

(Grönbæk & Rasmussen, 1962). The β -isomer contains two independent sets of complex ions, one of *cis*- and another of *trans*-planar configuration (Hazell, 1968). The Ni—S bond of the *cis* complex is significantly shorter than that of the *trans* complex [2.149 (1) and 2.169 (1) Å, respectively]. The molecular structures of *cis* and *trans* nickel dithiosemicarbazide dinitrate have been determined [Hazell (1972), Ni—S bond lengths 2.150 (5) and 2.185 (1) Å respectively].

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2-Thia[3]ferrocenophane S-Oxide

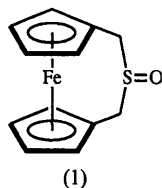
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Abstract. $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{SOCH}_2\text{-}\eta^5\text{-C}_5\text{H}_4)]$, $M_r = 260.1$, $P2_1/c$, $a = 13.195$ (2), $b = 7.476$ (2), $c = 10.541$ (2) Å, $\beta = 95.00$ (2)°, $V = 1035.9$ (7) Å³, $Z = 4$, $D_x = 1.668$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 16.13$ cm⁻¹, $F(000) = 536$, $T = 299$ K, $R = 0.028$ for 2465 observed data (of 3017 unique data). The η^5 -cyclopentadienyl ligands each exhibit a maximum deviation of 0.006 (2) Å from planarity. The bridging C atoms lie out of these planes by 0.114 (2) and 0.079 (2) Å toward Fe. The Fe atom lies 1.635 (1) Å from each plane. The two rings form a dihedral angle of 5.9 (5)°, and the Cp centroid—Fe—Cp centroid angle is 175.7°. The S=O distance is 1.501 (2) Å.

Experimental. The title compound (1) was prepared by 3-chloroperbenzoic acid oxidation of 2-thia[3]ferrocenophane (Ando, Hanyu, Kumamoto & Takata, 1986) and recrystallized from refluxing ethanol to afford yellow–orange needles, m.p. 474.5–475 K.



A needle fragment of dimensions 0.28 × 0.38 × 0.45 mm, was used for data collection on an Enraf–Nonius CAD-4 diffractometer with Mo $K\alpha$ radiation and a graphite monochromator. Cell dimensions

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were determined at 299 K by a least-squares fit to setting angles of 25 reflections having $19 > \theta > 12^\circ$. One quadrant of data having $1 < \theta < 30^\circ$, $0 \leq h \leq 18$, $0 \leq k \leq 10$, $-14 \leq l \leq 14$ was measured by ω - 2θ scans at speeds ranging from 0.45 to 4.0° min⁻¹ to measure all significant data with approximately equal precision. Three standard reflections (500, 040, 004) exhibited only a random fluctuation in intensity so no correction for decay was applied. Data reduction included corrections for background, Lorentz, polarization and absorption. Absorption corrections were based on ψ scans, with maximum transmission coefficients 91.56%.

The space group was determined by systematic absences $h0l$ with l odd, and $0k0$ with k odd. The structure was solved by heavy-atom methods and refined by full-matrix least squares based on F , with weights $w = 4F_o^2[\sigma^2(I) + (0.02F_o^2)^2]^{-1}$ using the *Enraf–Nonius Structure Determination Package* (Frenz, 1980), scattering factors of Cromer & Waber (1974), anomalous coefficients of Cromer (1974), and data having $I > 3\sigma(I)$. Heavy-atom coordinates were refined with anisotropic thermal parameters; H-atom coordinates were located by ΔF synthesis and were refined with isotropic thermal parameters. Final $R = 0.028$ ($R = 0.041$ for all 3017 data), $wR = 0.038$, $S = 1.810$ for 185 variables. Largest shift was 0.02σ in the final cycle, maximum and minimum residual density 0.45 and -0.37 e Å⁻³, extinction coefficient $g = 8.9$ (5) × 10⁻⁷, where the correction factor $(1 + gI_c)^{-1}$ was applied to F_c .

The fractional coordinates of the title compound are given in Table 1. Fig. 1 is a perspective drawing showing the atom numbering, and Fig. 2 is a unit-

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Table 1. Coordinates and equivalent isotropic thermal parameters

$$B_{eq} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
Fe	0.18310 (2)	0.02059 (3)	0.38809 (2)	2.041 (4)
S	0.43775 (4)	-0.01823 (7)	0.32863 (5)	3.314 (9)
O	0.5286 (1)	-0.0873 (3)	0.2675 (2)	4.92 (4)
C1	0.2510 (1)	0.1234 (2)	0.2397 (2)	2.51 (3)
C2	0.2436 (1)	0.2574 (2)	0.3350 (2)	2.84 (3)
C3	0.1392 (2)	0.2795 (3)	0.3545 (2)	3.37 (4)
C4	0.0814 (1)	0.1625 (3)	0.2704 (2)	3.42 (4)
C5	0.1500 (1)	0.0670 (3)	0.2002 (2)	3.00 (3)
C6	0.2805 (1)	-0.1778 (2)	0.4467 (2)	2.55 (3)
C7	0.2678 (1)	-0.0580 (3)	0.5500 (2)	2.84 (3)
C8	0.1625 (2)	-0.0543 (3)	0.5708 (2)	2.85 (3)
C9	0.1096 (1)	-0.1723 (3)	0.4821 (2)	2.84 (3)
C10	0.1821 (1)	-0.2490 (2)	0.4067 (2)	2.79 (3)
C11	0.3462 (1)	0.0455 (3)	0.1964 (2)	3.13 (4)
C12	0.3757 (1)	-0.2168 (3)	0.3867 (2)	3.52 (4)

Table 2. Bond distances (\AA), selected bond angles ($^\circ$) and selected torsion angles ($^\circ$)

Fe—C1	2.021 (2)	C1—C2	1.427 (3)
Fe—C2	2.040 (2)	C1—C5	1.424 (2)
Fe—C3	2.042 (2)	C1—C11	1.492 (3)
Fe—C4	2.043 (2)	C2—C3	1.420 (3)
Fe—C5	2.021 (2)	C3—C4	1.420 (3)
Fe—C6	2.023 (2)	C4—C5	1.412 (3)
Fe—C7	2.043 (2)	C6—C7	1.431 (3)
Fe—C8	2.047 (2)	C6—C10	1.431 (2)
Fe—C9	2.042 (2)	C6—C12	1.483 (3)
Fe—C10	2.025 (2)	C7—C8	1.426 (3)
S—O	1.501 (2)	C8—C9	1.424 (3)
S—C11	1.826 (2)	C9—C10	1.418 (3)
S—C12	1.827 (2)		
O—S—C11	105.2 (1)	O—S—C12	105.2 (1)
C11—S—C12	100.46 (9)	C2—C1—C5	107.1 (2)
C7—C6—C10	107.1 (2)	C2—C1—C11	126.9 (2)
C7—C6—C12	127.3 (2)	C5—C1—C11	125.9 (2)
C10—C6—C12	125.5 (2)	C1—C2—C3	108.1 (2)
C6—C7—C8	108.1 (2)	C2—C3—C4	108.2 (2)
C7—C8—C9	108.4 (2)	C3—C4—C5	107.7 (2)
C8—C9—C10	107.6 (2)	C1—C5—C4	108.8 (2)
C6—C10—C9	108.9 (2)	S—C11—C1	112.8 (1)
S—C12—C6	113.8 (1)		
O—S—C11—C1	-178.2 (2)	C11—S—C12—C6	-68.6 (2)
C12—S—C11—C1	72.7 (2)	C2—C1—C11—S	46.8 (3)
O—S—C12—C6	-177.7 (2)	C7—C6—C12—S	-55.4 (3)

cell diagram. Bond distances, selected bond angles and torsion angles are presented in Table 2.*

Related literature. For other examples of crystal structures of [3]ferrocenophanes see Hillman & Austin, (1987). Curiously, the 2-thia[3]ferrocenophane (Hillman & Austin, 1987) is also $P2_1/c$ with very similar cell dimensions except that a and c are interchanged. The molecular structure is also very similar to that of the title compound. The Fe—centroid distance in both compounds is approximately 1.63 \AA and the dihedral angle formed by the rings is 5.9 $^\circ$ in the title compound and 6.0 $^\circ$ in

* Lists of H-atom coordinates and thermal parameters, structure-factor amplitudes, bond distances and angles involving H, bond angles, torsion angles, and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54427 (24 pp.). Copies may be obtained through the Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

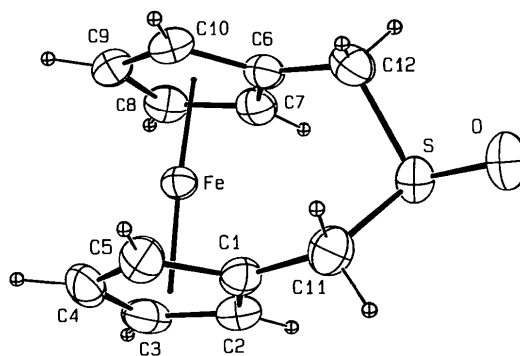
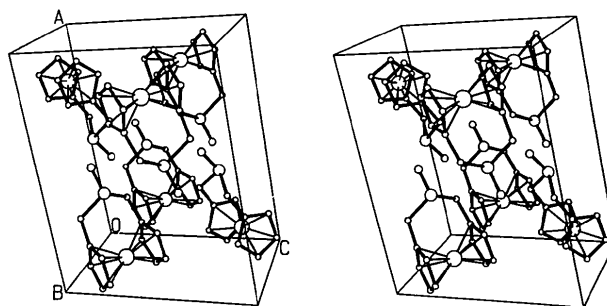


Fig. 1. ORTEP drawing (Johnson, 1965) of the molecule, representing heavy atoms as 50% probability ellipsoids and H atoms as spheres of arbitrary radius.

Fig. 2. PLUTO stereopair (Motherwell & Clegg, 1978) of the unit cell viewed slightly oblique to the b axis.

2-thia[3]ferrocenophane. Also, the average S—methylene-C bond distance is 1.826 \AA for the title compound compared to 1.82 \AA in 2-thia[3]ferrocenophane, with C—S—C bond angles of 100.46 and 101.6 $^\circ$ respectively.

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