

μ -Ethylthio- μ' -carbonyl-bis(η -cyclopentadienylcarbonyliron)(Fe–Fe) Tetraphenylborate

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Abstract. $[\text{Fe}_2(\eta\text{-C}_5\text{H}_5)_2(\text{CO})_3(\text{SC}_2\text{H}_5)]\text{B}(\text{C}_6\text{H}_5)_4$, monoclinic, $P2_1/n$, $a = 14.909$ (5), $b = 23.82$ (1), $c = 9.610$ (5) Å, $\beta = 91.4$ (2)°, $D_c = 1.37$ g cm⁻³ for $Z = 4$. The structure of the cation is remarkably similar to that reported for the corresponding hexafluoroantimonate, suggesting a high degree of rigidity of the cation.

Introduction. The preparation of the salt has been described (English, Haines & Nolte, 1975). A crystal $0.1 \times 0.15 \times 0.1$ mm was used for data collection. Cell parameters were obtained by least squares from the settings of 25 reflexions measured on a four-circle Philips PW1100 diffractometer. Intensities were measured with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å), ω - 2θ scan mode. 5814 reflexions were collected of which 3973 unique observed reflexions [$I_{\text{rel}} > 2\sigma(I_{\text{rel}})$] were employed in the structural analysis. No crystal decomposition was observed. Lorentz-polarization corrections were applied, but none for absorption.

The two Fe and the S atom positions were found from a Patterson map. Isotropic refinement of their coordinates was performed; the positions of 32 light atoms were revealed in a subsequent difference map. After further full-matrix least-squares refinement all non-hydrogen atoms had been revealed and several peaks appeared in a difference map in chemically reasonable positions for H atoms. R was 0.24. In the subsequent refinement the C_6H_5 and C_5H_5 rings were treated as rigid, perfect hexagons and pentagons, respectively, with $\text{C}-\text{C} = 1.395$ Å (Sheldrick, 1975); idealized H atom positions were calculated with $\text{C}-\text{H} = 1.080$ Å and all non-hydrogen atoms were refined anisotropically. After blocked-matrix least-squares refinement for the cation and anion parameters in alternate cycles, R was 0.109.

In the final blocked-matrix refinement geometric constraints were removed from the ring C atoms. R fell to its final value of 0.088. R_w was 0.096 with a

weighting scheme $w = 0.8321(\sigma^2 F + gF^2)$; the value of $g = 0.0094$ was chosen to give the smallest variation of $w\Delta^2$ with F .

The isotropic temperature factors of the H atoms of the phenyl, cyclopentadienyl, CH_3 and CH_2 groups, which were refined as four single variables, converged to $U = 0.081$ (7), 0.16 (2), 0.11 (3) and 0.19 (4) Å² respectively. The six highest peaks (1.2 to 1.6 e Å⁻³) in a difference map based on all the atoms could be ascribed to anisotropic thermal motion of the Fe and S atoms. The average shift/error in the last two cycles

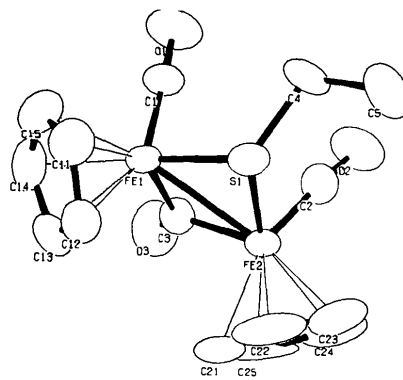


Fig. 1. ORTEP drawing of the cation with the atom labelling.

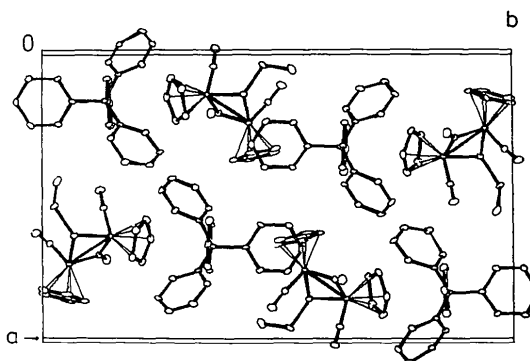


Fig. 2. Packing diagram of the unit cell, projected on (001).

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Table 1. Fractional atomic coordinates ($\times 10^4$) of the non-hydrogen atoms (with *e.s.d.*'s)

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
Fe(1)	1399 (1)	3538 (0)	1899 (1)	B(1)	8299 (5)	8650 (3)	2209 (9)
Fe(2)	2385 (1)	4417 (0)	1479 (1)	C(31)	9187 (4)	8355 (3)	1505 (7)
S(1)	1414 (1)	4313 (1)	3137 (2)	C(32)	9587 (5)	8559 (3)	323 (8)
O(1)	-207 (5)	3758 (3)	203 (10)	C(33)	10307 (5)	8268 (3)	-301 (8)
O(2)	1219 (5)	5115 (3)	-286 (7)	C(34)	10628 (5)	7788 (4)	255 (8)
O(3)	2181 (5)	3622 (3)	-839 (7)	C(35)	10251 (6)	7573 (4)	1432 (9)
C(1)	422 (6)	3683 (4)	909 (11)	C(36)	9535 (5)	7850 (3)	2066 (8)
C(2)	1654 (6)	4836 (3)	426 (10)	C(41)	8294 (5)	8590 (3)	3911 (8)
C(3)	2045 (5)	3784 (3)	251 (7)	C(42)	9091 (5)	8606 (3)	4720 (8)
C(4)	406 (6)	4738 (4)	2867 (10)	C(43)	9088 (7)	8576 (4)	6162 (9)
C(5)	575 (8)	5333 (4)	3336 (13)	C(44)	8300 (7)	8539 (4)	6853 (8)
C(11)	1232 (7)	2999 (4)	3628 (10)	C(45)	7506 (7)	8519 (4)	6122 (9)
C(12)	2176 (7)	3070 (4)	3353 (11)	C(46)	7512 (5)	8556 (3)	4657 (8)
C(13)	2313 (7)	2860 (4)	1997 (12)	C(51)	8268 (4)	9336 (3)	1943 (7)
C(14)	1473 (7)	2685 (4)	1448 (10)	C(52)	7470 (5)	9643 (3)	1937 (8)
C(15)	850 (7)	2769 (4)	2462 (11)	C(53)	7426 (6)	10218 (4)	1851 (9)
C(21)	3685 (6)	4098 (5)	1962 (19)	C(54)	8204 (7)	10527 (4)	1780 (10)
C(22)	3450 (7)	4469 (9)	2966 (14)	C(55)	9022 (6)	10250 (4)	1820 (10)
C(23)	3294 (8)	4976 (8)	2405 (26)	C(56)	9044 (5)	9665 (3)	1898 (8)
C(24)	3428 (8)	4945 (8)	999 (25)	C(61)	7440 (4)	8321 (3)	1476 (7)
C(25)	3674 (6)	4374 (9)	705 (15)	C(62)	6977 (5)	8515 (3)	288 (8)
				C(63)	6267 (6)	8209 (4)	-321 (9)
				C(64)	6021 (5)	7695 (4)	177 (9)
				C(65)	6473 (5)	7479 (4)	1346 (10)
				C(66)	7180 (5)	7785 (3)	1943 (9)

Table 2. Bond lengths (\AA) (with *e.s.d.*'s)

C(cp) denotes a cyclopentadienyl C atom.		
Fe(1)—Fe(2)	2.595 (2)	Fe(1)—C(cp) (ring 1)
S(1)—Fe(1)	2.195 (3)	(average) 2.10 (2)
S(1)—Fe(2)	2.193 (3)	Fe(2)—C(cp) (ring 2)
C(1)—Fe(1)	1.754 (9)	(average) 2.09 (2)
C(3)—Fe(1)	1.963 (7)	C(cp)—C(cp) (ring 1)
C(2)—Fe(2)	1.775 (9)	(average) 1.40 (3)
C(3)—Fe(2)	1.973 (7)	C(cp)—C(cp) (ring 2)
C(1)—O(1)	1.16 (1)	(average) 1.38 (3)
C(2)—O(2)	1.14 (1)	C—C (phenyl ring)
C(3)—O(3)	1.14 (1)	(average) 1.39 (1)
C(4)—S(1)	1.826 (9)	
C(5)—C(4)	1.51 (1)	

was in no case >0.2 . Scattering factors were from Cromer & Mann (1968) and anomalous dispersion corrections were applied to the Fe and S scattering curves. Final positional parameters are given in Table 1.* Fig. 1 shows the structure of the cation and the atom labelling, and Fig. 2 depicts the contents and outlines of the unit cell, projected on (001). Tables 2 and 3 list bond lengths and angles.

* Lists of structure factors, anisotropic thermal parameters and hydrogen atom positions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33420 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Bond angles ($^\circ$) (with *e.s.d.*'s)

Fe(1)—S(1)—Fe(2)	72.5 (1)	S(1)—Fe(1)—C(1)	97.2 (3)
Fe(1)—C(3)—Fe(2)	82.5 (3)	S(1)—Fe(1)—C(3)	100.8 (2)
Fe(1)—C(1)—O(1)	176.3 (9)	C(1)—Fe(1)—C(3)	85.5 (4)
Fe(2)—C(2)—O(2)	176.7 (8)	S(1)—Fe(2)—C(2)	94.1 (3)
Fe(1)—C(3)—O(3)	138.0 (6)	S(1)—Fe(2)—C(3)	100.6 (2)
Fe(2)—C(3)—O(3)	139.5 (6)	C(2)—Fe(2)—C(3)	86.7 (3)

Discussion. Previous studies (English, Haines & Nasimbeni, 1977) have shown that, although a characteristic bond length of some $2.55 \pm 0.1 \text{ \AA}$ is associated with the presence of a formal two-electron Fe—Fe bond, in complexes where two ligands bridge symmetrically across the metal—metal bond an appreciable variation in this bond length occurs, apparently depending upon the nature of the bridging ligand. Thus in [$\{\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2\}_2$] (*cis*) (Bryan, Greene, Newlands & Field, 1970) an Fe—Fe length of 2.462 \AA is observed, while the Fe atoms in [$\text{Fe}_2(\text{C}_5\text{H}_5)_2(\text{CO})_3(\text{GeMe}_2)$] are separated by 2.628 \AA (Adams, Brice & Cotton, 1974). However, the effects on the Fe—Fe distance of crystal packing in this type of compound were not known, and it was possible that the rather wide spread of bond lengths might be simply an artefact of packing dissimilarities in the various compounds, rather than due specifically to the nature of the bridging ligands. The preparation and crystallization of the title complex therefore presented an

opportunity of separating the two effects in the cation [Fe₂(C₅H₅)₂(CO)₃(SC₂H₅)₃]⁺, the structure of the SbF₆⁻ salt of which has already been determined (English, Haines & Nassimbeni, 1977). It was anticipated that the crystal packing in the tetraphenylborate salt would be grossly different from that in the SbF₆⁻ salt due to the much greater size of the anion.

As can be seen from the packing diagram (Fig. 2), this is indeed the case; the complex has not crystallized in a centred space group as does the corresponding SbF₆⁻ salt and the structure is somewhat less compact than the SbF₆⁻ structure [average volume occupied by a non-hydrogen atom = 18.54 Å³ for the B(C₆H₅)₄⁻ salt, = 17.67 Å³ for the SbF₆⁻ salt].

However, a comparison of bond lengths and angles in the cations in the two structures reveals no major differences. A slight increase of 0.015 Å in the Fe—Fe length is observed for the B(C₆H₅)₄⁻ salt, with a concomitant increase in the Fe(1)—S—Fe(2) angle. The Fe(1)—S—Fe(2)—C(3) ring is also more puckered; the angles between the planes defined by Fe(1), Fe(2), S and Fe(1), Fe(2), C(3); and by Fe(1), S, C(3), and Fe(2), S, C(3) being 18.3 and 22.4° as opposed to the corresponding values of 15.6 and 19.2° in the SbF₆⁻ salt.

In conclusion, therefore, it can be stated with some certainty that systems where two Fe atoms are bound

together and where two bridging ligands symmetrically span the metal—metal bond are stereochemically quite rigid. Gross differences in the metal—metal length can be ascribed to changes of electron density on the metal atoms due to different bridging ligands or overall charge, as structural parameters in such systems seem insensitive to crystal packing.

All calculations in this study were performed on the University of Cape Town's Univac 1106 computer with the *SHELX* (Sheldrick, 1975) program system.

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Bis(oxamide oximato)nickel(II)—Water—Dimethylformamide

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Abstract. Ni(C₂H₅N₄O₂)₂·H₂O·C₃H₇NO, FW 384.0, triclinic, *P*1̄, *a* = 8.116 (2), *b* = 9.902 (2), *c* = 9.856 (1) Å, α = 94.87 (2), β = 99.98 (1), γ = 100.98 (2)°, *V* = 760.08 Å³, *Z* = 2, *d*_c = 1.70 g cm⁻³. The structure was refined to *R* = 0.051 for 3734 reflections. There are two independent, centrosymmetric, planar complex molecules in the unit cell, one of them bound by hydrogen bonds to two water molecules. The water and the dimethylformamide do not coordinate to the metal.

Introduction. Oxamide oxime (diaminoglyoxime), a possible chelating ligand with two additional potentially

coordinating sites at the two amino N atoms, has been known since 1889 (Fischer, 1889; Ephraim, 1889). A summary of the methods of its preparation and a discussion of the conformation of the free molecule were published by Ungnade, Kissinger, Narath & Barham (1963). Pearse & Pflaum (1959) reported spectroscopic investigations on several transition-metal complexes (Fe, Co, Ni, Cu). The coordination chemistry of this ligand has recently aroused new interest (Sarisaban, 1976), and the first X-ray structure analysis of an oxamide oxime (OAOH₂) complex has been published: Co(OAOH₂)₂·OAOH₂ (Bekaroglu, Sarisaban, Koray & Ziegler, 1977). The Co atom has a square-