closer to parallel than in the Co structures (Table 3, planes 15 and 17 intersect at 11·4°, 16 and 18 at 15·1°) and the closest approach of each pair is 3·00 and 2·90 Å at C(151) and C(251) respectively. Close contacts are given in Table 4.

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The Crystal and Molecular Structure of Tetramethylammonium 1-η-Cyclopentadienyl-1-ferra-2-carbaundecaborate

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$[N(CH_3)_4]^+[\eta-(C_5H_5)FeCB_9H_{10}]^-$ is orthorhombic, space group $P2_12_12_1$, with $a = 10·092$ (5), $b = 11·116$ (6), $c = 15·377$ (5) Å and $Z = 4$. The structure was solved by the heavy-atom method and refined to $R_w = 0·053$ for 1760 counter reflections. The new ferracarbaborate anion was found to be the eleven-vertex polyhedron, where the metal atom occupies the vertex of highest coordination number and is also coordinated to the cyclopentadienyl ring. The carbon atom occupies the vertex of lowest coordination.

Introduction

The present study reports the results of an X-ray investigation of a tetramethylammonium salt of a new ferracarbaborate complex with eleven non-hydrogen atoms in the metallocarbaborate skeleton. Crystals were prepared at the Institute of Inorganic Chemistry of the Czechoslovak Academy of Sciences, at Řež near Prague.

Experimental

Preliminary data were obtained from oscillation and Weissenberg photographs (Co $K\alpha$ radiation, $\lambda = 1·790$ Å). Systematic absences correspond to the space group $P2_12_12_1$. Refined cell parameters were determined by the least-squares method from twenty reflections centred on the diffractometer. Crystal data are summarized in Table 1.

The intensities were collected at room temperature with a fragile crystal (0·1 × 0·2 × 0·1 mm) mounted on a four-circle Syntex $P2_1$ automatic diffractometer (Mo $K\alpha$ radiation, graphite monochromator). 1760 independent reflections were measured in the $\omega/2\theta$ scan mode to $2\theta = 50°$. The scan speed varied from 0·95 to 29·3° min^{-1} and was determined from a rapid prescan. The scanning interval was from 1° below $K\alpha_1$ to 1° above $K\alpha_2$ of the Mo $K\alpha$ doublet. 363 reflections were considered to be unobserved according to the criterion $I < 1·96\sigma(I)$ where $I = [TC - (B_1 + B_2)]R$ and $\sigma(I) =$

Table 1. *Crystal data*

$[N(CH_3)_4]^+[(C_5H_5)FeCB_9H_{10}]^-$	Orthorhombic, $P2_12_12_1$
$a = 10·092$ (5) Å	$Z = 4$
$b = 11·116$ (6)	$M_r = 314·6$
$c = 15·377$ (5)	$D_m = 1·210$ g cm^{-3}
$V = 1724·8$ $Å^3$	$D_c = 1·207$

$[(TC + B_1 + B_2)R^2 + (0.015I)^2]^{1/2}$ (TC = total count, R = rate of the scan, B_1 and B_2 = background counts measured at each end of the scan for 0·5 of the scan time). All unobserved reflections were used in the refinement. The intensities of three standard reflections, measured after every 50 reflections, showed no significant variations. All intensities were corrected for Lorentz and polarization effects, but not for absorption or extinction.

Structure determination and refinement

The position of the Fe atom was determined from a three-dimensional Patterson function. All remaining non-hydrogen atoms were located in a subsequent electron-density map calculated with phases given by the Fe atom. This determined the configuration of the metallocarbaborate polyhedron, the cyclopentadienyl ring and the position of the tetramethylammonium ion. The positional parameters were refined by a full-matrix least-squares method, initially with the scale and overall temperature factor estimated from a Wilson plot and then with individual isotropic temperature factors.

At this stage the C atom of the polyhedron was distinguished from the B atoms by its lower temperature factor and shorter bond distances.

The function minimized was $\sum w\Delta^2$ where $w = 1/\sigma^2$ and $\Delta = ||F_o| - |F_c||$. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic reduced $R_w = (\sum w\Delta^2/\sum w|F_o|^2)^{1/2}$ to 0·076. A difference Fourier synthesis revealed all 27 H atoms at expected positions. Ten of these are terminal H bonded to the B

and C atoms in the polyhedron, five are from the cyclopentadienyl ring and the remaining 12 belong to the $[N(CH_3)_4]^+$ ion. The final refinement, including positional parameters of all H atoms, reduced R_w to 0·053. Temperature factors assigned to H were the same as those of the atoms to which they were bonded.

The highest residual peak in the difference synthesis was 0·87 e Å^{-3} and was located in the vicinity of the Fe atom. Final positional parameters for non-hydrogen atoms are given in Table 2, H-atom positions are in Table 3.* Scattering factors (including anomalous dispersion correction for Fe) were taken from *International Tables for X-ray Crystallography* (1974).

All calculations were performed on the computers TESLA 200 and IBM 370/135 with the program system *TLS* (Sklenář, 1975).

Results and discussion

The structure of this new ferracarbaborate consists of $[\eta-(C_5H_5)FeCB_9H_{10}]^-$ and $[N(CH_3)_4]^+$ ions. As shown in Fig. 1, the anion is an eleven-vertex polyhedron, where nine boron atoms and one C atom form a decaborane-like framework, with six cage atoms bonded to

Table 2. *Final positional parameters for non-hydrogen atoms* ($\times 10^4$, *for* Fe *atom* $\times 10^5$) *and their e.s.d.'s*

	x	y	z
Fe	25507 (16)	42794 (9)	67858 (7)
C(2)	3536 (9)	4490 (9)	7834 (6)
B(3)	1472 (10)	5674 (12)	6345 (8)
B(4)	2088 (10)	4818 (10)	8179 (9)
B(5)	4166 (13)	5525 (15)	7290 (10)
B(6)	3088 (10)	6179 (10)	6484 (8)
B(7)	982 (12)	5446 (14)	7368 (9)
B(8)	3456 (11)	5838 (12)	8320 (9)
B(9)	1652 (12)	6856 (12)	7016 (8)
B(10)	1879 (11)	6388 (12)	8117 (9)
B(11)	3285 (12)	6898 (11)	7491 (9)
C(1P)	1681 (11)	2618 (12)	6679 (8)
C(2P)	3065 (11)	2411 (10)	6812 (8)
C(3P)	3642 (10)	3007 (11)	6085 (9)
C(4P)	2716 (13)	3488 (9)	5540 (6)
C(5P)	1448 (12)	3235 (12)	5931 (9)
N	2284 (8)	9483 (6)	4866 (4)
C(1T)	2628 (17)	440 (10)	4233 (7)
C(2T)	2267 (20)	8314 (10)	4400 (8)
C(3T)	3281 (11)	9472 (14)	5603 (8)
C(4T)	953 (13)	9717 (13)	5256 (8)

Table 3. *Final parameters for hydrogen atoms* ($\times 10^3$)

	x	y	z
H(C2)	394 (8)	389 (8)	824 (7)
H(B3)	93 (8)	576 (9)	566 (6)
H(B4)	174 (8)	444 (9)	866 (5)
H(B5)	516 (9)	550 (8)	714 (6)
H(B6)	361 (8)	645 (7)	587 (6)
H(B7)	995 (9)	502 (8)	740 (6)
H(B8)	386 (9)	597 (8)	902 (6)
H(B9)	121 (8)	771 (8)	684 (6)
H(B10)	140 (8)	669 (9)	858 (6)
H(B11)	387 (9)	766 (8)	752 (6)
H(C1P)	135 (11)	223 (11)	725 (7)
H(C2P)	379 (9)	218 (8)	720 (6)
H(C3P)	448 (9)	268 (9)	592 (7)
H(C4P)	233 (13)	396 (7)	504 (5)
H(C5P)	64 (10)	340 (9)	550 (6)
H(1C1T)	167 (11)	29 (10)	393 (8)
H(2C1T)	289 (11)	108 (9)	464 (6)
H(3C1T)	358 (11)	39 (10)	394 (9)
H(1C2T)	250 (11)	825 (9)	365 (7)
H(2C2T)	277 (14)	757 (9)	480 (9)
H(3C2T)	137 (12)	804 (11)	476 (8)
H(1C3T)	278 (9)	900 (9)	605 (6)
H(2C3T)	311 (9)	24 (9)	591 (6)
H(3C3T)	411 (10)	928 (16)	560 (8)
H(1C4T)	35 (9)	979 (9)	461 (6)
H(2C4T)	109 (11)	32 (11)	581 (7)
H(3C4T)	58 (11)	915 (15)	564 (8)

the Fe atom (see Table 4). The metal atom is also coordinated to the cyclopentadienyl ring. As expected the polyhedral Fe atom occupies the vertex of highest coordination number, with the C atom at the vertex of

Table 4. *Interatomic distances (Å) and angles (°)*

(a) Distances in polyhedron
Non-hydrogen atoms

Fe—C(2)	1·908 (9)	Fe—B(5)	2·274 (14)
Fe—B(3)	2·012 (11)	Fe—B(6)	2·229 (11)
Fe—B(4)	2·274 (12)	Fe—B(7)	2·234 (13)
C(2)—B(4)	1·596 (14)	B(3)—B(6)	1·738 (14)
C(2)—B(5)	1·558 (18)	B(3)—B(7)	1·669 (18)
C(2)—B(8)	1·676 (16)	B(3)—B(9)	1·680 (17)
B(4)—B(7)	1·814 (18)	B(7)—B(9)	1·791 (20)
B(4)—B(8)	1·799 (15)	B(7)—B(10)	1·800 (17)
B(4)—B(10)	1·760 (15)	B(8)—B(10)	1·733 (13)
B(5)—B(6)	1·802 (17)	B(8)—B(11)	1·744 (17)
B(5)—B(8)	1·773 (18)	B(9)—B(10)	1·787 (17)
B(5)—B(11)	1·793 (19)	B(9)—B(11)	1·803 (13)
B(6)—B(9)	1·827 (14)	B(10)—B(11)	1·806 (15)
B(6)—B(11)	1·754 (16)		

Hydrogen atoms

C(2)—H(C2)	1·00 (8)	B(7)—H(B7)	1·14 (9)
B(3)—H(B3)	1·19 (8)	B(8)—H(B8)	1·17 (9)
B(4)—H(B4)	0·92 (8)	B(9)—H(B9)	1·08 (8)
B(5)—H(B5)	1·03 (9)	B(10)—H(B10)	0·92 (8)
B(6)—H(B6)	1·12 (9)	B(11)—H(B11)	1·04 (8)

(b) Cyclopentadienyl (ring) distances

Fe—C(1P)	2·051 (13)	C(1P)—C(2P)	1·430 (13)
Fe—C(2P)	2·141 (11)	C(2P)—C(3P)	1·425 (15)
Fe—C(3P)	2·092 (9)	C(3P)—C(4P)	1·364 (15)
Fe—C(4P)	2·115 (9)	C(4P)—C(5P)	1·441 (16)
Fe—C(5P)	2·078 (13)	C(5P)—C(1P)	1·360 (16)
C(1P)—H(C1P)	1·03 (9)	C(4P)—H(C4P)	1·01 (9)
C(2P)—H(C2P)	0·98 (9)	C(5P)—H(C5P)	1·06 (9)
C(3P)—H(C3P)	0·95 (8)		

(c) Distances within the $[N(CH_3)_4]^+$ cation

N—C(1T)	1·483 (11)	N—C(3T)	1·516 (12)
N—C(2T)	1·484 (13)	N—C(4T)	1·495 (13)
C(1T)—H(1C1T)	1·09 (9)	C(3T)—H(1C3T)	1·01 (9)
C(1T)—H(2C1T)	0·98 (10)	C(3T)—H(2C3T)	0·99 (9)
C(1T)—H(3C1T)	1·06 (9)	C(3T)—H(3C3T)	0·86 (10)
C(2T)—H(1C2T)	1·18 (11)	C(4T)—H(1C4T)	1·17 (10)
C(2T)—H(2C2T)	1·16 (10)	C(4T)—H(2C4T)	1·10 (9)
C(2T)—H(3C2T)	1·10 (11)	C(4T)—H(3C4T)	0·94 (11)

(d) Angles around the Fe atom

Type	Range	Mean value	Number of angles
Fe—C(P)—C(P)	66·7–73·5	70·4 (2·1)	10
C(P)—Fe—C(P)	64·8–66·4	65·6 (0·7)	5
	37·9–40·2	39·1 (0·9)	5
B—Fe—B	45·9–48·0	47·1 (0·9)	4
C(2)—Fe—B	42·6–43·8	43·2 (0·8)	2

(e) Cyclopentadienyl ring angles

Type	Range	Mean value	Number of angles
C(P)—C(P)—C(P)	102·2–112·6	108·0 (4·3)	5

Table 4 (*cont.*)

(f) Cage angles

Type	Range	Mean value	Number of angles
B—B—B	56·2–64·6	60·0 (1·9)	30
	94·2–111·8	106·8 (5·2)	25
C—B—B	53·6–60·0	56·8 (3·1)	4
	106·2–115·0	110·1 (3·9)	6
B—C—B	66·4–66·6	66·5 (0·1)	2
	–	112·5	1

(g) Angles within the $[N(CH_3)_4]^+$ cation

Type	Range	Mean value	Number of angles
C(T)—N—C(T)	107·3–111·2	109·5 (1·4)	6
H—C(T)—N	88·2–129·5	107·3 (12·7)	12
H—C(T)—H	83·8–133·3	110·6 (17·3)	12

lowest coordination bonded to only four other polyhedral atoms. The same arrangement was predicted on the basis of the ^{11}B NMR spectra for $1\text{-}(C_5H_5)\text{-}1\text{-Co-}2,3\text{-}C_2B_8H_{10}$ (Evans, Dunks & Hawthorne, 1973) and for some other related compounds (Dustin, Evans, Jones, Wiersema, Gong, Chan & Hawthorne, 1974; Evans & Hawthorne, 1973, 1974).

All important bond distances, together with mean values for angles, are reported in Table 4. In the polyhedron the differences in coordination number are reflected in the differences in bond lengths exhibited by these atoms, a feature generally observed for metallocarbaboranes (Wade, 1976). The B(3) atom, as well as
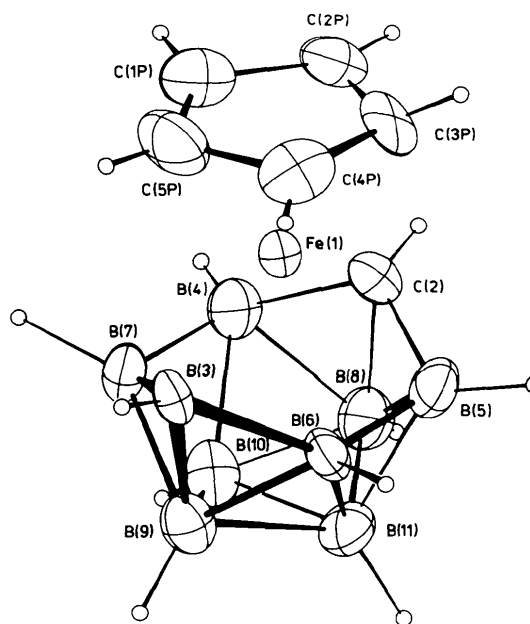

Fig. 1. Structure and numbering of the $[(C_5H_5)FeCB_9H_{10}]^-$ anion. Bonds to Fe are omitted for clarity.

Table 5. *Important planes in the anion*

(a) Cage plane $0.7848x + 0.3133y - 0.5347z = -2.0722$

Atoms	Fe(1)	C(2)	B(3)	B(8)	B(9)
Deviations (Å)	0.004	−0.004	−0.002	0.002	+0.000

$\chi^2 = 0.47$

(b) Cage plane $0.0047x - 0.8658y - 0.5004z = -10.9136$

Atoms	B(4)	B(5)	B(6)	B(7)
Deviations (Å)	−0.007	0.007	−0.007	0.007

$\chi^2 = 1.02$

(c) Cyclopentadienyl $0.0500x + 0.8575y + 0.5120z = 7.8288$

Atoms	C(1P)	C(2P)	C(3P)	C(4P)	C(5P)
Deviations (Å)	0.010	−0.013	0.011	−0.006	−0.003

$\chi^2 = 2.94$

Angles between planes: $a–b$ 90.00, $a–c$ 88.04, $b–c$ 176.76°.

O Fe   O N   ● C   O B   ∘ H

Fig. 2. Packing of ions within the unit cell. A projection along **b**, with the origin top left.

C(2), occupies the low-coordination positions of the polyhedron. Table 4 shows that the Fe—B(3) bond length is 2.012 Å, while the mean distance of Fe to other B atoms is 2.252 Å. The Fe—C bond length of 1.908 Å is shorter than the Fe—B(3) bond distance, which is in agreement with previous results observed for the $1,6\text{-}(\eta\text{-}C_5H_5)_2\text{-}1,6,2,3\text{-}Fe_2C_2B_6H_8$ ferracarbaborane (Callahan, Evans, Lo, Strouse & Hawthorne, 1975). Similar results are observed for the B—B distances. The average B(3)—B distance (1.695 Å) is shorter than the average B—B distance for other B atoms, which was found to be 1.785 Å. Hence, a longer interatomic distance was observed between atoms having a greater number of bonding interactions. The mean C—B bond length is 1.610 Å, the average terminal B—H and C—H distances are 1.07 and 1.00 Å respectively.

Table 5 shows that the cyclopentadienyl ring is nearly planar. The average Fe—C(P) distance is 2.095 Å, the perpendicular distance of Fe from the ring plane is 1.721 Å. Mean C(P)—C(P) and C(P)—H(CP) distances are 1.404 and 1.01 Å, respectively. The polyhedron has an almost perfect non-crystallographic mirror plane defined by Fe, C(2), B(3), B(8) and B(9) (see Table 5). The same table shows a planarity of the B(4), B(5), B(6) and B(7) atoms. This latter plane is parallel to the C_5H_5 plane and both are perpendicular to the Fe, C(2), B(3), B(8), B(9) plane.

For the cation $[N(CH_3)_4]^+$ the average C—N distance is 1.495 Å; the C(T)—H(CT) distances range from 0.86 to 1.18 Å with a mean value of 1.05 Å. The shortest interionic distance is 2.220 Å. The packing of the ions within the unit cell is indicated in Fig. 2.
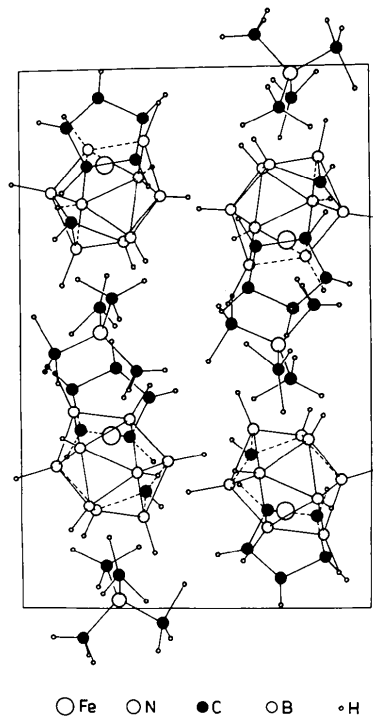
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