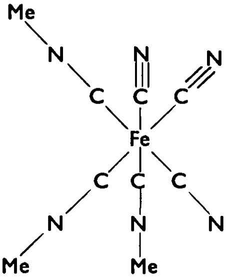
140. *Structure of Compounds of Ferrocyanide Type. Part II.** *Crystal Structure of β-Tetramethyl Ferrocyanide.*

By R. Hulme and H. M. Powell.

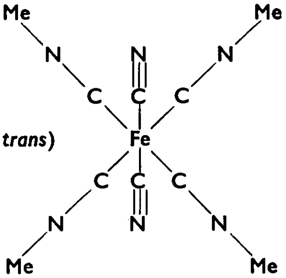
β-Tetramethyl ferrocyanide is orthorhombic, *a* = 8·45, *b* = 13·24, *c* = 11·62 Å, has space-group *Pbca*, and the unit cell contains four neutral molecules $Fe(CNMe)_4(CN)_2$. These are centrosymmetric and have the *trans*-octahedral form. Atomic co-ordinates, derived from electron-density sections and projections, are recorded for all the atoms, together with the interatomic distances. The mean Fe–C distance, 1·8 Å, is shorter than the probable single-bond distance. The FeCNMe sequence departs from linearity by a small bend at the nitrogen atom.

Two isomers of tetramethyl ferrocyanide, α- and β-, were prepared by Hartley.[1] Hölzl[2] obtained the α-form and another substance, stated to have the same composition but to be different from both the α- and the β-form. Hartley's compounds, which do not ionise, were presumed to be octahedral complexes, (I) and (II), and reasons have been given[3] for supposing that α- has the *cis*-form. Space-group considerations show[4] that the molecule of the β-form must be centrosymmetric, and therefore *trans*. Atomic positions were given only for iron, and the present investigation has been undertaken to confirm the configuration by locating the lighter atoms.



(I; *cis*)

(II; *trans*)



The material used was part of Hartley's original preparation. Unsolvated crystals were obtained by dissolving the powder in hot dry methanol and cooling the solution slowly from 65° to 40°. At room temperature a compound with methanol crystallises.

The crystals, which are orthorhombic, show forms {111}, {011}, and {100} small. They cleave parallel to (010), and have weak negative double refraction with acute bisectrix parallel to [010].

Several small crystals were used to obtain a set of 15° oscillation photographs with copper-K_α radiation. All three principal axes were used in turn as oscillation axis. A

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* Part I, *J.*, 1945, 799.

[1] Hartley, *J.*, 1913, **103**, 1196.

[2] Hölzl, *Monatsh.*, 1927, **48**, 72.

[3] Glasstone, *J.*, 1930, 321.

[4] Powell and Stanger, *J.*, 1939, 1105.

FIG. 1. *Electron density projection on* (100); *atomic positions shown on the right. Dotted contour at* 3 e/Å^2 (*approx.*), *thereafter at intervals of* 0·8 e/Å^2. *Four times this interval round the iron atoms.*

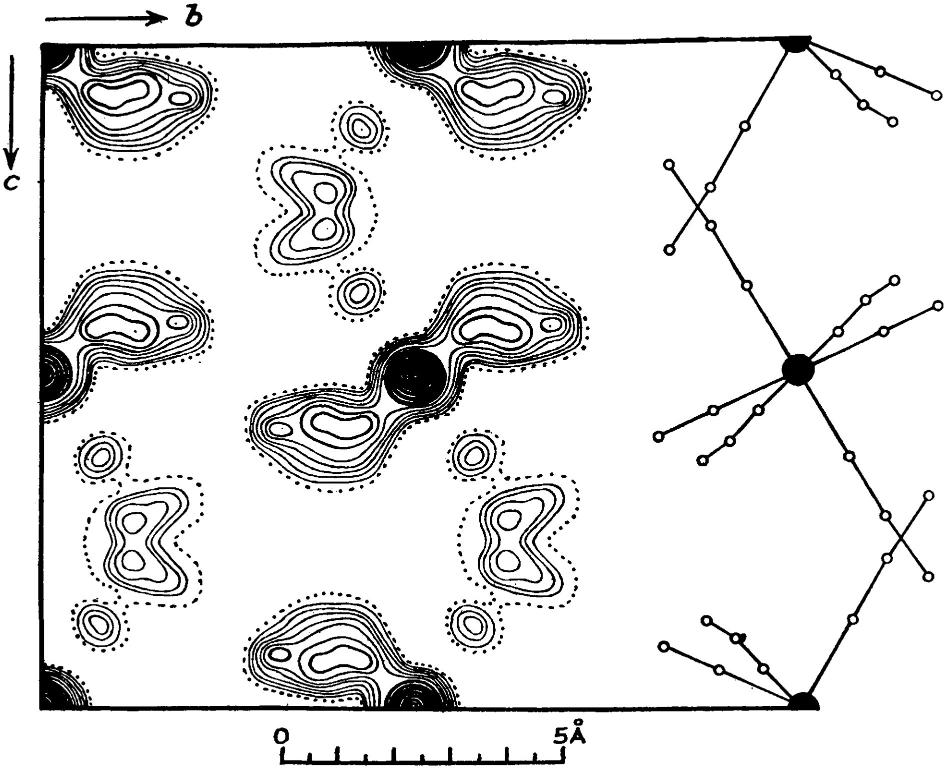


FIG. 2. *Electron density projection on* (001); *atomic positions shown on the right. Dotted contour at* 0 e/Å^2, *thereafter at intervals of* 0·6 e/Å^2. *Eight times this interval round the iron atoms.*

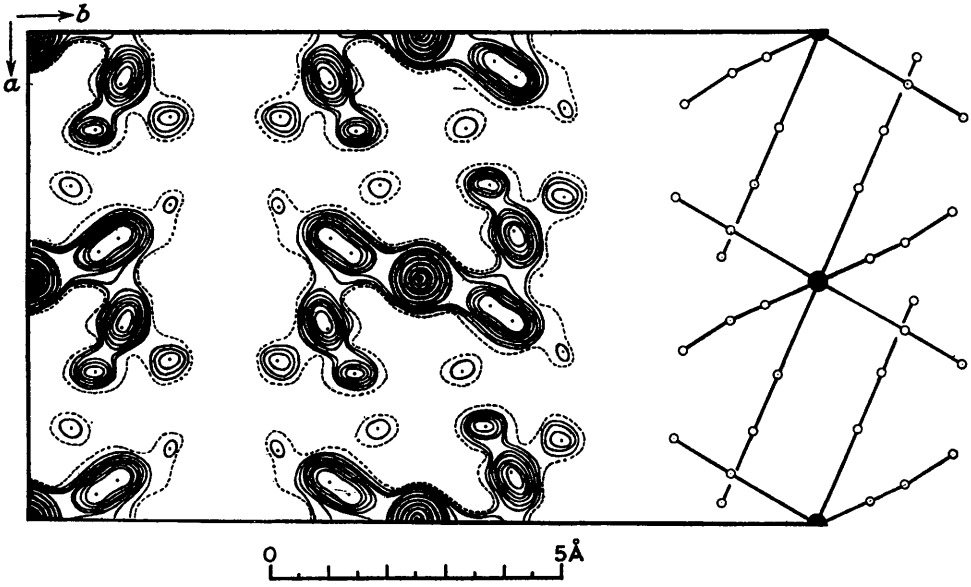


FIG. 3. *Electron density projection on* (010): *atomic positions shown on the right. Dotted contour at* 1 e/Å^3, *thereafter at intervals of* 1·2 e/Å^3. *Four times this interval round the iron atoms.*

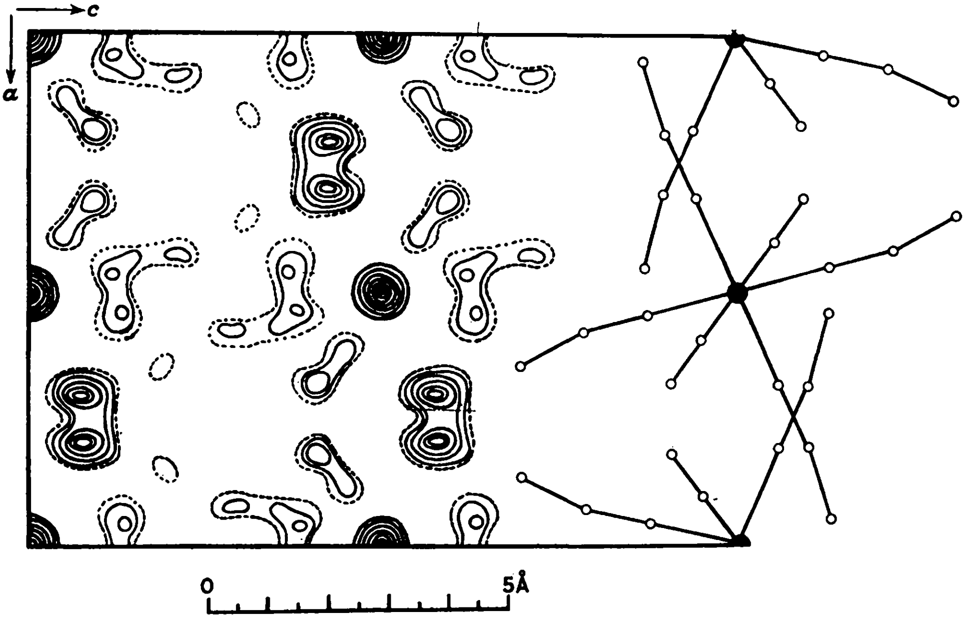
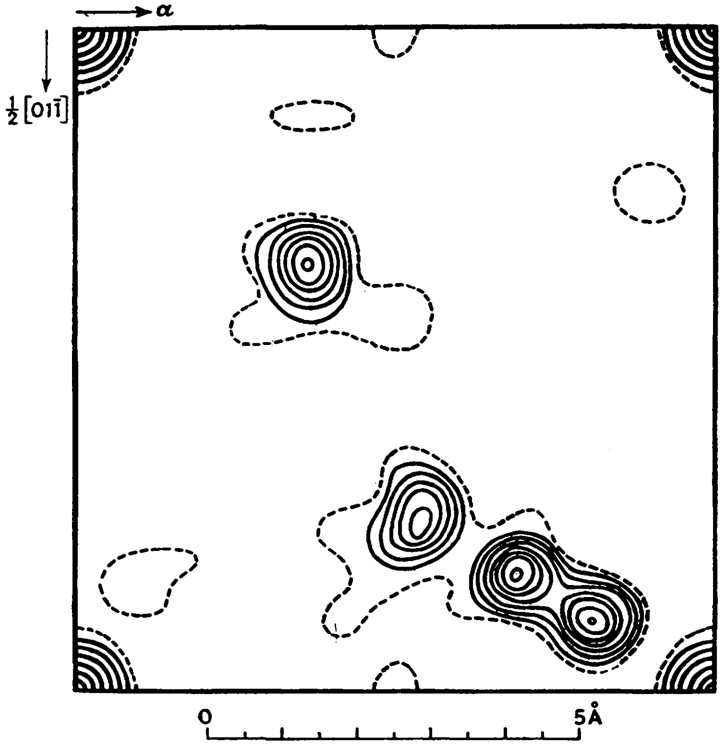


FIG. 4. *Section showing electron density in the plane* (011). *Dotted contour at about* 1 e/Å^3 *and thereafter at intervals of* 1 e/Å^3, *with iron contours* (*thick lines*) *at seven times this interval. Adjoining one iron atom are the peaks for* $C^2N^2Me^2$. *The prominent isolated peak is a methyl group,* Me^1, *of another molecule.*



suitable range of intensities was covered by the multiple-film technique combined with long and short exposures. Intensities of *X*-ray reflexions were estimated visually, and correlation between different films was made by comparison of common reflexions. To facilitate this procedure an overlap of 5° was allowed in photographs obtained by oscillation of the crystal about any one axis.

The unit cell dimensions, $a = 8{\cdot}45 \pm 0{\cdot}02$, $b = 13{\cdot}24 \pm 0{\cdot}01$, $c = 11{\cdot}62 \pm 0{\cdot}02$ Å, are in close agreement with values previously reported and combined with density 1·372 g./c.c. give the cell contents as four molecules. The absent spectra, *hk*0 when *h* is odd, *h*0*l* when *l* is odd, and 0*kl* when *k* is odd, correspond to the space-group P*bca*.

In this case absent spectra establish the space-group unambiguously, but the presence of the symmetry centre required by this space-group has been confirmed [5] in tests of a method depending on the probability distribution of *X*-ray intensities.

The general position in the space-group is 8-fold and the four iron atoms must therefore occupy special positions. The two possibilities, which are equivalent, differ only in the formal choice of origin, and the iron atoms are, therefore, assigned to the positions 000, $\frac{1}{2}\frac{1}{2}0$, $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$. The remaining atoms lie in general positions *xyz* and equivalents. In the previous investigation it was concluded from packing considerations that the CN and $CNCH_3$ arms of the molecule were approximately linear and had the expected octahedral configuration, but the positions of these carbon and nitrogen atoms were not determined.

As a first step towards the determination of the parameters for the lighter atoms an evaluation of the electron-density projection on (100) was attempted. The observed 0*kl* structure factors are of two kinds. Those with $k + l$ even have the maximum positive contribution from the iron atoms and accordingly they were given the positive sign as though it were determined by the iron contributions alone. The remainder with $k + l$ odd have no iron contribution and their signs are determined by the carbon and nitrogen atoms whose positions it is desired to find. As is to be expected, most of these structure factors are relatively small but one, F_{023}, is of great importance since it is larger than any other observed F value, including those to which iron contributes. It indicates a concentration of the lighter atoms in planes nearly parallel to (023). For a first attempted projection this F value, alone of those for which $k + l$ is odd, was included in the Fourier summation. Since it must have one or the other sign it was arbitrarily taken as negative but its inclusion in the summation with the positive sign gives a projection which would be identical if the origin were changed to a suitable iron atom, *e.g.*, that at $0\frac{1}{2}\frac{1}{2}$. The resulting projection gave a general indication of the approximate directions of the arms of the molecule. With the help of this information and packing considerations a provisional set of atomic parameters was estimated.

With these as basis, the method of F synthesis was applied to the three principal projections. The electron density was calculated at intervals of 1/60th of the unit cell dimensions. The projection on (100) required two successive approximations, that on (001) three. A single summation was made for (010). The three final projections are shown in Figs. 1—3.

TABLE 1. *Co-ordinates in* Å.

	x	*y*	*z*		*x*	*y*	*z*
Fe	0	0	0	C^2	1·61	−0·69	−0·63
				N^2	2·60	−1·08	−1·21
C^1	0·40	−0·88	1·49	Me^2	3·85	−1·64	−1·50
N^1	0·61	−1·52	2·56				
Me^1	1·18	−2·22	3·63	C^3	0·79	1·48	0·63
				N^3	1·53	2·42	1·10

The eight non-equivalent atoms or groups of the asymmetric unit in general positions are designated C^1, C^2, C^3, N^1, N^2, N^3, Me^1 and Me^2 as in Table 1, the superscripts being

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[5] Howells, Phillips, and Rogers, *Acta Cryst.*, 1950, **3**, 210.

TABLE 2. *Observed structure amplitudes and calculated structure factors for* hkl.
(*In each set of three columns the first lists values of* l, *the second* F_{obs}, *and the third* $F_{\text{calc.}}$.)

	00*l*	
2	79	96
4	17	−10
6	18	12
8	30	47
10	50	51

	10*l*	
2	27	30

	20*l*	
0	81	93
2	30	32
4	62	68
6	93	79
8	82	73
10	30	19
14	21	11

	30*l*	
2	39	−22
4	22	−24
6	33	−30
12	19	21

	40*l*	
0	36	34
2	68	73
4	36	30
6	52	44
8	69	71
10	31	29
12	28	26

	50*l*	
4	25	25
6	15	−31

	60*l*	
0	58	55
2	65	58
4	30	17
6	21	33
8	25	29
10	34	47

	70*l*	
6	15	11
8	39	10

	80*l*	
0	31	−19
2	25	23
4	39	56
6	44	58
8	15	10

	90*l*	
4	18	−18

	10,0*l*	
0	24	28
2	29	50
4	26	35

	11*l*	
1	82	119
2	14	14
3	77	94
4	24	−27
5	84	73
6	34	−30
7	51	28
9	45	39
10	25	32

	21*l*	
1	84	−88
2	70	−64
3	27	−22
4	33	40
6	38	29

	31*l*	
1	54	64
2	63	60
3	48	34
4	19	− 7
5	52	61
7	66	53
9	58	58
11	43	46

	41*l*	
0	31	23
1	33	−28
4	24	− 9
6	30	−27
7	41	−15
8	59	14
9	18	−19
10	27	25

	51*l*	
1	43	44
3	58	60
4	16	− 1
5	43	49
7	48	41
9	20	18

	61*l*	
0	34	−25
4	22	21
5	31	27
7	23	38

	71*l*	
1	40	28
3	46	43
4	9	23
5	27	19
7	32	47

	81*l*	
4	30	3

	91*l*	
3	27	37

	02*l*	
0	90	128
2	105	115
3	128	−155
4	83	62
5	51	−14
6	62	46
7	35	31
8	62	56
10	28	18
11	23	7
12	33	13

	12*l*	
2	38	37
3	13	− 5
4	65	51
5	15	−19
10	41	− 2

	22*l*	
0	77	89
1	34	33
2	56	60
3	23	14
4	54	52
5	20	21
6	63	57
8	71	54
10	40	43

	32*l*	
1	13	− 6
2	40	−38
3	46	−37
5	14	− 1
7	51	16
9	30	37

	42*l*	
0	83	80
1	26	−27
2	54	50
3	27	18
4	46	46
5	11	17
6	48	50
8	42	37
10	33	39

	52*l*	
1	32	31
2	24	−16
3	32	−47

	62*l*	
0	47	37
1	23	−17
2	50	51
4	42	46
6	33	38
8	30	33

	72*l*	
1	32	30
2	15	15

	82*l*	
0	29	16
2	32	33

	92*l*	
4	30	35

	10,2*l*	
0	32	35

	13*l*	
1	80	90
2	61	64
3	43	38
4	43	−33
5	65	62
6	30	−37
7	77	75
8	18	−22
9	45	36
10	20	33
11	30	33

	23*l*	
0	8	− 1
1	71	76
2	29	−29
3	26	15
5	21	10
9	23	− 4

	33*l*	
1	85	84
2	13	7
3	58	61
5	24	5
7	51	57
8	25	22
9	45	58

	43*l*	
0	27	12
2	30	−34
3	25	−24
6	27	− 5
8	44	26
10	30	20

	53*l*	
1	61	59
2	22	22
3	52	58
4	27	17
5	45	53
7	25	33

	63*l*	
8	22	−13

	73*l*	
1	32	44
3	30	24
5	38	54

	83*l*	
0	28	7
4	26	−13

	04*l*	
0	53	−64
1	11	−14
2	83	99
3	22	− 2
4	70	84
5	31	−18
6	69	67

TABLE 2. (*Continued.*)

	04*l*	
7	30	−38
8	43	37
9	21	13
10	31	32

	14*l*	
1	79	87
3	26	−34
5	31	−30
6	31	26
7	36	−22

	24*l*	
0	33	23
1	31	29
2	73	76
3	20	14
4	56	59
5	19	− 4
6	47	50
8	40	35
10	38	48

	34*l*	
1	14	−11
2	15	2
3	27	−26
5	21	21
6	27	32
7	21	13

	44*l*	
0	79	71
2	51	50
4	56	65
5	13	− 9
6	37	41
8	22	17

	54*l*	
1	17	−12
6	23	28
7	18	19

	64*l*	
0	68	63
2	36	40
4	44	55
5	22	3
6	30	27

	74*l*	
1	30	38
2	15	−19
5	18	−30

	84*l*	
0	32	52
1	18	−12
2	26	26

	15*l*	
1	54	67
2	19	15
3	65	61
5	20	14
7	60	71
9	32	46
11	39	46

	25*l*	
0	23	6
1	22	25
2	32	41
3	11	13
4	15	−18
5	56	13
6	22	−14
10	23	−22

	35*l*	
1	38	37
2	16	−29
3	45	53
4	55	18
5	57	81
7	44	50
9	29	14

	45*l*	
1	33	39
4	25	−33

	55*l*	
1	72	82
2	22	2
3	33	32
5	28	25
9	23	43

	65*l*	
0	20	36
1	42	26
4	30	−17

	75*l*	
1	29	35
3	27	41
4	18	−14
5	26	41

	06*l*	
0	31	40
2	45	39
4	49	66
5	30	−38
6	50	67
8	30	17
9	18	24
10	41	50

	16*l*	
1	13	9
2	20	−22
3	23	25
4	37	−45
9	18	−25

	26*l*	
0	49	42
1	17	19
2	62	67
3	39	36
4	49	54
6	40	42
8	27	36

	36*l*	
2	33	42
3	18	19
4	22	1
5	16	−13

	46*l*	
0	37	28
1	41	10
2	52	60
4	43	54
5	35	−15
6	23	30
8	25	39

	56*l*	
2	14	14
4	31	21

	66*l*	
0	43	59
2	30	31
3	22	−34
4	30	38
6	21	32

	86*l*	
0	35	56
2	22	24
6	19	30

	17*l*	
1	39	36
2	29	−37
3	58	73
4	14	25
5	40	58
9	18	33

	27*l*	
0	16	29
2	19	15
3	14	15

	37*l*	
1	45	46
2	21	30
3	53	62
5	37	70

	47*l*	
4	17	−10

	57*l*	
1	39	39
2	18	−26
3	32	32
4	30	−39
5	23	29

	67*l*	
3	27	7

	77*l*	
1	33	35
3	17	37

	08*l*	
0	30	31
2	27	30
3	17	12
4	68	76
6	31	50
8	37	42

	18*l*	
2	28	− 5
3	14	27

	28*l*	
0	86	99
1	56	−13
2	49	53
4	39	37

	38*l*	
5	34	−18

	48*l*	
0	36	43
1	41	−11
2	36	33
4	25	32
5	15	− 1

	58*l*	
2	15	27

	68*l*	
2	25	31
4	22	32

	88*l*	
0	40	41

	19*l*	
1	39	41
3	42	48
5	42	76

	29*l*	
5	44	−32

	39*l*	
1	37	40
3	49	65
5	23	28

	49*l*	
0	40	−43
1	31	−24
4	15	36

	59*l*	
2	32	− 5
3	29	35
4	15	−10

	69*l*	
1	24	−14

	89*l*	
0	22	−11

	0,10*l*	
0	51	51
2	31	40
4	30	39
6	14	19
8	18	39

	1,10*l*	
2	31	−15
3	42	−15

	2,10*l*	
0	45	46
2	37	42
3	20	−43
4	33	55

TABLE 2. (*Continued.*)

	4,10*l*	
0	26	31
1	41	3
2	25	28
4	23	33
	6,10*l*	
0	24	19
1	13	− 1
2	21	31
	8,10*l*	
0	19	22
	1,11*l*	
1	27	43
3	23	36
4	15	−24
5	15	24

	2,11*l*	
2	22	−12
3	29	−17
	3,11*l*	
1	33	51
3	33	30
	4,11*l*	
2	29	−18
	5,11*l*	
1	21	26
2	26	− 2
	0,12*l*	
0	25	35
2	34	30
6	32	33

	1,12*l*	
2	31	8
	2,12*l*	
0	23	9
2	33	41
4	20	48
	4,12*l*	
0	29	24
1	15	− 3
2	21	41
	6,12*l*	
0	28	50
	1,13*l*	
1	13	25

	2,13*l*	
3	21	− 2
	3,13*l*	
1	43	19
	2,14*l*	
0	23	34
	4,14*l*	
0	26	47
	0,16*l*	
0	30	58
	2,16*l*	
0	19	39

used to group together atoms belonging to the same arm of the molecule. From the three projections an indication may be obtained of the values of all 24 parameters, 18 of which may be derived from resolutions, some good and some moderate, of individual atoms. Since interatomic distances and bond angles were required, three-dimensional F synthesis methods were applied to improve the resolution and to remove the remaining uncertainties due to overlap in the projections.

It may be seen that each arm of the molecule lies in or close to a plane of low indices. All the atomic positions may be determined from the sections (110), (021) and (011) since in these one or other of the equivalent arms will appear, $C^1N^1Me^1$ in (110) and (021), $C^2N^2Me^2$ in (011) and C^3N^3 in (110). Me^1 also lies close to (011), and (021) contains N^1.

Signs for the F_{hkl} structure factors were evaluated from the best parameters derivable from the projections. There were 420 observed F_{hkl} magnitudes. Each of these was included the required number of times in the summation to allow for the corresponding negative indices, appropriate sign changes being made where necessary. Transformations of axes were made so that each section became a section at zero along the new axis of some suitable cell. Electron density was calculated at intervals of 1/120th of the section edges. Modifications in the parameters required six successive approximations for (011), four for (021) and four for (110). The final sections are reproduced in Figs. 4—6.

Table 1 gives the final atomic co-ordinates for all the atoms in the structure. These co-ordinates have, for the most part, been determined from sections, but a few values are derived either partly or wholly from projections. Where the same co-ordinate has been observed more than once with equal accuracy, an average value has been entered in this Table.

Structure factors for all the observed reflections have been calculated on the basis of these atomic co-ordinates. The numerical F values have been evaluated with the help of the appropriate tables, and a proportion of them have been checked by means of a crystal-structure factor calculator.[6] The Hartree atomic scattering factors [7] have been used throughout, except that Hönl's correction [8] has been applied to the atomic scattering factor for iron. The scattering of a methyl group was taken as equal to that of a nitrogen atom, located in the position of the methyl carbon atom. A temperature factor $\exp - B(\sin\theta)^2/\lambda^2$ with $B = 1$, was applied to the calculated F values. The structure then gives the following reliability factors: *h*0*l* 0·21, *hk*0 0·26, 0*kl* 0·24, all observed *hkl* 0·26. Table 2 lists observed and calculated F values. Further refinement was not

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[6] Hughes and Hulme, to be published.

[7] " Internationale Tabellen," 1935.

[8] James, " The Crystalline State," Bell, London, 1948, II, 608.

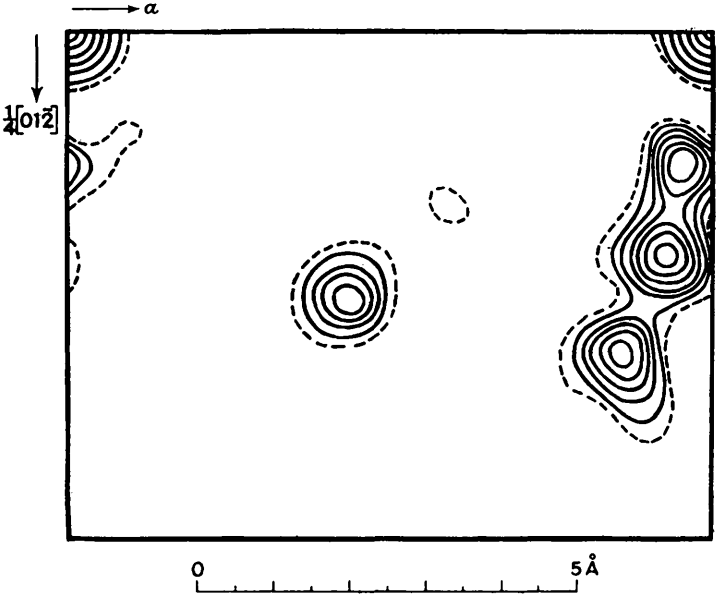

FIG. 5. *Section showing electron density in the plane* (021). *Dotted contour at about* 1 e/Å^3 *and thereafter at intervals of* 1 e/Å^3, *with iron contours* (*thick lines*) *at seven times this interval. Adjoining an iron atom are the peaks for* C^{1}N^{1}Me^1. *The isolated peak is an* N^1 *atom of another molecule.*

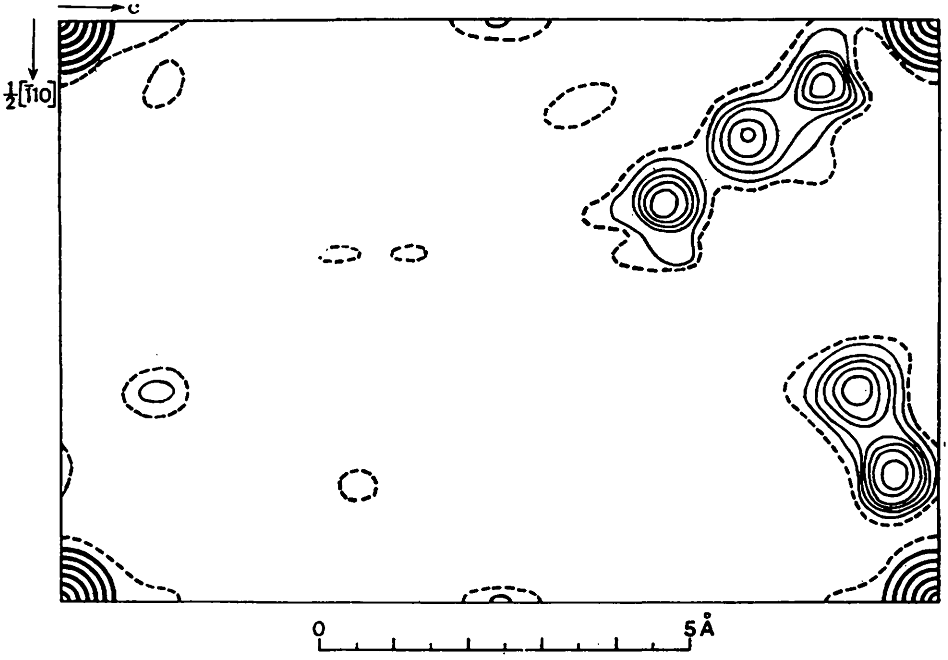

FIG. 6. *Section showing electron density in the plane* (110). *Dotted contour at about* 1 e/Å^3 *and thereafter at intervals of* 1 e/Å^3, *with iron contours* (*thick lines*) *at seven times this interval. Adjoining one iron atom are the peaks for* C^{1}N^{1}Me^1. *Another iron atom has neighbouring peaks for* C^{3}N^3.

attempted, this degree of accuracy being sufficient to establish the *trans*-octahedral configuration for β-tetramethyl ferrocyanide.

From the final co-ordinates listed in Table 1, interatomic distances, to within 0·1 Å, and bond angles to within 5°, were obtained.

The iron–carbon distances in the FeCNMe arms and the FeCN groups vary ($1{\cdot}8_0$, $1{\cdot}8_5$, $1{\cdot}8_0$ Å for Fe to C^1, C^2, and C^3 respectively) but they give an average value, 1·8 Å, which is close to that found[9] in $[Fe(CNMe)_6]^{++}$. The distance is considerably less than 2·0 Å, a probable value for the iron–carbon single bond, and is in better agreement with a structural formula, similar to that suggested by Pauling[10] for the ferrocyanide ion, in which the iron–carbon link has a bond order of 1½. The carbon–nitrogen distances are $1{\cdot}2_5$, $1{\cdot}2_0$, and $1{\cdot}3_0$ Å, respectively, giving an average distance of 1·3 Å. This is greater than the corresponding triple-bond distance, 1·17 Å, found in methyl *iso*cyanide.[11] Both the nitrogen–methyl group distances are 1·4 Å, agreeing well with the value, 1·43 Å, found by Wheatley[12] for a terminal nitrogen–methyl group distance. It is significantly less than 1·48 Å, the single-bond distance.[13] The minimum observed distance, $3{\cdot}4_5$ Å, between atoms in different molecules is normal.

The angles, C^1FeC^2, C^1FeC^3, and C^2FeC^3, are calculated from the parameters to be 85°, 91°, and 92° respectively, but the differences from 90° are probably all within the accuracy of measurement. The molecule has two sets of FeCNMe arms unrelated by symmetry, and in both the sequence is linear except for a bend at the nitrogen atom. The angles $C^1N^1Me^1$ and $C^2N^2Me^2$ are 167° and 166°, giving a mean bend of about 13°. This is considerably larger than the maximum error in the structure and is therefore significant. A similar but smaller bend was inferred in the $[Fe(CNMe)_6]^{++}$ ion.[9]

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[9] Powell and Bartindale, *J.*, 1945, 799.
[10] " The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, 1939, 234.
[11] Gordy, *Rev. Mod. Phys.*, 1948, **20**, 668.
[12] Wheatley, *Acta Cryst.*, 1954, **7**, 68.
[13] Cox and Jeffrey, *Proc. Roy. Soc.*, 1951, **207**, *A*, 110.