Journal of Organometallic Chemistry, 276 (1984) 393–397
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

SYNTHESIS AND STRUCTURE OF DITHIODIIRON HEPTACARBONYL

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(Received May 29th, 1984)

Summary

In addition to $Fe_2(CO)_6S_2$ and $Fe_3(CO)_9S_2$, a novel dithiodiiron heptacarbonyl complex, $Fe_2(CO)_6(S_2CO)$, was isolated in a small yield from the products of the reaction of S_8 with $Fe_3(CO)_{12}$ in THF. The structure of this complex was established by X-ray analysis.

Results and discussion

We found that the reaction of S_8 with $Fe_3(CO)_{12}$ in THF generates, besides $Fe_2(CO)_6S_2$ (I) and $Fe_3(CO)_9S_2$ (II) [1], a new dithiodiiron heptacarbonyl complex, $Fe_2(CO)_6(S_2CO)$ (III), in a low yield (< 1%).

III is present in the reaction mixture in a small amount; this complex is labile and upon heating, easily transforms into I in solution. Its IR spectrum (ν(CO) 1775 cm^{-1}) allows us to suppose that compound III has a bridged structure, a CO molecule being introduced into the Fe–Fe bond, as in the case of the $Fe_2(CO)_7(C_4H_4N_2)$ cluster [2].

This supposition is also based on earlier published work on the isolation and identification of dinuclear iron carbonyl complexes with nitrogen-containing bridges of the $Fe_2(CO)_7L$ type [3]. The formation of an intermediate containing a $Fe_2(CO)_7$

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* Deceased (June 1983).

0022-328X/84/$03.00

TABLE 1

ATOMIC COORDINATES ($\times 10^4$, for Fe $\times 10^5$) AND ANISOTROPIC TEMPERATURE FACTORS IN THE FORM $T = \exp[-1/4(B_{11}h^2a^{*2} + \ldots + 2B_{23}b^*c^*kl)]$ OF COMPOUND III

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	12263(6)	76642(11)	1538(5)	3.18(3)	3.19(3)	2.59(2)	−0.21(3)	0.04(3)	−0.14(2)
S(1)	2429(1)	8905(3)	2500	3.23(8)	3.45(8)	3.77(8)	−0.54(7)	0	0
S(2)	1744(1)	5073(3)	2500	3.68(9)	3.07(8)	4.44(9)	0.04(8)	0	0
O(1)	387(4)	11528(7)	1121(4)	8.8(3)	4.3(2)	7.4(3)	1.2(3)	−1.9(2)	1.0(2)
O(2)	−575(3)	5756(7)	1030(3)	4.3(2)	6.4(3)	5.8(3)	−1.3(2)	−0.2(2)	−1.6(2)
O(3)	2236(4)	7230(8)	−455(3)	8.3(3)	8.4(3)	4.9(2)	−1.5(3)	3.0(2)	−1.6(2)
O(4)	3638(4)	5766(10)	2500	3.7(3)	6.3(3)	11.2(4)	0.6(3)	0	0
C(1)	713(5)	10037(9)	1291(4)	4.8(3)	4.1(3)	3.7(2)	−0.3(3)	−0.7(2)	0.1(2)
C(2)	124(4)	6464(9)	1223(4)	4.0(3)	4.2(3)	3.2(3)	−0.3(3)	0.1(2)	−0.5(2)
C(3)	1829(5)	7352(9)	306(4)	5.3(3)	4.5(3)	3.9(3)	−0.7(3)	0.5(2)	−0.7(2)
C(4)	2861(7)	6380(14)	2500	3.6(4)	4.8(5)	5.2(5)	0.2(4)	0	0

group was assumed in the scheme of reductional decyclization of sulfur organic compounds [4]. The complex $Fe_2(CO)_7$ (1,3-dithiacyclohexane) has been reported but has not been characterized [5]. The formation of III as an intermediate with a Fe–CO–Fe fragment can be surmised in the reaction that yields I:

$$S_8 + Fe_3(CO)_{12} \rightarrow [S_2Fe_2(CO)_7] \rightarrow S_2Fe_2(CO)_6 + CO$$

However, an X-ray study demonstrates that this complex is generated by the introduction of a CO molecule into the S–S bond. Previously, cases have been described of the analogous introduction of CO into the N–S bond in $Fe_2(CO)_6S(CO)NR$ [6] and into the N–N bond in $Fe_2(CO)_6[RN(CO)NR]$ complexes [7–11].

Compound III is the single example of an iron carbonyl cluster with a dithiocarbonyl ligand. It is a yellow-orange coloured crystalline compound which dissolves easily in organic solvents, it is relatively stable in the solid state, and upon standing in solution transforms into I. The structure of III is shown in Fig. 1; the atomic coordinates and anisotropic temperature factors are listed in Table 1, bond lengths in Table 2, and bond angles in Table 3.

The X-ray study demonstrates that the dinuclear complex III has an ordinary Fe–Fe bond supported by the S atoms of the bridged dithiocarbonyl ligand S_2CO, i.e. III has the structural formula $Fe_2(CO)_6(S_2CO)$. III has a molecular symmetry of C_{2v} and a crystallographic one of C_s (the plane *m* includes atoms of the S_2CO ligand which pass normally to the Fe–Fe bond).

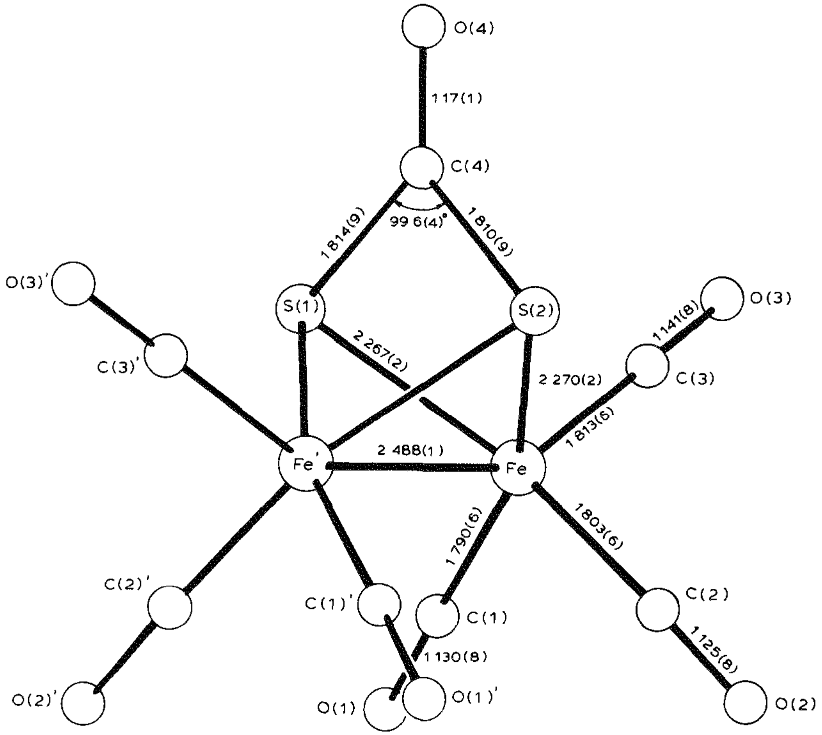

Fig. 1. Structure of $Fe_2(CO)_6(S_2CO)$.

The coordination of the iron atoms in III is identical to that found in $Fe_2(CO)_6S_2$ (I) [12], where the S_2 ligand is bridged between the Fe atoms, i.e. typical of complexes of the $Fe_2(CO)_6X_2$ type [13] (where X = S, RS and R is an organic ligand). The Fe–S bond lengths are 2.267(2) and 2.270(2) Å, slightly shorter than those found in I (2.22 Å), but agree well with the corresponding dimensions in $Fe_2(CO)_6(RS)_2$ type molecules (2.25 ÷ 2.26 Å) [13], where the atoms of the S-bridge are bonded to the carbon atom. In the complex $Fe_2(CO)_6L$ (L = $4\text{-MeC}_6H_4N(CO)S$) [6], the $Fe(CO)_3$ fragments are bonded by the Fe–Fe bond (2.431(4) Å) with bridged atoms N and S of the bridged ligand L, and the Fe–S bond length is 2.279(5) Å.

The length of the ordinary Fe–Fe bond in III, 2.4875(9) Å, is shorter than those found in I (2.55 Å) and in other $Fe_2(CO)_6X_2$ [13] derivatives (the Fe–Fe bond length varies from 2.537 to 2.720 Å). The geometric parameters of the bridged S_2CO ligand in III are C=O 1.17(1) and S–C 1.812(9) Å (average), similar to those found in $Pt(PPh_3)_2(S_2CO)$ and $Pt(S_2CO)$(diphoc) [14], where the S_2CO ligand is coordinated with the Pt atom in a chelate manner (C=O 1.195, S–C 1.803 and 1.755 Å). The Pt–S distances (average 2.34 Å) also agree well with those of Fe–S in III (the covalent radius of Fe (1.34 Å) is shorter, ~ 0.09 Å, than that of Pt (1.43 Å) [15]).

Experimental

The IR spectrum was recorded in hexane on a UR-20 spectrophotometer. The mass spectrum was recorded on an LKB 2091 instrument with a direct inlet to the ion source, at 50 °C and at an ionization energy of 70 eV. The UV spectrum was taken in heptane on a Specord UV-Vis. Crystals of III were crystallized from

TABLE 2

BOND LENGTHS [a] OF COMPOUND III

Bond	d (Å)	Bond	d (Å)	Bond	d (Å)
Fe–Fe′	2.4875(9)	Fe–C(2)	1.803(6)	O(1)–C(1)	1.130(8)
Fe–S(1)	2.267(2)	Fe–C(3)	1.813(6)	O(2)–C(2)	1.125(8)
Fe–S(2)	2.270(2)	S(1)–C(4)	1.814(9)	O(3)–C(3)	1.141(8)
Fe–C(1)	1.790(6)	S(2)–C(4)	1.810(9)	O(4)–C(4)	1.17(1)

[a] Atom Fe′ is Fe taken from crystallographic plane *m* and has coordinates $x, y, \frac{1}{2} - z$.

TABLE 3

BOND ANGLES [a] OF COMPOUND III

Angle	ω (°)	Angle	ω (°)	Angle	ω (°)
Fe′FeS(1)	56.73(4)	S(2)FeC(1)	156.9(2)	Fe′S(2)Fe	66.44(5)
Fe′FeS(2)	56.78(5)	S(2)FeC(2)	93.0(2)	FeS(2)C(4)	84.5(3)
Fe′FeC(1)	100.2(2)	S(2)FeC(3)	103.8(2)	FeC(1)O(1)	178.9(6)
Fe′FeC(2)	102.9(2)	C(1)FeC(2)	90.8(3)	FeC(2)O(2)	178.4(5)
Fe′FeC(3)	151.1(2)	C(1)FeC(3)	98.1(3)	S(1)C(4)S(2)	99.6(4)
S(1)FeS(2)	75.15(6)	C(2)FeC(3)	99.1(3)	FeC(3)O(3)	176.7(6)
S(1)FeC(1)	93.9(2)	Fe′S(1)Fe	66.55(5)	S(1)C(4)O(4)	130.4(6)
S(1)FeC(2)	159.6(2)	FeS(1)C(4)	84.5(3)	S(2)C(4)O(4)	130.0(6)
S(1)FeC(3)	99.9(2)				

[a] Atom Fe′ is Fe taken from crystallographic plane *m* and has coordinates $x, y, \frac{1}{2} - z$.

pentane at $-5\,^\circ$C. X-Ray diffraction studies were performed on a Syntex-P$\bar{1}$ diffractometer (λ(Mo-K_α), graphite monochromator, $\theta/2\theta$-scanning, $3 \leqslant 2\theta \leqslant 54^\circ$, 720 reflections with $F^2 \geqslant 2\sigma$). The crystals are orthorhombic, a 14.131(7), b 6.764(3), c 12.900(8) Å, $Z = 4$, V 1233(1) Å^3, space group *Pnam* (the molecule has crystallographic symmetry C_s). The structure was solved by the heavy atom method and refined by the least-squares method in full matrix anisotropic approximation to $R = 0.029$ ($R_w = 0.036$).

Synthesis of III

A mixture of 105 g (0.41 mol) of S_8 and 252 g (0.5 mol) of $Fe_3(CO)_{12}$ in 1 l THF was stirred for 4 h at 60 °C. Excess THF was removed in vacuo, and the residue was Soxhlet-extracted with pentane. After removal of pentane, the residue was chromatographed on a silica gel column (eluant hexane). Isolated: first fraction (I), m.p. 45 °C; second fraction (II), m.p. 115 °C (cf. [16]); third fraction (III). Yield of I + II, 40%.

III: M.p. 82 °C (pentane). Mass spectrum (m/e): 372 (M^+), 344 ($M^+ - $CO), 316 ($M^+ - 2$CO), 288 ($M^+ - 3$CO), 260 ($M^+ - 4$CO), 232 ($M^+ - 5$CO), 204 ($M^+ - 6$CO), 176 ($M^+ - 7$CO; $Fe_2S_2^+$), 144 (Fe_2S^+), 56 (Fe^+). IR spectrum (ν,cm^{-1}): 2095, 2060, 2023, 1985, 1972 (C≡O), 1775 (C=O), 620, 582, 570, 559, 515, 480, 462. UV spectrum (λ, nm): 215,336. Found: C, 22.80; Fe, 30.34; S, 16.84. $C_7Fe_2S_2O_7$ calcd.: C, 22.60; Fe, 30.03; S, 17.24%.

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