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The Structure of 8,8'-μ-Methoxo-3,3'-*commo*-bi[1,2-dicarba-3-ferra-*closo*-dodecaborane(11)]

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Abstract. $OCH_3(B_9C_2H_{10})_2Fe$, $M_r = 349.89$, orthorhombic, $P2_12_12_1$, $a = 12.128$ (2), $b = 21.521$ (3), $c = 6.991$ (4) Å, $V = 1825$ (1) Å^3, $Z = 4$, $D_c = 1.27$ Mg m^{-3}. The structure was refined to $R = 5.6\%$ for 2167 counter reflections. Two dicarbollide ligands sharing the Fe atom as a common apex are linked by a monoatomic oxygen bridge to which a CH_3 group is bound. The molecule is compared with its Co analogue.

Introduction. In 1976 we reported the crystal structure of the uncharged zwitterionic compound 8,8'-OCH$_3$-(B$_9$C$_2$H$_{10}$)$_2$Co (Šubrtová, Petříček, Línek & Ječný, 1976). Thus we found the first case of a metallocarborane with a monoatomic bridge in which the pentagonal faces of the two dicarbollide ligands are mutually inclined. However, the crystals which we studied were not good enough to obtain the necessary experimental data for the refinement of this structure and the precise estimation of all distances and angles. For this reason we studied the ionic compound C$_{11}$H$_{38}$B$_{18}$CoNO with the anion O(B$_9$C$_2$H$_{10}$)$_2$Co$^-$ where the same inclination (28°) of the dicarbollide ligands occurs (Petřina, Petříček, Malý, Šubrtová, Línek & Hummel, 1981).

The purpose of the present study was to determine the molecular dimensions of the sandwich metallocarborane in which the central atom is Fe, and to compare these with the situation in the Co sandwich regarding the inclination of ligand planes and bond lengths between the central ion and the ligand vertices.

Crystals were prepared from (C$_2$B$_9$H$_{11}$)Fe$^-$ and formaldehyde in the presence of hydrochloric acid, as for the Co analogue (Plešek, Heřmánek, Baše, Todd & Wright, 1976).

Whereas the structure of the Co analogue could be deduced from ^{1}H and ^{11}B NMR spectroscopy, this was not possible for the Fe compound since the central ion is paramagnetic. Hence only X-ray diffraction can give information about this structure.

Experimental. The brown transparent crystals are air stable and do not decompose in X-rays. Preliminary lattice constants and the space group were obtained from photographs (Fe $K\alpha$ radiation); final cell parameters were calculated by least squares from 50 reflections centred on the diffractometer (Shoemaker, 1970).

A crystal 0.1 × 0.1 × 0.5 mm was used for intensity measurement on a Hilger & Watts diffractometer with Mo $K\alpha$ radiation (Zr filter). The ω–2θ scan technique was used with a constant scan speed of 2° min^{-1} over a range of 2° to measure 2531 independent reflections to $2\theta = 56°$. 364 reflections were classified as unobserved [$I < 2\sigma_1(I)$; $\sigma(I)$ was calculated from counting statistics]. Backgrounds were measured at the scan limits for half of the scan time.

The intensities of three standard reflections measured after every ten reflections showed no significant variation. The data were corrected for Lorentz and polarization factors but were not corrected for absorption or extinction.

The structure was solved by the heavy-atom method. The coordinates of the Fe atom were determined from Patterson maps. An electron density synthesis based on

these parameters provided the positions of all remaining non-hydrogen atoms. The C atoms of the polyhedron were distinguished from B atoms by their higher electron densities, lower temperature factors and shorter bond distances.

Table 1. *Fractional atomic coordinates* $(\times 10^4)$ *and equivalent isotropic thermal parameters* (*Hamilton,* 1959), *with e.s.d.'s in parentheses*

	x	y	z	B_{eq} (Å^2)
Fe	447·4 (5)	1535·0 (2)	2338·4 (8)	2·33 (1)
O	2135 (3)	1287 (2)	4682 (5)	3·5 (1)
C	3188 (5)	993 (3)	5006 (12)	6·1 (2)
C(1)	909 (5)	2106 (3)	−104 (8)	3·6 (1)
C(2)	383 (5)	2507 (2)	1533 (8)	3·6 (1)
B(4)	1906 (5)	1628 (3)	673 (8)	3·5 (1)
B(5)	2252 (6)	2313 (3)	−513 (9)	4·0 (1)
B(6)	1237 (6)	2884 (3)	−45 (11)	4·3 (1)
B(7)	902 (5)	2374 (3)	3723 (9)	3·1 (1)
B(8)	1965 (4)	1790 (3)	3231 (7)	2·7 (2)
B(9)	2939 (5)	2135 (3)	1667 (10)	3·9 (2)
B(10)	2517 (6)	2901 (3)	1161 (10)	4·1 (2)
B(11)	1284 (6)	3044 (3)	2429 (12)	4·3 (1)
B(12)	2332 (5)	2595 (3)	3512 (9)	3·7 (2)
C(1')	−1088 (4)	1132 (2)	3322 (8)	3·2 (1)
C(2')	−566 (4)	742 (2)	1636 (8)	3·5 (1)
B(4')	−202 (5)	1300 (3)	5081 (8)	3·0 (1)
B(5')	−1197 (5)	709 (3)	5379 (10)	3·7 (1)
B(6')	1450 (6)	363 (3)	3167 (12)	4·4 (1)
B(7')	774 (5)	575 (3)	2008 (8)	2·9 (2)
B(8')	1055 (4)	938 (3)	4269 (8)	2·8 (1)
B(9')	205 (5)	574 (3)	6050 (9)	3·6 (2)
B(10')	−579 (7)	−17 (3)	4857 (11)	4·7 (1)
B(11')	−230 (5)	8 (2)	2399 (11)	4·1 (1)
B(12')	806 (6)	128 (3)	4154 (11)	4·0 (2)

Table 2. *Fractional coordinates* $(\times 10^3)$ *for hydrogen atoms*

	x	y	z
H(C1)	34 (7)	200 (3)	−119 (11)
H(C2)	−23 (7)	256 (3)	166 (12)
H(B4)	218 (7)	120 (3)	−8 (12)
H(B5)	257 (6)	230 (3)	−217 (12)
H(B6)	102 (7)	324 (4)	−81 (12)
H(B7)	53 (7)	243 (4)	514 (13)
H(B9)	379 (6)	201 (3)	171 (12)
H(B10)	298 (7)	324 (3)	88 (11)
H(B11)	95 (7)	344 (3)	287 (11)
H(B12)	272 (7)	270 (3)	473 (12)
H(C1')	−182 (7)	143 (3)	306 (11)
H(C2')	−84 (7)	78 (3)	49 (12)
H(B4')	−31 (7)	165 (3)	597 (11)
H(B5')	−172 (7)	81 (3)	637 (12)
H(B6')	−224 (6)	29 (3)	246 (13)
H(B7')	121 (7)	50 (3)	78 (12)
H(B9')	43 (6)	52 (3)	750 (11)
H(B10')	−70 (6)	−35 (3)	561 (12)
H(B11')	−31 (6)	−34 (3)	137 (11)
H(B12')	139 (6)	−17 (3)	432 (11)
H(OC1)	330 (7)	76 (4)	587 (12)
H(OC2)	374 (7)	134 (4)	530 (12)
H(OC3)	307 (7)	53 (3)	406 (12)

Refinement was carried out with a local version of the full-matrix least-squares program *ORFLS* (Busing, Martin & Levy, 1962). The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F)$ derived from $\sigma_2(I) = [\sigma_1^2(I) + (0.015I)^2]^{1/2}$. Initial scale and overall temperature factors were estimated from the Wilson plot. A subsequent difference synthesis revealed the positions of all 23 H atoms.

A common isotropic temperature factor for the H atoms was fixed at $B = 5$ Å^2. All non-hydrogen atoms were refined with anisotropic temperature factors. Final $R = 0.056$ for the 2167 observed reflections.

The maximum residual electron density in the final difference synthesis was 0.9 e Å^{-3} and was located in the vicinity of the Fe atom. Final atomic coordinates are given in Tables 1 and 2.* Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The calculations were carried out on Tesla 200 and EC 1040 computers.

Discussion. The structure of OCH$_3$(B$_9$C$_2$H$_{10}$)$_2$Fe is built up of two dicarbollide ligands with the Fe atom as common apex. These ligands are also linked by a monoatomic oxygen bridge to which a CH$_3$ group is bound (Fig. 1). The pentagonal planes C(1)—C(2)—B(4)—B(7)—B(8) and C(1')—C(2')—B(4')—B(7')—B(8') are inclined at an angle of 31·2 (5)°, which is larger than the 28·3 (4)° found in the isostructural Co analogue. This ligand-plane inclination is undoubtedly
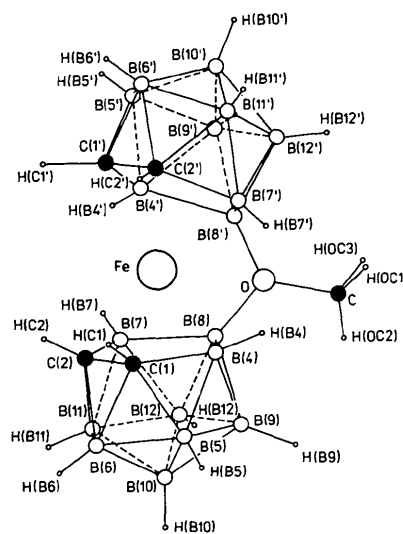
Fig. 1. Structure of a molecule of OCH$_3$(B$_9$C$_2$H$_{10}$)$_2$Fe with numbering following the IUPAC system (Adams, 1972).

caused by the short oxygen bridge between the ligands. The distortion of the icosahedron is also evident from a consideration of the next 'parallel' planes B(5)–B(6)–B(11)–B(12)–B(9) and B(5')–B(6')–B(11')–B(12')–B(9') which are also mutually inclined, but with a somewhat smaller angle (see Table 4).

Comparison with the Co analogue (Petřina *et al.*, 1981) shows that whereas the perpendicular distances of the Fe atom from the pentagonal planes are both 1·531 (6) Å, the corresponding distances for the Co atom are 1·462 (5) Å. The Fe–C bond lengths are in the range 2·159 (5)–2·176 (6) Å while Co–C lengths are in the range 2·077 (8)–2·101 (8) Å. The Fe–B(4), B(7),B(4'),B(7') distances are in the range 2·117 (5)–2·133 (6) Å while the Co–B(4),B(7),B(4'),B(7') distances are in the range 2·083 (9)–2·113 (9) Å. All these bond lengths are longer in the Fe compound. This is a consequence of looser bonding between the ligands and the central ion for the Fe compound since Fe^{3+}, unlike Co^{3+}, contains an unpaired electron. The metal–B(8) and metal–B(8') distances are nearly the same for both metals. The reason for this is obviously the influence of the oxygen bridges linking B(8) and B(8').

The mean values of the distances within the cages are B–B = 1·778 (9), B–C = 1·703 (8), C–C = 1·625 (8), C–H = 0·95 (8) and B–H = 1·03 (8) Å, which are in good agreement with those found in related compounds (Petřina *et al.*, 1981; Churchill &

Gold, 1971). All bond distances and selected angles are given in Table 3. The methyl C atom is located at a distance of 0·699 (6) Å from the plane Fe–B(8)–O–B(8'). The directions of the bonds B(8)–O and B(8')–O deviate by 5° from the directions connecting the antipodal atoms B(6)–B(8) and B(6')–B(8') respectively. This is clear evidence of the steric strain imposed by the monoatomic oxygen bridge.

Important least-squares planes and deviations of atoms from the planes are given in Table 4. The C(1)–C(2) and C(1')–C(2') bonds are bisected symmetrically by the plane Fe–B(8)–O–B(8'). Thus the title compound can be classified according to the
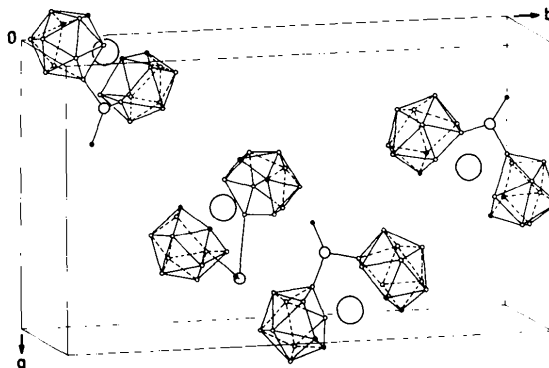

Fig. 2. Packing of the molecules in the unit cell.

Table 3. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

The values given in the second column refer to atoms denoted by primes.

(a) Metal–cage distances

Fe–C(1)	2·176 (6)	2·165 (5)	Fe–B(4)	2·128 (6)	2·133 (6)	Fe–B(8)	2·019 (5)	2·004 (6)
Fe–C(2)	2·167 (5)	2·159 (5)	Fe–B(7)	2·122 (6)	2·117 (5)			

(b) OCH_3-group distances

O–B(8)	1·498 (7)	1·536 (6)	C–H(OC1)	0·80 (8)		C–H(OC3)	1·20 (8)	
O–C	1·444 (7)		C–H(OC2)	1·01 (8)				

(c) Cage distances

C(1)–C(2)	1·569 (8)	1·580 (7)	B(4)–B(9)	1·802 (9)	1·774 (8)	B(7)–B(12)	1·804 (9)	1·782 (9)
C(1)–B(4)	1·678 (8)	1·672 (8)	B(5)–B(6)	1·770 (10)	1·743 (10)	B(8)–B(9)	1·773 (8)	1·797 (8)
C(1)–B(5)	1·713 (9)	1·708 (9)	B(5)–B(9)	1·779 (9)	1·788 (9)	B(8)–B(12)	1·800 (9)	1·772 (8)
C(1)–B(6)	1·724 (9)	1·716 (8)	B(5)–B(10)	1·753 (10)	1·771 (9)	B(9)–B(10)	1·762 (10)	1·794 (9)
C(2)–B(6)	1·718 (9)	1·720 (9)	B(6)–B(10)	1·767 (10)	1·784 (11)	B(9)–B(12)	1·784 (9)	1·792 (9)
C(2)–B(7)	1·679 (8)	1·684 (8)	B(6)–B(11)	1·764 (11)	1·749 (9)	B(10)–B(11)	1·766 (10)	1·770 (11)
C(2)–B(11)	1·709 (8)	1·716 (7)	B(7)–B(8)	1·834 (8)	1·796 (8)	B(10)–B(12)	1·785 (10)	1·778 (11)
B(4)–B(5)	1·743 (10)	1·767 (8)	B(7)–B(11)	1·763 (9)	1·744 (8)	B(11)–B(12)	1·767 (9)	1·775 (10)
B(4)–B(8)	1·823 (8)	1·804 (8)						
C(1)–H(C1)	1·05 (8)	1·11 (8)	B(6)–H(B6)	0·97 (8)	1·09 (8)	B(10)–H(B10)	0·95 (9)	0·91 (8)
C(2)–H(C2)	0·76 (9)	0·87 (8)	B(7)–H(B7)	1·09 (9)	1·02 (8)	B(11)–H(B11)	1·00 (7)	1·05 (8)
B(4)–H(B4)	1·11 (8)	0·99 (7)	B(9)–H(B9)	1·07 (8)	1·06 (8)	B(12)–H(B12)	1·00 (8)	0·96 (8)
B(5)–H(B5)	1·22 (8)	0·97 (8)						

Selected bond angles

Fe–O–C	149·4 (4)		B(8)–Fe–B(8')	68·3 (2)		Fe–B(8)–O	98·0 (3)	97·3 (3)
			B(8)–O–B(8')	96·2 (3)		B(8)–O–C	123·0 (4)	124·7 (4)

Table 4. *Important planes in the molecule and atomic deviations* (Å) *from them*

Atoms marked with an asterisk were not included in the least-squares calculation.

(*a*) Plane C(1), C(2), B(4), B(7), B(8); $\chi^2 = 11\cdot2$

$$0\cdot6769x + 0\cdot7191y - 0\cdot1574z - 4\cdot0162 = 0$$

C(1)	−0·001 (5)	B(7)	−0·011 (6)
C(2)	0·008 (5)	B(8)	0·010 (5)
B(4)	−0·007 (6)	Fe*	−1·531 (6)

(*b*) Plane C(1′), C(2′), B(4′), B(7′), B(8′); $\chi^2 = 1\cdot8$

$$0\cdot2576x + 0\cdot8443y - 0\cdot4699z - 0\cdot6298 = 0$$

C(1′)	−0·003 (5)	B(7′)	−0·004 (5)
C(2′)	0·005 (5)	B(8′)	0·002 (6)
B(4′)	0·001 (6)	Fe*	1·531 (6)

(*c*) Plane B(5), B(6), B(9), B(11), B(12); $\chi^2 = 5\cdot04$

$$0\cdot6652x + 0\cdot7257y - 0\cdot1756z - 5\cdot4990 = 0$$

B(5)	−0·007 (7)	B(11)	−0·008 (6)
B(6)	0·009 (7)	B(12)	0·004 (6)
B(9)	0·002 (6)	B(10)*	0·920 (6)

(*d*) Plane B(5′), B(6′), B(9′), B(11′), B(12′); $\chi^2 = 0\cdot35$

$$0\cdot2722x + 0\cdot8454y - 0\cdot4595z + 0\cdot8336 = 0$$

B(5′)	−0·000 (6)	B(11′)	0·002 (6)
B(6′)	−0·001 (7)	B(12′)	−0·002 (6)
B(9′)	0·002 (6)	B(10′)*	−0·949 (6)

(*e*) Plane Fe, O, B(8), B(8′); $\chi^2 = 132\cdot31$

$$0\cdot4294x - 0\cdot5437y - 0\cdot7211z + 2\cdot7238 = 0$$

Fe	−0·018 (1)	C(1)*	0·786 (6)
O	−0·030 (4)	C(2)*	−0·783 (6)
B(8)	0·024 (5)	C(1′)*	−0·842 (6)
B(8′)	0·024 (5)	C(2′)*	0·736 (6)
C*	0·699 (6)		

Angles between planes (°): (*a*)–(*b*) 31·2 (5); (*c*)–(*d*) 28·9 (4); (*a*)–(*e*) 89·2 (1·4); (*b*)–(*e*) 90·5 (1·3).

nomenclature of Janoušek, Plešek, Heřmánek, Baše, Todd & Wright (1981), as having the *e* 1–2′ conformation for both ligands.

The packing of the molecules within the unit cell is shown in Fig. 2.

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Structure of Tetrakis(1,3-thiazolidine-2-thione)palladium(II) Dichloride–1,3-Thiazolidine-2-thione (1:2)

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Abstract. [Pd(C$_3$H$_5$NS$_2$)$_4$]Cl$_2$.2(C$_3$H$_5$NS$_2$), M_r = 892·6, triclinic, space group P$\bar{1}$, a = 11·075 (3), b = 9·363 (3), c = 8·531 (3) Å, α = 102·78 (2), β = 85·50 (2), γ = 94·87 (2)°, U = 858 Å^3, Z = 1, D_c = 1·73, D_m = 1·74 (1) Mg m^{-3}, μ(Mo $K\alpha$) = 1·41 mm^{-1}. The structure was refined to R = 0·046 for 2013 counter reflections. It consists of discrete [Pd(C$_3$H$_5$NS$_2$)$_4$]$^{2+}$ cations, Cl$^-$ anions and uncoordinated C$_3$H$_5$NS$_2$ solvent molecules, linked by a network of NH$\cdots$Cl hydrogen bonds. All four ligands are S-bonded to the metal with Pd–S bonds of 2·322 (2) and 2·327 (2) Å, to give a square-planar PdS$_4$ unit with