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An Additional Isomer of the Neutral Dicarbollide Analogue of Ferrocene $[Fe\{C_2B_9H_{10}(SMe_2)\}_2]$

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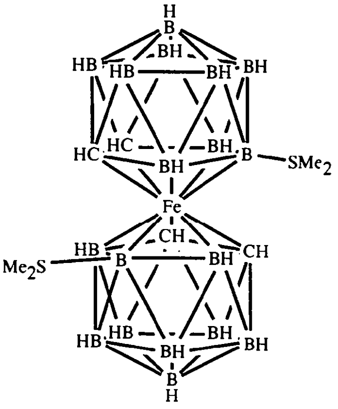
Abstract

The title compound, 8,8′-bis(dimethyl sulfido)-3,3′-ferra-*commo*-bis[3,1,2-ferradicarba-*closo*-dodecaborane(11)], has the expected overall geometry in which two $\{FeC_2B_9\}$ icosahedra are linked *via* a common Fe atom; additionally, the whole cluster has crystallographically imposed C_2 symmetry. The structure is compared with those of its geometric isomers and of some related compounds.

Comment

There is, at present, considerable interest in the structural behaviour of metallacarbaborane sandwich complexes and their derivatives, and in particular their possible application as novel molecular materials (see for example, Yan & Mingos, 1995). Prompted by the recent structural accounts of one such compound, *commo*-$[3,3'$-$Fe\{4$-(Me_2S)-$1,2$-$C_2B_9H_{10}\}_2]$, as its *DD/LL*- (Yan *et al.*, 1994) and *meso*- (Yan, Mingos & Williams, 1995) isomers, hereinafter (I) and (II), respectively, and its varied structural behaviour, we report our own determination of the molecular geometry of the title compound, (III), a structural isomer of the ferracarbaboranes (I) and (II).



(III)

A perspective view of a whole molecule of (III), showing the atomic numbering scheme, is presented in Fig. 1. The molecule is chiral and has crystallographically imposed twofold symmetry, with Fe3 lying on a C_2 axis, which coincides with the crystallographic *c* axis. Thus, the two η^5-$\{C_2B_3\}$ faces binding to the Fe atom have a staggered conformation and the cage C atoms are not fully *cisoid*; the C1—C2 and C1^i—C2^i vectors, and likewise the pendant dimethyl sulfide

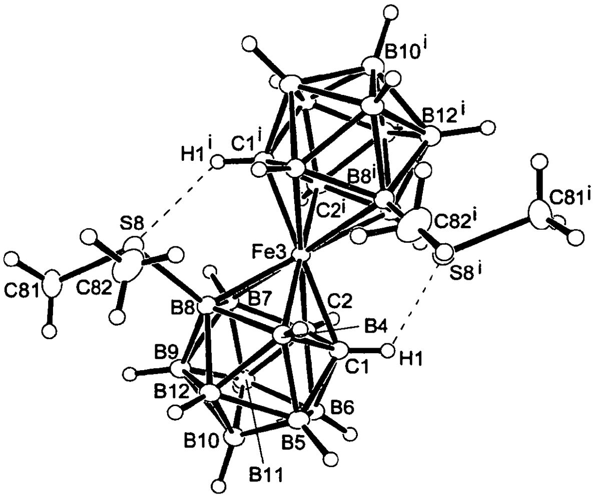


Fig. 1. Perspective view of a single molecule of (III) drawn with 40% probability ellipsoids and with H atoms shown as small circles of artificial radii for clarity. [Symmetry code: (i) $2 - x$, $2 - y$, z.]

ligands, have a quasi-*gauche* configuration [symmetry code: (i) $2-x$, $2-y$, z]. The chirality is crystallographically imposed. In solution, there is mutual contrarotation of the $\{C_2B_9H_{10}(SMe_2)\}$ residues about an axis approximately defined by B10, Fe3 and B10^i.

The mean planes defined by the atoms of the two ligating faces are almost parallel, being inclined at 3.1 (8)° to each other. The Fe atom is located 1.498 (1) Å above the mean C_2B_3 plane, a displacement that is similar to those of 1.500 (1) and 1.498 (1) Å in (I) and (II), respectively. The same parameter is 1.475 (1) Å in the 'parent' dianion $[Fe(C_2B_9H_{11})_2]^{2-}$, (IV), and is 1.50 (4) and 1.56 (4) Å in the 8,8′-$(NEt_3)_2$- relative of (III), hereinafter (V) (Kang *et al.*, 1991). The rather greater steric demands of the pendant amine ligands in (V) appear to contribute to considerable geometric distortions in comparison with the analogue (III) (see below). [Although the determination of the structure of (V) was not highly accurate, the magnitude of these distortions is quite significant.]

The five ligating atoms in (III) are, in fact, not exactly coplanar: the face is folded about B4···B7 in an 'envelope' conformation, with the C2—C1—B4—B8/B4—B8—B7 dihedral angle being 4.82 (13)°. The lower B5—B6—B11—B9—B12 pentagonal belt, in contrast, approaches planarity rather more closely. The largest deviation from the mean C_2B_3 plane in (III) is 0.034 (1) Å (B8), which is rather larger than any deviation reported previously in (I), (II) and (IV) (<0.016 Å). Therefore, (III) has a greater puckering of the ligating face than (I), (II) and (IV). The coordinating faces of the carbaborane ligands in the $(NEt_3)_2$ derivative (V) are even more folded [dihedral angles 7 (3) and 6 (3)°], with correspondingly greater deviations of up to 0.052 Å. This may arise from the greater ligand strength of amine *versus* sulfide ligands towards boranes. Distances from the Fe vertex to the coordinating atoms of the carbaborane ligand in (III) are compared in Table 3 with the corresponding parameters for the related species (I), (II), (IV) and (V). Table 3 shows that there appears to be little effect on these separations arising either from greater folding of the carbaborane face or from changes in the position of the B-bound ligand. A slightly smaller separation of the Fe vertex from the carbaborane ligand in anionic (IV) than in neutral (I), (II), (III) and (V) has been attributed to electrostatic factors (Kang *et al.*, 1991). We note in this context that a number of other dialkyl sulfido relatives of (III) have been prepared, namely the anionic monosubstituted 8-SR_2- (R = Me, Et, ^{n}Pr) analogues, as well as the 8,8′-$(SEt_2)_2$- compound, but these, unfortunately, were not structurally characterized (Hawthorne *et al.*, 1971).

The cage C atoms in (III) are separated by 1.616 (2) Å, a typical value [*cf.* 1.602 (6) and 1.633 (6) Å in (I), 1.615 (2) Å in (II), 1.616 (12) Å in (IV), and 1.66 (4) and 1.58 (4) Å in (V)]. Cluster B—B and C—B distances lie within the ranges 1.757 (3)–1.808 (2) and 1.698 (2)–1.740 (2) Å, respectively, which also do not differ greatly from those reported previously.

Geometric parameters associated with the pendant SMe_2 group are close to those expected, and to those observed in (I) and (II). We find no significant intermolecular contacts involving the S atom, such as those reported for (II). However, the S-atom lone pair is directed approximately towards the protonic C-bound H atom H1^i, with an intramolecular S8···H1^i separation of 2.91 (2) Å.

Experimental

To a solution of 10-(Me_2S)-*nido*-7,8-$C_2B_9H_{11}$ (1.0 g, 5.2 mmol) (Plešek *et al.*, 1993) and $FeCl_2.4H_2O$ (1.0g, 5.0 mmol) in Me_2SO (15 ml) was added solid KOH (5 g, 90 mmol) and the resulting slurry was stirred for 30 min at 353 K. After cooling to room temperature, H_2O (50 ml) was added, followed by concentrated aqueous HCl (6 ml) and benzene (40 ml) to leave an undissolved violet solid (*A*) on the interface of the two layers. This was isolated by filtration and kept for further purification. The layers were separated and the nearly colourless bottom layer discarded. The purple (upper) layer was reduced in volume and applied to a silica gel column and eluted with benzene to collect two fractions. The colourless fractions of R_f = 0.46 (analytical TLC, silica gel G, benzene) were identified as the starting dicarbaborane. The remaining violet band was washed with acetone and the effluent combined with the original violet solid *A*. The acetone solution thus obtained was filtered and the acetone removed by evaporation to give 463 mg (47%) of violet crystals, identified as $[Fe(C_2B_9H_{10}SMe_2)_2]$, (III). Mass spectrometry $(m/z)_{max}$ found 446, $^{12}C_8{}^1H_{32}{}^{11}B_{18}{}^{32}S_2{}^{56}Fe$ requires 446. NMR spectroscopy (acetone-d_6): $\delta(^1H)$ +3.62 (*s*, 4H, CH_{cage}), +2.58 (*s*, 12H, Me_2S); $\delta(^{11}B)$ +0.8 [*s*, 1B, B(8)], −9.6 [*d*, 1B, B(10)], −12.0 [*d*, 2B, B(4,7)], −14.9 [*d*, 2B, B(9,12)], −23.1 [*d*, 2B, B(5,11)], −26.2 p.p.m. [*d*, 1B, B(6)] (assigned by [^{11}B–^{11}B]-COSY measurements). Single crystals suitable for X-ray diffraction analysis were grown by overlayering a concentrated CH_2Cl_2 solution with cyclohexane (243 K).

Crystal data

$[Fe(C_4H_{16}B_9S)_2]$
M_r = 442.89
Orthorhombic
$P2_12_12$
a = 13.1891 (9) Å
b = 10.5406 (8) Å
c = 8.0819 (8) Å
V = 1123.5 (2) Å^3
Z = 2
D_x = 1.310 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 30 reflections
θ = 16.16–20.02°
μ = 0.852 mm^{-1}
T = 200 (2) K
Plate
0.68 × 0.42 × 0.27 mm
Red

Data collection

Stoe Stadi-4 four-circle diffractometer
ω/θ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
T_{min} = 0.652, T_{max} = 0.764

1969 reflections with $I > 2\sigma(I)$
R_{int} = 0.012
θ_{max} = 25°
$h = -15 \rightarrow 15$
$k = -12 \rightarrow 12$
$l = -9 \rightarrow 9$

4680 measured reflections
1988 independent reflections

3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.017$
$wR(F^2) = 0.045$
$S = 1.127$
1988 reflections
176 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0277P)^2 + 0.1595P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.001$

$\Delta\rho_{\max} = 0.169$ e Å^{-3}
$\Delta\rho_{\min} = -0.179$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = −0.002 (12)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Fe3	1	1	0.85134 (3)	0.01434 (8)
C1	0.95212 (10)	0.81551 (12)	0.8559 (2)	0.0192 (3)
C2	1.01601 (11)	0.85553 (13)	1.0184 (2)	0.0201 (3)
B4	1.01568 (12)	0.85163 (14)	0.6787 (2)	0.0179 (3)
B5	1.0082 (2)	0.6911 (2)	0.7557 (2)	0.0222 (3)
B7	1.12901 (12)	0.9226 (2)	0.9685 (2)	0.0188 (3)
S8	1.21579 (2)	1.02464 (3)	0.62051 (4)	0.01928 (9)
B6	1.0062 (2)	0.6951 (2)	0.9740 (2)	0.0236 (3)
B8	1.13275 (12)	0.9133 (2)	0.7508 (2)	0.0171 (3)
C81	1.34379 (11)	0.9681 (2)	0.6363 (2)	0.0357 (4)
C82	1.18746 (12)	0.9822 (2)	0.4104 (2)	0.0350 (4)
B9	1.19733 (12)	0.79514 (14)	0.8697 (2)	0.0215 (3)
B10	1.11972 (12)	0.65694 (14)	0.8715 (2)	0.0234 (3)
B11	1.12125 (13)	0.7621 (2)	1.0436 (2)	0.0240 (4)
B12	1.12685 (13)	0.7515 (2)	0.6896 (2)	0.0205 (3)

Table 2. *Selected geometric parameters (Å, °)*

Fe3—C1	2.044 (2)	B5—B12	1.771 (3)
Fe3—C2	2.045 (2)	B5—B10	1.780 (3)
Fe3—B4	2.105 (2)	B7—B8	1.763 (2)
Fe3—B7	2.111 (2)	B7—B11	1.799 (2)
Fe3—B8	2.135 (2)	B7—B9	1.803 (2)
C1—C2	1.616 (2)	S8—B8	1.919 (2)
C1—B4	1.702 (2)	B6—B10	1.757 (3)
C1—B5	1.709 (2)	B6—B11	1.765 (3)
C1—B6	1.740 (2)	B8—B12	1.777 (2)
C2—B7	1.698 (2)	B8—B9	1.789 (2)
C2—B11	1.714 (2)	B9—B11	1.761 (2)
C2—B6	1.732 (2)	B9—B10	1.780 (2)
B4—B8	1.773 (2)	B9—B12	1.787 (2)
B4—B5	1.804 (2)	B10—B11	1.778 (3)
B4—B12	1.808 (2)	B10—B12	1.778 (2)
B5—B6	1.765 (2)		
C1$^{\rm i}$—Fe3—C1	177.96 (9)	C2—B7—B8	103.80 (11)
C1—Fe3—C2$^{\rm i}$	131.60 (6)	C81—S8—C82	100.39 (9)
C1—Fe3—C2	46.57 (6)	C81—S8—B8	107.16 (8)
C2$^{\rm i}$—Fe3—C2	97.40 (9)	C82—S8—B8	104.35 (7)
C1—Fe3—B4	48.40 (6)	B7—B8—B4	108.87 (11)
C2—Fe3—B7	48.19 (6)	B7—B8—S8	121.99 (11)
B4—Fe3—B8	49.44 (6)	B4—B8—S8	122.74 (10)
B7—Fe3—B8	49.05 (6)	B12—B8—S8	117.30 (10)
C2—C1—B4	111.61 (11)	B9—B8—S8	116.64 (10)
C1—C2—B7	111.91 (11)	S8—B8—Fe3	114.55 (8)
C1—B4—B8	103.58 (11)		

Symmetry code: (i) $2 - x, 2 - y, z$.

Table 3. *Comparison of Fe—C and Fe—B distances (Å) in ferracarbaborane sandwich complexes*

	(III)	(I)	(II)	(IV)	(V)
Fe3—C1	2.044 (2)	2.057 (4) 2.029 (5)	2.039 (1)	2.015 (8)	2.04 (4) 2.07 (4)
Fe3—C2	2.045 (2)	2.034 (4) 2.051 (4)	2.037 (1)	2.047 (8)	2.03 (4) 2.06 (4)
Fe3—B4	2.105 (2)	2.100 (5) 2.084 (5)	2.103 (2)	2.073 (10)	2.14 (4) 2.13 (4)
Fe3—B7	2.111 (2)	2.094 (5) 2.126 (5)	2.104 (2)	2.112 (10)	2.12 (4) 2.23 (4)
Fe3—B8	2.135 (2)	2.139 (5) 2.157 (4)	2.150 (2)	2.144 (10)	2.26 (4) 2.28 (5)

Data were collected using an on-line profile-fitting method (Clegg, 1981). Methyl H atoms were constrained to calculated positions with free rotation and isotropic displacement parameters equal to $1.5U_{\rm eq}$ of the parent C atom. Borane terminal H atoms were located *via* difference Fourier syntheses and all associated parameters were refined freely.

Data collection: *DIF*4 (Stoe & Cie, 1988*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1988*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEX*5 (McArdle, 1995). Software used to prepare material for publication: *SHELXL*93 and *PLATON* (Spek, 1995) .

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1497). Services for accessing these data are described at the back of the journal.

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