$ group. The arrangement is such that atom C_{10} occupies the sixth octahedral site about Fe(II), but the Fe–C distance of 2·48 Å is clearly too long for any simple interaction.

The six C–O separations (average 1·14 Å) are in good agreement with other typical metal carbonyls.

The octahedral arrangement about Fe(II) results in considerable co-planarity. The major atom-bearing plane, that which contains C_1–C_8, O_5–O_8, and Fe(II) lies nearly parallel to the b axis (Fig. 6) and it is this feature which accounts for the very high intensity of reflexion 30$\bar{4}$.

The molecules pack in infinite chains parallel to b, the molecules being linked by hydrogen bonds between the C–OH groups of the successive molecules
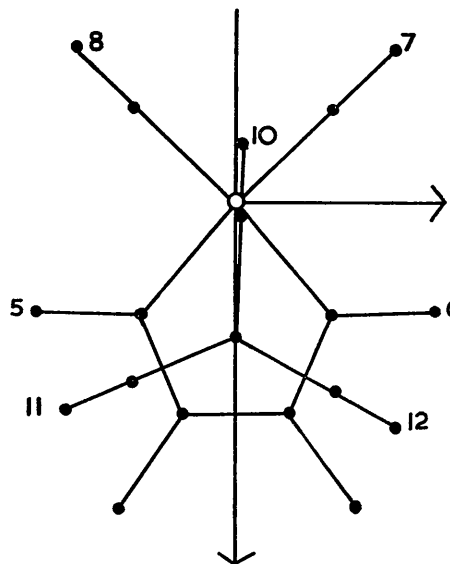

Fig. 7. The molecule is referred to a set of orthogonal axes with Fe(II) as origin, such that $0x'$ passes through the mid-point of C_2–C_3 and $0y'$ is parallel to C_2–C_3. The molecule is here viewed down $0z'$. The oxygen atoms are numbered in accordance with Fig. 5. Atoms C_9 and O_9 coincide with the origin in this projection.

(O_5–O_6 separation 2·85 Å). The only other short O–O distance is that between O_5 of one molecule and, significantly, O_{10}, the 'bent' CO, of the next. The infra-red spectrum of the solid clearly shows the presence of hydrogen bonds which are broken when the solid is dissolved in solvents such as CS_2.

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Syntheses for the Deconvolution of the Patterson Function.
Part III: Theory for Centrosymmetric Crystals

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This part deals with the syntheses for the deconvolution of the Patterson function when the structure is centrosymmetric. The interesting result is obtained that the isomorphous β-synthesis gives just the structure with no background at all.

1. Introduction

In Parts I and II (Ramachandran & Raman, 1959) of this series of papers, three classes of Fourier syntheses were proposed, which can be used when part of the structure is known for the determination of the remaining atoms in the structure. In Part II, the theory was fully worked out for the case of a non-centrosymmetric crystal. It is the purpose of the present paper to extend the theory to the case of a centrosymmetric crystal.

Let us suppose that the unit cell of the crystal contains N atoms. It is convenient to take $N = 2n$ in view of the centrosymmetry. The structure is then given by atoms of strength f_j at $\pm \mathbf{r}_j$ where $j = 1$ to $n (= N/2)$.

Let us next investigate the nature of the Fourier synthesis calculated with the product $F_P F_Q$ as the coefficient where F_P and F_Q refer to the structure factors of two centrosymmetric structures, P and Q respectively. Let f_{pi} denote the strengths of the equivalent atoms at $\pm \mathbf{r}_{pi}$.† In working out the modulation of the two structures P and Q, it is convenient to divide each of them into its two non-equivalent parts, whose structure factors may be denoted by F_P, $F_{P'}$, F_Q, $F_{Q'}$ respectively. Then,

$$F_P F_Q = (F_P + F_{P'})(F_Q + F_{Q'})$$
$$= F_P F_Q + F_P F_{Q'} + F_{P'} F_Q + F_{P'} F_{Q'}. \quad (1)$$

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† The symbols p, q are the number of atoms of type P and Q in the asymmetric unit. The symbols P and Q agree with those in the earlier part, being the total number of atoms of each type. Clearly, $P = 2p$, $Q = 2q$.

Applying the principle of modulation (Raman, 1959), the peaks in the resultant structure are obtained as follows:

$$f_{pi}f_{qj} \text{ at } \pm(\mathbf{r}_{pi} + \mathbf{r}_{qj}) \; \} \; i = 1 \text{ to } p \; (= P/2)$$
$$f_{pi}f_{qj} \text{ at } \pm(\mathbf{r}_{pi} - \mathbf{r}_{qj}) \; \} \; j = 1 \text{ to } q \; (= Q/2) .$$

The peaks therefore correspond to sums and differences of vectors of the atoms p_i, q_j and their inverses. This particular property of the resultant structure plays an important part in the interpretation of the Patterson diagram in centrosymmetric crystals, as we shall see below.

2. The Patterson function and the squared structure

It is interesting to note that the Patterson function and the squared structure become identical, when a structure is centrosymmetric. The reason for this is that a centrosymmetric structure is identical with its inverse, so that the structure factor F_N is the same as its complex conjugate F_N^*. It follows that the Patterson function becomes identical with the squared structure. It suffices therefore to study the properties of either one. Interpreting the Patterson function of a centrosymmetric structure as the modulation of the structure with itself we get the following peaks:

a strong peak $\sum\limits_{1}^{N} f_{Nj}^2$ at the origin,

$N (= 2n)$ peaks of strength f_{nj}^2 at $\pm 2r_{nj}$ these referring to the interatomic vectors between equivalent atoms related by inversion and