Crystal and Molecular Structure of Tetramethylammonium Carbidohexadecacarbonylhexaferrate(2−), $[Me_4N]_2[Fe_6(CO)_{16}C]$, a Hexanuclear Iron Cluster Complex with an Encapsulated Six-co-ordinate Carbon Atom

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The title compound crystallizes in the centrosymmetric orthorhombic space group *Pnma*, with a = 10·098(15), b = 18·788(20), c = 36·712(36) Å, and Z = 8. The structure was solved by packing considerations and was refined to R 11·9% for the 1584 independent nonzero reflections. The asymmetric unit consists of two half-anions of $[Fe_6(CO)_{16}C]^{2-}$ (the remaining halves being generated by crystallographic mirror planes) and two $[Me_4N]^+$ cations. The $[Fe_6(CO)_{16}C]^{2-}$ anion has 13 terminal carbonyl ligands [two per iron atom, except for Fe(4) which bears three], and 3 'semi-bridging' carbonyls. Nonbridged Fe–Fe bonds range from 2·646(10) to 2·743(10) Å, bridged Fe–Fe bonds from 2·553(10) to 2·632(10) Å. The encapsulated carbido-carbon atom is octahedrally co-ordinated to six iron atoms, with individual Fe–C distances from 1·805(38) to 1·968(38) Å.

THE reduction of $Ru_3(CO)_{12}$ in tetrahydrofuran with such mononuclear carbonyl anions as $[Mn(CO)_5]^-$, followed by acidification, gives rise [1,2] to the hexanuclear hydridocarbonyl complex $H_2Ru_6(CO)_{18}$ [equation (1)]. The

$$Ru_3(CO)_{12} \xrightarrow{[Mn(CO)_5]^-} [Ru_6(CO)_{18}]^{2-}(?) \xrightarrow{H^+} H_2Ru_6(CO)_{18} \quad (1)$$

reaction of $Fe(CO)_5$ with $[Mn(CO)_5]^-$, however, proceeds by a different course, yielding [3] the species $[Fe_6(CO)_{16}C]^{2-}$ [equation (2)]. Recent work has shown [4] that

$$Fe(CO)_5 \xrightarrow[\text{diglyme}]{[Mn(CO)_5]^-} [MnFe_2(CO)_{12}]^- \xrightarrow[\text{1 h}]{\text{reflux}} [Fe_6(CO)_{16}C]^{2-} \quad (2)$$

acidification of $[Fe_6(CO)_{16}C]^{2-}$ yields the known pentanuclear cluster complex [5] $Fe_5(CO)_{15}C$ rather than the expected hydrido-species, $H_2Fe_6(CO)_{16}C$.

We now report the results of a single-crystal X-ray diffraction study of $[Me_4N]_2[Fe_6(CO)_{16}C]$. A preliminary account of this work has appeared previously.[3]

EXPERIMENTAL

Crystal Data.—$C_{25}H_{24}Fe_6N_2O_{16}$, M = 943·556, Orthorhombic, a = 10·098(15), b = 18·788(20), c = 36·712(36) Å, U = 6965·0 Å^3, D_m = 1·82(2) (by flotation), Z = 8, D_c = 1·799. Space group *Pnma* (D_{2h}^{16}, No. 62). Mo-K_α radiation, λ = 0·7107 Å, μ(Mo-K_α) = 24·38 cm^{-1}.

Collection and Processing of Data.—Two crystals were used in the course of data collection. Crystal (A) (0·20 × 0·60 × 0·06 mm relative to $\vec{a}, \vec{b}, \vec{c}$; volume 7·2 × 10^{-6} cm^3) was mounted along a, while crystal (B) (0·26 × 0·86 × 0·12 mm relative to $\vec{a}, \vec{b}, \vec{c}$; volume 22·4 × 10^{-6} cm^3) was mounted on its b axis.

Intensity data were collected with a 0·01°-incrementing Supper–Pace Buerger automated diffractometer using equi-inclination Weissenberg geometry and a stationary-background, ω-scan, stationary-background counting sequence, as described previously.[6] The angle scanned here was chosen as $\omega(hkl) = [1·4 + 0·7/L(hkl)]°$.

Intensity data to sin θ 0·36 were collected; of 3151 reflections in levels 0—6kl collected from crystal (A), 2108 were $<3\sigma$ above background and were rejected; of 3849 reflections in levels h0—18l collected from crystal (B), 2318 were rejected. Data were corrected for Lorentz and polarization effects and absorption corrections were applied (using the Gaussian quadrature numerical integration method of Burnham [7]). Resulting transmission factors were in the ranges 0·348—0·872 [crystal (A)] and 0·529—0·750 [crystal (B)].

Data were merged to a common scale by a least-squares process,[8] the R-factor for scaling being 6·74% (based on F^2). The final data set consisted of 1584 independent non-zero reflections.

The compound is unstable in air (*ca.* 10% decomposition in 2—3 days as a solid) and crystals were sealed into Lindemann capillaries under nitrogen. The crystals were far from ideal for X-ray diffraction, being thin fragile plates with rather high mosaicity. Crystals decomposed slowly in the Mo X-ray beam; this process was accelerated by exposing the crystals to Cu-K_α radiation. (Note

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[1] M. R. Churchill, J. Wormald, J. Knight, and M. J. Mays, *Chem. Comm.*, 1970, 458.

[2] M. R. Churchill and J. Wormald, *J. Amer. Chem. Soc.*, 1971, **93**, 5670.

[3] M. R. Churchill, J. Wormald, J. Knight, and M. J. Mays, *J. Amer. Chem. Soc.*, 1971, **93**, 3073.

[4] R. P. Stewart, U. Anders, and W. A. G. Graham, *J. Organometallic Chem.*, 1971, **32**, C49.

[5] E. H. Braye, L. F. Dahl, W. Hübel, and D. L. Wampler, *J. Amer. Chem. Soc.*, 1962, **84**, 4633.

[6] M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, 1968, **7**, 1123.

[7] C. W. Burnham, *Amer. Mineral.*, 1966, **51**, 159.

[8] A. D. Rae, *Acta Cryst.*, 1965, **19**, 683.

that no decomposition correction *per se* was applied; this error is taken up in scaling together the separate Weissenberg levels, *vide supra*.) The worst problem, however, was the very small proportion of reflections which gave a statistically significant intensity.

Solution and Refinement of the Structure.—Data were placed on an approximately absolute scale by means of a Wilson plot.[9] This, and all subsequent calculations were carried out on an IBM 360/65 computer at Harvard University using the CRYM system of crystallographic routines (written under the direction of Dr. R. E. Marsh at the California Institute of Technology.)

TABLE 1

Atomic co-ordinates and thermal parameters

(*a*) Positional and isotropic thermal parameters

Atom	x	y	z	B/Å^2
(i) Anion (A)				
Fe(1)	0·26911(60)	0·14922(27)	0·13163(16)	
Fe(2)	0·27183(87)	1/4	0·07877(25)	
Fe(3)	0·45745(88)	1/4	0·12825(28)	
Fe(4)	0·27249(92)	1/4	0·18306(24)	
Fe(5)	0·08728(92)	1/4	0·13063(30)	
O(1)	0·0038(31)	0·0964(17)	0·1267(9)	8·5(9)
O(2)	0·3789(31)	0·0564(18)	0·0767(10)	7·6(9)
O(3)	0·3537(33)	0·0461(19)	0·1851(11)	8·2(9)
O(4)	0·1945(34)	0·1491(18)	0·0258(11)	9·8(10)
O(5)	0·5452(50)	1/4	0·0509(14)	6·8(12)
O(6)	0·6384(36)	0·1342(20)	0·1367(11)	8·7(10)
O(7)	0·5133(86)	1/4	0·2117(23)	19·6(29)
O(8)	0·1530(45)	0·1442(25)	0·2301(14)	11·8(14)
O(9)	−0·1255(64)	1/4	0·1881(20)	14·1(21)
O(10)	−0·0946(41)	1/4	0·0761(12)	6·8(10)
C(1)	0·0951(43)	0·1346(22)	0·1291(12)	4·8(10)
C(2)	0·3188(47)	0·0934(25)	0·0946(15)	6·3(12)
C(3)	0·3129(48)	0·0921(26)	0·1645(15)	6·3(12)
C(4)	0·2228(42)	0·1881(21)	0·0506(13)	6·8(11)
C(5)	0·4603(74)	1/4	0·0648(20)	5·3(18)
C(6)	0·5703(41)	0·1827(23)	0·1328(12)	4·5(10)
C(7)	0·4142(108)	1/4	0·1976(31)	15·8(32)
C(8)	0·2117(49)	0·1795(26)	0·2105(15)	6·4(12)
C(9)	−0·0478(85)	1/4	0·1702(25)	9·7(23)
C(10)	−0·0035(57)	1/4	0·0909(17)	5·0(13)
C(11)	0·2690(42)	1/4	0·1323(12)	0·9(9)
(ii) Anion (B)				
Fe(1)	0·22882(60)	0·14944(27)	0·62676(17)	
Fe(2)	0·38182(82)	1/4	0·59595(25)	
Fe(3)	0·13491(87)	1/4	0·58088(25)	
Fe(4)	0·06947(89)	1/4	0·65308(25)	
Fe(5)	0·32554(91)	1/4	0·66860(26)	
O(1)	0·3560(33)	0·0918(18)	0·6926(11)	7·7(9)
O(2)	0·3713(34)	0·0477(21)	0·5812(11)	8·0(15)
O(3)	−0·0021(31)	0·0601(16)	0·6278(9)	6·5(12)
O(4)	0·5832(38)	0·1477(21)	0·5759(12)	11·9(11)
O(5)	0·3143(57)	1/4	0·5172(19)	12·5(17)
O(6)	−0·0012(36)	0·1381(19)	0·5444(11)	11·0(11)
O(7)	−0·1721(49)	1/4	0·6104(14)	9·3(13)
O(8)	−0·0073(35)	0·1454(19)	0·7061(11)	8·7(10)
O(9)	0·2796(48)	1/4	0·7488(17)	8·2(13)
O(10)	0·6040(41)	1/4	0·6744(12)	5·0(10)
C(1)	0·3149(56)	0·1320(31)	0·6684(18)	8·1(16)
C(2)	0·3102(52)	0·0903(28)	0·5968(16)	7·7(10)
C(3)	0·0960(48)	0·0937(25)	0·6278(14)	8·8(10)
C(4)	0·4926(55)	0·1866(26)	0·5854(16)	9·3(15)
C(5)	0·2975(69)	1/4	0·5495(23)	7·8(19)
C(6)	0·0614(47)	0·1849(24)	0·5589(14)	7·5(12)
C(7)	−0·0644(58)	1/4	0·6307(17)	5·4(14)
C(8)	0·0264(48)	0·1825(26)	0·6823(15)	6·4(12)
C(9)	0·2961(73)	1/4	0·7131(24)	7·6(19)
C(10)	0·4877(51)	1/4	0·6689(15)	1·9(11)
C(11)	0·2250(45)	1/4	0·6279(13)	1·3(9)
(iii) The cations				
N(1)	0·8013(37)	−0·0146(20)	0·2055(11)	6·5(10)
C(1N)	0·6603(51)	0·0163(27)	0·2121(15)	7·4(14)
C(2N)	0·9042(71)	0·0599(37)	0·2085(20)	12·7(22)
C(3N)	0·8124(65)	−0·0466(35)	0·1642(21)	10·9(19)
C(4N)	0·8325(51)	−0·0808(25)	0·2313(15)	7·2(14)
N(2)	0·7421(38)	−0·0432(22)	0·5390(12)	8·4(11)

TABLE 1 (*Continued*)

(*b*) Anisotropic thermal parameters * (× 10^4) for the iron atoms

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
(i) Anion (A)						
Fe(1)	112·9 (8·2)	22·4 (1·9)	5·4 (0·5)	5·8 (6·8)	0·2 (4·2)	0·4 (1·8)
Fe(2)	120·8 (12·8)	23·1 (2·7)	6·6 (0·9)	0	−9·8 (6·3)	0
Fe(3)	98·7 (12·4)	39·8 (3·5)	7·9 (1·1)	0	−4·6 (6·6)	0
Fe(4)	110·5 (12·4)	26·9 (2·9)	4·8 (0·9)	0	11·9 (5·9)	0
Fe(5)	103·8 (12·7)	40·1 (3·7)	9·7 (1·2)	0	−10·5 (7·8)	0
(ii) Anion (B)						
Fe(1)	104·6 (8·1)	24·0 (1·9)	5·9 (0·6)	−1·3 (6·8)	8·0 (4·2)	0·2 (1·9)
Fe(2)	92·1 (11·4)	33·6 (3·2)	5·4 (0·9)	0	19·0 (6·0)	0
Fe(3)	115·8 (12·7)	34·4 (3·3)	4·2 (0·8)	0	5·7 (5·9)	0
Fe(4)	114·4 (12·6)	13·2 (2·4)	7·4 (1·0)	0	7·4 (6·0)	0
Fe(5)	108·5 (12·0)	33·0 (3·2)	4·9 (0·9)	0	8·3 (5·8)	0

* In the form: $\exp[-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}hl - \beta_{23}kl]$.

The use of Sayre's equation (for the 262 reflections with $E \geqslant 1{\cdot}2$) led to an electron-density map suggesting a pair of octahedra sharing a vertex at (1/4,1/4,1/8) and interrelated by reflection across $y = 1/4$; this 'pseudosolution' was rejected. A 'sharpened' Patterson map showed peaks about the origin consistent with an octahedron in which the C_4 axes lay along (100), (010), and (001); the same pattern recurred about 0,1/2,1/4 (corresponding to the vectors $1/2 + 2x$, $1/2$, $2z$). There were more complex patterns, apparently of general peaks, about (1/2,0,1/4) and (1/2,1/2,1/4). The Patterson map thus led to the location of an octahedron of iron atoms, centered on $x = 1/4$ and $z = 1/8$, but with y undetermined.

The structure was finally solved by a consideration of intermolecular packing and symmetry. The unit cell contained eight hexanuclear anions and sixteen Me_4N^+ cations, and had approximate dimensions 10 × 19 × 37 Å. Since a Howells–Phillips–Rogers plot[10] was equivocal both space groups $Pn2_1a$ and $Pnma$ were considered. Three possibilities presented themselves.

(1) Using space group $Pn2_1a$, one Fe_6 cluster could arbitrarily be centred at $y = 0$. Symmetry would place the four related molecules at (1/4,0,1/8), (1/4,1/2,5/8), (3/4,1/2,7/8), and (3/4,0,3/8). (The choice of $x = 1/4$ and $z = 1/8$ is dictated by the necessity of keeping the centres of the anions as far apart as possible; it is also consistent with the results from the Patterson map.) Maintaining a 9 Å separation in the y-direction, a second cluster can be introduced into the asymmetric unit at (1/4,1/2,1/8) with symmetry relations to (1/4,0,5/8), (3/4,0,7/8), and (3/4,1/2,3/8).

(2) Using the same primary disposition in the centrosymmetric space group $Pnma$, the mirror plane at $y = 1/4$ automatically generates the second set from the first, and the asymmetric unit contains only one Fe_6 cluster.

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[9] A. J. C. Wilson, *Nature*, 1942, **150**, 152.

[10] E. R. Howells, D. C. Phillips, and D. Rogers, *Acta Cryst.*, 1950, **3**, 210.

(3) Again using space group *Pnma*, the Fe_6 clusters are bisected at their equatorial belts by the mirror planes at $y = 1/4$ and $3/4$. In this case, the asymmetric unit would consist of two half-octahedra.

Possibility (2) could be excluded immediately, since the mirror plane reproduced not only the stereochemistry but also the orientation of the cluster. Combined with the symmetry planes parallel to (xy) and (yz) in the cluster itself, this generated such planes at $x = 1/2$ and $z = 1/4$ and $3/4$, producing systematic weaknesses, not validated by the experimental data. This provided the vital clue, that the degeneracy must be broken by changing the orientation of the second cluster. The Patterson map had rather suggested the same orientation for both, since there was not a complete second set of peaks about the origin.

The (B) cluster was introduced at (1/4,1/4,5/8), but with its C_4 axes directed along 101, y, and $\bar{1}01$. The asymmetric unit thus consisted of cluster (A): Fe(1), Fe(2)*, Fe(3)*, Fe(4)*, and Fe(5)*; cluster (B): Fe(1), Fe(2)*, Fe(3)*, Fe(4)*, and Fe(5)*, where all atoms marked with an asterisk lay in the special position 4*c* (symmetry C_s or *m*) of space group *Pnma*; these were given fixed population factors of 1/2. With B 3·24 Å^2 for each iron atom, as suggested by the Wilson plot, a structure-factor calculation gave R 51·0%, with no reflections systematically calculating as F_c 0. Two cycles of least-squares refinement of the iron atom co-ordinates merely rotated the (B) cluster about its vertical axis by some 13° and improved R to 40·4%. An observed Fourier map revealed the positions of all the lighter atoms of the $[Fe_6(CO)_{16}C]^{2-}$ anions.

Each cluster has ten independent carbonyl groups, of which four are in the 4*c* special position and six are symmetry-duplicated by the mirror plane. The carbido-carbon atom was immediately discernible at the centre of the cluster. The tetramethylammonium cations each occupied general positions, thus producing the required sixteen in the unit cell. The carbon atoms of one could not be located.

Full-matrix least-squares refinement of atomic co-ordinates, isotropic thermal parameters, and the overall scale factor reduced R to 12·9% in four cycles. The y co-ordinates of atoms in the special position were not, of course, refined.

Finally, the iron atoms were given anisotropic thermal parameters in *Pnma*, the reflection data being too sparse to justify anisotropic refinement of the lighter atoms. Convergence was achieved in two cycles at R 11·9%. The anisotropic thermal parameters of atoms in the special position were constrained by $\beta_{12} = \beta_{23} = 0$. There was no evidence of excessive amplitude in the y direction. These iron atoms are therefore required to lie in the special position and the centrosymmetric space group is established. Final suggested shifts were $< 0{\cdot}1\ \sigma$. Final positional and thermal parameters are collected in Table 1.[*]

Hamilton R factor ratio tests justify the anisotropic refinement of the iron atoms at the 90% confidence level. The scattering curve for iron was corrected for anomalous dispersion throughout ($\Delta f' = -0{\cdot}4$ e, $\Delta f'' = +1{\cdot}0$ e). A final difference-Fourier showed no features $> 1{\cdot}1$ eÅ^{-3}. Despite repeated efforts, the carbon atoms of the second cation were not located, nor were the methyl hydrogen atoms of the first. The data are obviously not as good as might be desired but the principal features of the compound are nevertheless established.

RESULTS AND DISCUSSION

The complex crystallizes in space group *Pnma*, which has eight equipoints. The asymmetric unit contains two independent tetramethylammonium cations and two half-clusters of iron atoms with their carbonyl ligands, crystallographically independent of each other.

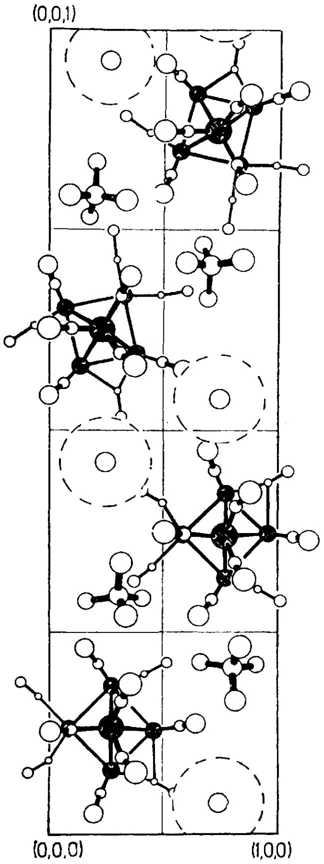

FIGURE 1 Partial unit cell contents viewed down *b*. Dashed circles indicate approximate radii of disordered $[Me_4N]^+$ ions

The half-clusters border on the mirror plane at $y = 1/4$ of the space group, in such a way that this symmetry operation generates the remaining half of each of two octahedral clusters, with their equatorial belts in the plane. The unit cell and that part of its contents lying between $y = 0$ and $1/2$ are shown in Figure 1.

The clusters are differently oriented with respect to the a and c axes. The first cluster (A) is centred on (0·27,1/4,0·13) and the second (B) on (0·23,1/4,0·63). The carbon atoms of one of the tetramethylammonium ions were disordered and could not be located.

The two clusters are closely similar; their dimensions are given together in Tables 2 and 3 and mean values are quoted in all discussions. The poor quality of the reflection data has made atomic co-ordinates and hence geometrical data subject to large σ. A clear picture of

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[*] Observed and calculated structure factor amplitudes are listed in Supplementary Publication No. SUP 21108 (4 pp.). For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are supplied as full size copies).

the stereochemistry nevertheless emerges and is represented in Figure 2 which gives a general view of an $[Fe_6(CO)_{16}C]^{2-}$ anion. The mirror plane includes Fe(2)—(5) and C(11), as well as the carbonyl groups CO(5), CO(7), CO(9), and CO(10). Atoms related by the mirror plane to those in the original asymmetric unit are marked with a prime.

TABLE 2

Bond lengths (Å)

(*a*) In the anions

Atoms	Anion (A)	Anion (B)	Mean *
(i) Iron–iron bonds			
Fe(1)–Fe(2)	2·706(9)	2·688(9)	2·697 ± 0·009
Fe(1)–Fe(3)	2·682(9)	2·695(9)	2·688 ± 0·009
Fe(1)–Fe(4)	2·669(9)	2·654(9)	2·661 ± 0·009
Fe(1)–Fe(5)	2·632(10)	2·621(9)	2·626 ± 0·009
Fe(2)–Fe(3)	2·609(10)	2·553(10)	2·581 ± 0·028
Fe(3)–Fe(4)	2·743(10)	2·729(10)	2·736 ± 0·010
Fe(4)–Fe(5)	2·682(11)	2·646(10)	2·664 ± 0·018
Fe(5)–Fe(2)	2·662(11)	2·725(10)	2·693 ± 0·032
(ii) Fe–C Bonds in semi-bridging CO groups			
Fe(1)–C(1)	1·780(43)	1·791(60)	1·785 ± 0·051
Fe(5)–C(1)	2·163(43)	2·213(60)	2·188 ± 0·051
Fe(2)–C(5)	1·969(60)	1·905(63)	1·937 ± 0·061
Fe(3)–C(5)	2·326(61)	2·005(63)	2·165 ± 0·161
(iii) Fe–C Bonds in terminal CO groups			
Fe(1)–C(2)	1·786(50)	1·767(55)	
Fe(1)–C(3)	1·670(50)	1·695(48)	
Fe(2)–C(4)	1·630(43)	1·676(54)	
Fe(3)–C(6)	1·706(44)	1·640(48)	
Fe(4)–C(7)	1·527(91)	1·581(49)	
Fe(4)–C(8)	1·769(51)	1·714(51)	
Fe(5)–C(9)	1·992(72)	1·657(66)	
Fe(5)–C(10)	1·721(49)	1·636(43)	
	Mean	1·698 ± 0·101	
(iv) C–O Bonds in bridging groups			
C(1)–O(1)	1·170(53)	1·235(69)	1·202 ± 0·061
C(5)–O(5)	0·997(72)	1·195(81)	1·097 ± 0·099
(v) C–O Bonds in terminal groups			
C(2)–O(2)	1·131(61)	1·158(66)	
C(3)–O(3)	1·218(61)	1·173(57)	
C(4)–O(4)	1·201(56)	1·219(67)	
C(6)–O(6)	1·149(57)	1·205(60)	
C(7)–O(7)	1·125(114)	1·317(64)	
C(8)–O(8)	1·142(69)	1·165(63)	
C(9)–O(9)	1·021(91)	1·320(79)	
C(10)–O(10)	1·068(59)	1·191(54)	
	Mean	1·175 ± 0·080	
(vi) Fe–C distances to the carbido-carbon atom			
Fe(1)–C(11)	1·888(35)	1·884(38)	1·886 ± 0·037
Fe(2)–C(11)	1·963(36)	1·968(38)	1·965 ± 0·037
Fe(3)–C(11)	1·907(36)	1·949(38)	1·928 ± 0·037
Fe(4)–C(11)	1·862(36)	1·821(38)	1·841 ± 0·037
Fe(5)–C(11)	1·834(36)	1·805(38)	1·820 ± 0·037

(*b*) In the cations

Atoms	
N(1)–C(1N)	1·554(65)
N(1)–C(2N)	1·744(81)
N(1)–C(3N)	1·632(78)
N(1)–C(4N)	1·590(64)
Mean	1·630 ± 0·071

* The σ associated with a mean value is given in the form ±X.XXX Å and is the larger of (i) the mean of the individual σ values of the two (or more) independent values or (ii) the internal σ calculated by the expression $\sigma\ (\text{mean}) = [\Sigma(\chi_i - \bar{\chi})^2/N]^{1/2}$, where χ_i is the *i*th value and $\bar{\chi}$ is the mean of *N* equivalent values.

TABLE 3

Bond angles (°)

(*a*) In the anions

Atoms	Angle (A)	Angle (B)	Mean
(i) Within the Fe_6 clusters, triangular faces			
Fe(1)–Fe(2)–Fe(3)	60·6(0·3)	61·8(0·3)	61·2 ± 0·6
Fe(2)–Fe(3)–Fe(1)	61·5(0·3)	61·6(0·3)	61·5 ± 0·3
Fe(3)–Fe(1)–Fe(2)	57·9(0·3)	56·6(0·2)	57·2 ± 0·6
Fe(1)–Fe(3)–Fe(4)	58·9(0·3)	58·6(0·2)	58·8 ± 0·3
Fe(3)–Fe(4)–Fe(1)	59·4(0·3)	60·1(0·3)	59·8 ± 0·3
Fe(4)–Fe(1)–Fe(3)	61·7(0·3)	61·3(0·3)	61·5 ± 0·3
Fe(1)–Fe(4)–Fe(5)	58·9(0·3)	59·3(0·3)	59·1 ± 0·3
Fe(4)–Fe(5)–Fe(1)	60·3(0·3)	60·5(0·3)	60·4 ± 0·3
Fe(5)–Fe(1)–Fe(4)	60·8(0·3)	60·2(0·3)	60·5 ± 0·3
Fe(1)–Fe(5)–Fe(2)	61·5(0·3)	60·3(0·3)	60·9 ± 0·6
Fe(5)–Fe(2)–Fe(1)	58·7(0·3)	57·9(0·2)	59·3 ± 0·6
Fe(2)–Fe(1)–Fe(5)	59·8(0·3)	61·7(0·3)	61·2 ± 0·5
(ii) Within the Fe_6 clusters, equatorial belts			
Fe(1)–Fe(2)–Fe(1′)	88·5(0·3)	89·0(0·2)	88·7 ± 0·3
Fe(2)–Fe(1)–Fe(4)	90·7(0·3)	90·2(0·2)	90·4 ± 0·3
Fe(1)–Fe(4)–Fe(1′)	90·0(0·3)	90·5(0·3)	90·2 ± 0·3
Fe(1)–Fe(3)–Fe(1′)	89·5(0·3)	88·7(0·3)	89·1 ± 0·4
Fe(3)–Fe(1)–Fe(5)	89·4(0·3)	89·7(0·2)	89·5 ± 0·3
Fe(1)–Fe(5)–Fe(1′)	91·7(0·3)	91·9(0·2)	91·8 ± 0·3
Fe(2)–Fe(3)–Fe(4)	91·2(0·3)	89·6(0·2)	89·9 ± 0·3
Fe(3)–Fe(4)–Fe(5)	87·1(0·3)	88·4(0·3)	87·7 ± 0·6
Fe(4)–Fe(5)–Fe(2)	91·4(0·3)	91·5(0·3)	91·5 ± 0·3
Fe(5)–Fe(2)–Fe(3)	90·3(0·3)	90·5(0·3)	90·4 ± 0·3
(iii) Angles involving the carbido-carbon atom			
Fe(1)–C(11)–Fe(1′)	178·5(1·0)	176·6(1·1)	180·0 ± 1·1
Fe(2)–C(11)–Fe(4)	178·1(1·1)	173·6(1·1)	175·8 ± 2·2
Fe(3)–C(11)–Fe(5)	173·6(1·0)	173·4(1·1)	173·5 ± 1·2
(iv) Between the cluster and the CO ligands			
Fe(2)–Fe(1)–C(1)	94·6(1·4)	101·8(1·9)	98·2 ± 3·6
Fe(3)–Fe(1)–C(1)	143·6(1·4)	146·2(1·9)	144·9 ± 1·7
Fe(4)–Fe(1)–C(1)	99·1(1·4)	96·5(1·9)	97·8 ± 1·7
Fe(5)–Fe(1)–C(1)	54·7(1·4)	56·5(1·9)	55·6 ± 1·7
Fe(2)–Fe(1)–C(2)	82·0(1·6)	84·7(1·8)	83·4 ± 1·7
Fe(3)–Fe(1)–C(2)	100·3(1·6)	102·3(1·8)	101·3 ± 1·7
Fe(4)–Fe(1)–C(2)	161·4(1·6)	162·5(1·8)	162·0 ± 1·7
Fe(5)–Fe(1)–C(2)	127·2(1·6)	129·8(1·8)	128·5 ± 1·7
Fe(2)–Fe(1)–C(3)	163·9(1·8)	153·5(1·7)	158·7 ± 5·2
Fe(3)–Fe(1)–C(3)	107·2(1·8)	99·7(1·7)	103·5 ± 3·7
Fe(4)–Fe(1)–C(3)	86·5(1·7)	87·4(1·7)	87·0 ± 1·7
Fe(5)–Fe(1)–C(3)	130·8(1·8)	136·5(1·7)	133·6 ± 2·8
Fe(1)–Fe(2)–C(4)	87·4(1·6)	89·1(1·9)	88·2 ± 1·7
Fe(3)–Fe(2)–C(4)	131·2(1·6)	126·9(1·9)	129·0 ± 2·2
Fe(5)–Fe(2)–C(4)	103·9(1·6)	111·4(1·9)	107·6 ± 3·7
Fe(1)–Fe(2)–C(5)	101·3(1·8)	96·8(1·9)	99·0 ± 2·2
Fe(3)–Fe(2)–C(5)	59·1(1·8)	50·9(1·9)	55·0 ± 4·1
Fe(5)–Fe(2)–C(5)	149·2(1·8)	141·2(1·9)	145·2 ± 4·0
Fe(1)–Fe(3)–C(5)	94·2(1·8)	93·1(1·5)	93·6 ± 1·7
Fe(2)–Fe(3)–C(5)	47·6(1·8)	46·6(1·5)	47·1 ± 1·7
Fe(4)–Fe(3)–C(5)	139·0(1·8)	137·8(1·5)	138·4 ± 1·7
Fe(1)–Fe(3)–C(6)	87·1(1·5)	86·9(1·7)	87·0 ± 1·6
Fe(2)–Fe(3)–C(6)	123·2(1·5)	123·2(1·7)	123·2 ± 1·6
Fe(4)–Fe(3)–C(6)	112·4(1·5)	116·6(1·7)	114·5 ± 1·6
Fe(1)–Fe(4)–C(7)	105·0(3·4)	109·1(1·8)	107·0 ± 2·6
Fe(3)–Fe(4)–C(7)	67·6(3·4)	72·7(1·8)	70·2 ± 2·6
Fe(5)–Fe(4)–C(7)	154·7(3·4)	161·1(1·8)	157·9 ± 3·2
Fe(1)–Fe(4)–C(8)	82·5(1·7)	81·8(1·7)	82·2 ± 1·7
Fe(3)–Fe(4)–C(8)	130·7(1·7)	131·9(1·8)	131·3 ± 1·8
Fe(5)–Fe(4)–C(8)	99·5(1·7)	96·5(1·7)	98·0 ± 1·7
Fe(1)–Fe(5)–C(9)	117·8(2·1)	120·6(2·3)	119·2 ± 2·2
Fe(2)–Fe(5)–C(9)	178·8(2·1)	178·3(2·3)	178·5 ± 2·2
Fe(4)–Fe(5)–C(9)	87·5(2·1)	92·1(2·3)	89·7 ± 2·3
Fe(1)–Fe(5)–C(10)	112·5(1·7)	112·2(1·5)	112·4 ± 1·6
Fe(2)–Fe(5)–C(10)	76·6(1·6)	78·3(1·5)	77·5 ± 1·6
Fe(4)–Fe(5)–C(10)	168·0(1·7)	167·9(1·6)	168·0 ± 1·7
Fe(1)–Fe(5)–C(1)	42·2(1·2)	42·5(1·6)	42·4 ± 1·4
Fe(2)–Fe(5)–C(1)	87·5(1·2)	90·4(1·6)	88·5 ± 1·4
Fe(4)–Fe(5)–C(1)	89·6(1·2)	87·2(1·6)	88·4 ± 1·4

TABLE 3 (*Continued*)

Atoms	Angle (A)	Angle (B)	Mean
(v) Interligand angles			
C(1)–Fe(1)–C(2)	98·5(2·1)	100·9(2·6)	99·7 ± 2·3
C(1)–Fe(1)–C(3)	101·5(2·2)	104·7(2·5)	103·1 ± 2·3
C(2)–Fe(1)–C(3)	95·8(2·4)	89·7(2·4)	92·7 ± 3·1
C(4)–Fe(2)–C(4′)	90·8(2·6)	90·3(2·5)	90·5 ± 2·6
C(4)–Fe(2)–C(5)	97·4(2·4)	95·2(2·7)	96·3 ± 2·6
C(5)–Fe(3)–C(6)	95·2(2·1)	95·0(2·5)	95·1 ± 2·3
C(6)–Fe(3)–C(6′)	95·3(2·1)	96·1(2·6)	95·7 ± 2·3
C(7)–Fe(4)–C(8)	97·3(3·8)	96·2(2·5)	96·7 ± 3·1
C(8)–Fe(4)–C(8′)	96·5(2·2)	95·1(2·4)	95·8 ± 2·3
C(1)–Fe(5)–C(9)	92·5(2·4)	89·7(2·8)	91·1 ± 2·6
C(1)–Fe(5)–C(10)	89·9(2·0)	92·8(2·2)	91·4 ± 2·1
C(9)–Fe(5)–C(10)	104·7(2·7)	100·0(2·8)	102·4 ± 2·8
(vi) Angles in bridging CO groups			
Fe(1)–C(1)–O(1)	151·0(3·7)	152·6(4·9)	151·8 ± 4·3
Fe(5)–C(1)–O(1)	125·8(3·3)	126·2(4·2)	126·0 ± 3·8
Fe(1)–C(1)–Fe(5)	83·2(2·1)	81·0(2·3)	82·1 ± 2·2
Fe(2)–C(5)–O(5)	164·2(5·7)	145·3(5·3)	154·7 ± 9·6
Fe(3)–C(5)–O(5)	121·5(5·0)	133·2(5·1)	127·2 ± 5·7
Fe(2)–C(5)–Fe(3)	74·3(4·1)	81·5(4·3)	77·9 ± 4·2
(vii) Angles in terminal CO groups			
Fe(1)–C(2)–O(2)	161·9(4·4)	171·0(4·9)	
Fe(1)–C(3)–O(3)	171·9(4·4)	174·2(4·3)	
Fe(2)–C(4)–O(4)	169·9(4·0)	171·4(4·8)	
Fe(3)–C(6)–O(6)	174·8(4·1)	174·9(4·3)	
Fe(4)–C(7)–O(7)	173·2(8·8)	176·9(4·3)	
Fe(4)–C(8)–O(8)	165·8(4·8)	169·0(4·6)	
Fe(5)–C(9)–O(9)	173·1(6·9)	176·9(5·5)	
Fe(5)–C(10)–O(10)	152·8(4·5)	170·6(4·3)	
	Mean 170·5 ± 5·9		

(*b*) In the cations

Atoms	Angle
C(1N)–N(1)–C(2N)	103·7(3·7)
C(1N)–N(1)–C(3N)	110·1(3·8)
C(1N)–N(1)–C(4N)	112·3(3·6)
C(2N)–N(1)–C(3N)	108·2(4·0)
C(2N)–N(1)–C(4N)	117·9(3·8)
C(3N)–N(1)–C(4N)	104·6(3·7)
	Mean 109·5 ± 4·8

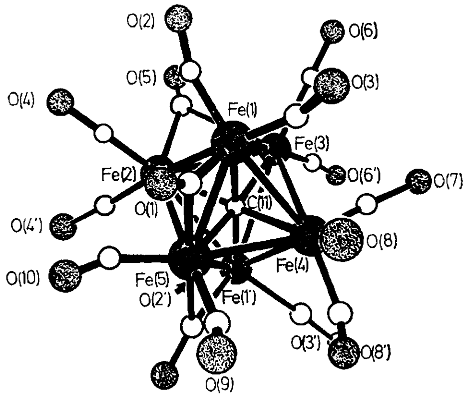

FIGURE 2 A general view of the $[Fe_6(CO)_{16}C]^{2-}$ anion. Carbon atoms in the carbonyl groups are numbered as their attached oxygen atoms. The central carbido-carbonyl atom is labelled C(11)

There are several interesting features in the dianion. The octahedral iron framework is very nearly regular. Close to its geometrical centre lies a carbido-carbon atom, bonded to all six metal atoms. One iron atom, Fe(4), carries three terminal CO ligands, while all the others carry two. There are also three semi-bridging carbonyl groups (the term ' semi-bridging ' will be discussed later), spanning Fe(1)–Fe(5), Fe(5)–Fe(1′), and Fe(2)–Fe(3). The first two of these are symmetry-related.

The mean lengths of nonbridged Fe–Fe bonds range from 2·661 ± 0·009 to 2·736 ± 0·010 Å, those of semi-bridged Fe–Fe bonds from Fe(2)–Fe(3) 2·581 ± 0·028 to Fe(1)–Fe(5) 2·626 ± 0·009 Å. Semi-bridging therefore seems to induce a significant contraction. This is also observed[11] in $[Fe_4(CO)_{13}]^{2-}$ where the mean comparable lengths are 2·58 ± 0·01 and 2·50 ± 0·01 Å.

The thirteen terminal carbonyl groups, of which six are three symmetry-related pairs, seem essentially normal, with mean dimensions Fe–C 1·698 ± 0·101, C–O = 1·175 ± 0·080 Å, and Fe–C–O 170·5 ± 5·9°. Comparable values in $[Fe_4(CO)_{13}]^{2-}$ are 1·72 ± 0·05, 1·18 ± 0·04 Å, and 174·4 ± 3·8°.

The remaining carbonyl groups have been called ' semi-bridging ' because of their geometries. CO(1) [and thus CO(1′)] is mainly bonded to Fe(1) [*viz.* Fe(1′)], with Fe(1)–C(1) 1·785 ± 0·051 Å. CO(5) is mainly bonded to Fe(2), with Fe(2)–C(5) 1·937 ± 0·061 Å. The bonds of lower order are Fe(5)–C(1) 2·188 ± 0·051 and Fe(3)–C(5) 2·165 ± 0·161 Å. Discrepancies between the two clusters spoil the accuracy for CO(5). The relevant bond angles are: Fe(1)–C(1)–O(1) 151·8 ± 4·3° and Fe(2)–C(5)–C(5) 154·7 ± 9·6°; Fe(5)–C(1)–O(1) 126·0 ± 3·8° and Fe(3)–C(5)–O(5) 127·2 ± 5·7°. Clearly, these are no normal terminal carbonyl groups, nor yet the fully bridging kind found in *e.g.* $(C_{10}H_8)_2Fe_4(CO)_{10}$ in which Fe–C 1·923(6), Fe′–C 1·938(6), C–O 1·175(8) Å, Fe–C–O 141·0(0·5), and Fe′–C–O 138·0(0·6)°.[12] Evidence has been accumulated for a number of iron carbonyl species in which the geometry of semi-bridging CO groups ranges from one extreme to the other. Thus distances in the black isomer of $(Ph_2C_2)_2Fe_3(CO)_8$ are[13] Fe–C 1·84 and 1·77, Fe′–C 1·99 and 1·99 Å. In the two isomers of $Fe_3(CO)_{11}(PPh_3)$ distances are[14] Fe–C 1·83, 1·89, and Fe–C′ 2·08, 1·94; Fe–C 1·74, 1·79, and Fe′–C 1·98, 1·94 Å. These bridging CO groups are only slightly asymmetric, but in $[Fe_4(CO)_{13}]^{2-}$ the asymmetry is more pronounced[11] with Fe–C 1·82 ± 0·02, Fe′–C 2·28 ± 0·04 Å, and Fe–C–O 154·6 ± 2·7°. In $Fe_3(CO)_{12}$ it is similar, with Fe–C 2·08(2), 2·18(2) and Fe′–C 2·24(2), 2·36(2) Å.[15] Epstein and Dahl[16] find Fe–C 1·741(20) and Fe′–C 2·388(20) Å in $Fe(CO)_3(PhC_2C_6H_4C_2Ph)_2Fe(CO)$, with Fe–C–O 166·4(1·7)°. Finally, in $Fe(CO)_3(HOC_2Me)_2Fe(CO)_3$ (ref. 17) and $Fe(CO)_3(C_6H_4CHCPh)_2Fe(CO)_3$ (ref. 18)

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Fe–C is 1·73—1·74 and Fe′–C 2·48—2·49 Å, with the CO groups virtually linear.

TABLE 4

Non-bonding contacts (Å) within the crystal

(*a*) Within the anions, to 2·8 Å

Atoms	(A)	(B)	Mean
Fe(3) · · · C(7)	2·582(77)	2·718(50)	2·650 ± 0·068

(*b*) Between atoms of the asymmetric unit, to 3·5 Å

Atoms	
O(3)A · · · C(1N)	3·30

(*c*) Between symmetry-related asymmetric units (not x, $\frac{1}{2} - y$, z), to 3·5 Å

O(1)A · · · O(2$^{\mathrm{I}}$)B	3·41	O(2)A · · · C(1$^{\mathrm{I}}$)B	3·39
O(5)B · · · O(9$^{\mathrm{II}}$)B	3·37	O(7)B · · · C(8$^{\mathrm{V}}$)B	3·35
O(5)B · · · O(9$^{\mathrm{III}}$)B	3·37	O(1)A · · · C(2N$^{\mathrm{VII}}$)	3·24
O(3)A · · · O(3$^{\mathrm{I}}$)B	3·35	O(8)A · · · C(1N$^{\mathrm{VI}}$)	3·20
O(7)B · · · O(9$^{\mathrm{IV}}$)B	3·35	O(8)A · · · C(2N$^{\mathrm{VII}}$)	3·07
O(6)B · · · O(7$^{\mathrm{IV}}$)B	3·33	C(4N) · · · O(3B$^{\mathrm{VIII}}$)	3·46
O(6)B · · · O(7$^{\mathrm{V}}$)B	3·33	C(4N) · · · O(7$^{\mathrm{IX}}$)B	3·44
O(3)A · · · O(1$^{\mathrm{I}}$)B	3·26	C(4N) · · · O(7$^{\mathrm{X}}$)B	3·44
O(6)B · · · O(9$^{\mathrm{II}}$)B	3·26	C(3N) · · · O(1$^{\mathrm{I}}$)B	3·41
O(6B) · · · O(9$^{\mathrm{III}}$)B	3·26	C(1N) · · · O(8$^{\mathrm{I}}$)B	3·41
O(2)A · · · O(1$^{\mathrm{I}}$)B	3·14	C(4N) · · · O(3$^{\mathrm{X}}$)B	3·39
O(2)A · · · C(2$^{\mathrm{I}}$)B	3·43	C(2)A · · · O(2$^{\mathrm{I}}$)B	3·30
O(3)A · · · C(1$^{\mathrm{I}}$)B	3·40	C(4N) · · · O(8$^{\mathrm{X}}$)B	3·14

Roman numeral superscripts denote the following equivalent positions:

I	$\frac{1}{2} - x, -y, \frac{1}{2} + z$	VI	$\frac{1}{2} + x, y, \frac{1}{2} - z$
II	$-1 + x, y, z$	VII	$1 + x, y, z$
III	$-1 + x, \frac{1}{2} - y, z$	VIII	$1\frac{1}{2} - x, -y, \frac{1}{2} + z$
IV	$-\frac{1}{2} + x, y, 1\frac{1}{2} - z$	IX	$1 - x, \frac{1}{2} + y, 1 - z$
V	$-\frac{1}{2} + x, \frac{1}{2} - y, 1\frac{1}{2} - z$	X	$1 - x, -y, 1 - z$

The distortion of the Fe_6 skeleton, although slight, does seem related to the presence of the semi-bridging CO groups. The carbido-carbon atom, C(11), lies just off-centre in the octahedron. It does, of course, lie in the mirror plane and is thus equidistant from Fe(1) and Fe(1′); within that plane, bonding distances to the other iron atoms decrease in the order Fe(2) > Fe(3) > Fe(4) > Fe(5), with Fe(1) taking a median position (see Table 2). The straight-through angles of Table 3 (section A.iii) also illustrate the deviations.

Only one of the tetramethylammonium ions was completely located. It has the expected dimensions, with mean N–C 1·630 ± 0·071 Å, and mean C–N–C 109·5 ± 4·8°. Only the nitrogen atom of the other cation could be located; the carbon atoms are presumably subject to spherical disorder about the nitrogen atom.

Intermolecular distances in the crystal are consistent with normal van der Waals packing radii. They are listed in Table 4. The failure to find the methyl carbons of the second tetramethylammonium cation renders the list incomplete. The packing is, however, very regular and no abnormally short contacts are likely to have been missed. The approximate expected carbon positions about N(2) are shown by dashed circles in Figure 1, which also shows the unit cell contents about the $y = 1/4$ mirror plane; the crystallographic centre of symmetry at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ will reproduce the same contents about $y = 3/4$, in such a way that a cluster of type (A) will lie above one of type (B) and *vice versa*. Tetramethylammonium ions are regularly interspersed close to the $y = 0$ and $y = 1/2$ planes. The co-ordination pattern is thus 6 : 12.

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