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Synthesis and structure of the trinuclear cluster $Fe_3(\eta^4\text{-}C_6H_8)(\mu\text{-}CO)_2(CO)_6(\mu_3\text{-}S)$

A.I. Nekhaev *, S.D. Alekseeva, B.I. Kolobkov
A.V. Topchiev Institute of Petrochemical Synthesis, Academy of Sciences of the USSR, Leninsky Prospekt 29, Moscow (USSR)

G.G. Aleksandrov
All-Union Scientific Research Institute of Antibiotics, Nagatinskaya St., 3a, Moscow (USSR)

M.T. Toshev and H.B. Dustov
Bukhara Technological Institute of Food and Light Industry, Leninsky Komsomol Prospekt 15, Bukhara (USSR)

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Abstract

Along with the dithiolatodiironhexacarbonyl complex $Fe_2(C_6H_8S_2)(CO)_6$, μ_3-thio-η^4-cyclohexa-1,3-diene-(Fe^1)-di-μ-carbonyl(Fe^1,Fe^2;Fe^1,Fe^3)hexacarbonyltriiron $Fe_3(\eta^4\text{-}C_6H_8)(\mu\text{-}CO)_2(CO)_6(\mu_3\text{-}S)$ has been isolated and characterized by an X-ray study from the interaction products of cyclohexa-1,3-diene with sulfur and $Fe_3(CO)_{12}$.

Results and discussion

Earlier we reported [1] that the interaction of cyclohexa-1,3-diene and cycloocta-1,5-diene with sulfur and $Fe_3(CO)_{12}$ results in the implantation of sulfur atoms at one double bond of the diene, with the formation of the corresponding dithiolatodiironhexacarbonyl complexes.

The present paper reports the isolation and establishment of the structure of a new complex $Fe_3(\eta^4\text{-}C_6H_8)(\mu\text{-}CO)_2(CO)_6(\mu_3\text{-}S)$ (II), which was formed in the reaction of cyclohexa-1,3-diene with sulfur and $Fe_3(CO)_{12}$ (Eq. 1) with a yield of 3%.

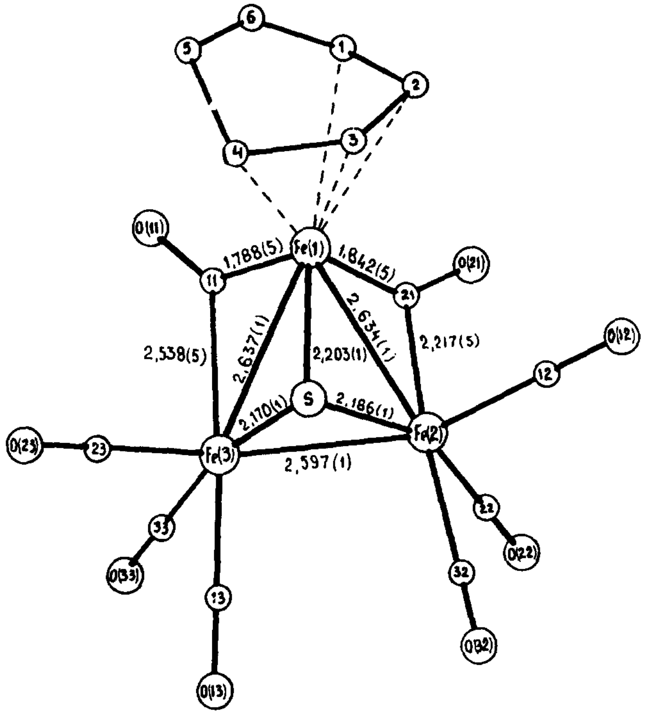
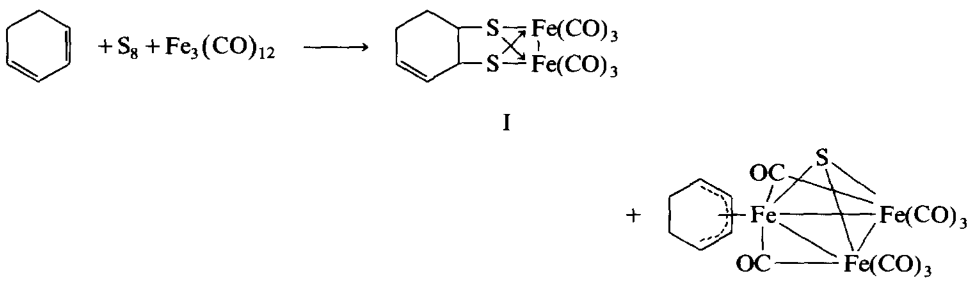


Fig. 1. The structure of $Fe_3(\eta^4\text{-}C_6H_8)(\mu\text{-}CO)_2(CO)_6(\mu_3\text{-}S)$.



$$+ Fe_2(CO)_6S_2 + Fe_3(CO)_9S_2 + Fe_3(CO)_{10}S\,^{*} + Fe_2(CO)_6(S_2CO) \qquad (1)$$

III IV V VI

Ironcarbonyl complexes of diene hydrocarbons (cyclohexa-1,3-diene, cycloocta-1,5-diene or norbornadiene) could not be formed in the presence of sulfur [1], owing to the fact that sulfur is a more favourable reagent for ironcarbonyl. As a result of their interaction, the formation of compounds III–VI occurred [2,3], and sulfur underwent activation which allowed it to join to the double bond under mild conditions [1,2].

The route to the formation of the trinuclear complex II is not clear. Since the ironcarbonyl complex of cyclohexa-1,3-diene could not be found among the pro-

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* Complex V was present in the reaction mixture only if the latter contained $Fe_3(CO)_{12}$ [1,2].

ducts of the reaction, it seems possible that the substitution of two CO groups of thiodecacarbonyltriiron (V) by the η^4-C_6H_8 ligand takes place in situ. The substitution of two terminal CO-groups by norbornadiene was observed previously for bis(methylthiotricarbonyliron) [4].

A cluster of the form $Fe_2(\eta^5\text{-}MeC_5H_4)Mn(\mu\text{-}CO)_2(CO)_6(\mu_3\text{-}S)$ (VII) was formed with a yield of 8% as a result of reaction [5,6] and was structurally similar to complex II:

$$MeC_5H_4Mn(CO)_2S^tBu + Fe_3(CO)_{12} \xrightarrow[\text{toluene}]{60\,°C} \text{VII} \qquad (2)$$

Isoelectronic and isostructural complexes $Fe_2(\eta^5\text{-}C_5H_5)Mn(\mu\text{-}CO)_2(CO)_6(\mu_3\text{-}PR)$ ($R = C_6H_{11}$ [7], C_6H_5 [8]) are known for compound VII, and all three complexes have been subjected to an X-ray study. The row of trinuclear carbene compounds with a core similar to that of II are also known. These are $Fe_3(\eta^5\text{-}L)(\mu\text{-}CO)_2(CO)_6(\mu_3\text{-}CR)$ complexes, where L = cyclopentadienyl or substituted cyclopentadienyl, $R = CH_3$, $CH{=}CH_2$, C_2H_5, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$ [9].

It was established by an X-ray structural study that in a molecule of II (Fig. 1) ligands of different types are simultaneously present: η^4-cyclohexa-1,3-diene, μ_3-S, and bridged and terminal carbonyl groups. There is an unusual (for the products of the reaction of unsaturated hydrocarbons with elemental sulfur and $Fe_3(CO)_{12}$) π-coordination of cyclohexa-1,3-diene ligand with one of the iron atoms in the trinuclear cluster II. Three iron atoms form a nearly equilateral triangle with three metal–metal bonds. The sulfur atom is situated 1.58 Å from the triangular plane and forms a μ_3-bridge for the triangle. Thus the Fe_3S core of the molecule is a tetrahedron with three Fe atoms and a μ_3-bridging S atom at its apices.

Both carbonyl groups on the Fe(1) atom coordinated by η^4-type bonds with the butadiene system of cyclohexa-1,3-diene are unsymmetrical bridging ones, and the Fe(2) and Fe(3) atoms, in addition to forming bonds with their own terminal carbonyl groups, take part in the interaction with C(11) and C(21) atoms (the Fe(3)–C(11) and Fe(2)–C(21) distances are 2.538(5) and 2.217(5) Å, respectively). As a result of the interaction with other Fe atoms the linearity of these semi-bridging Fe(1)–CO fragments was disturbed (the angles Fe(1)–C(11)–O(11) and Fe(1)–C(21)–O(21) are 166.2(4) and 152.3(4)°, respectively). It seems that this interaction compensates, on the one hand, the surplus electronic density on the Fe(1) atom, and, on the other hand, its deficiency on atoms Fe(2) and Fe(3).

In accordance with the presence of a surplus of electronic density on the Fe(1) atom, the bonds in which it participates are slightly longer in comparison with analogous steric equivalents. For example, the Fe(1)–Fe(2) and Fe(1)–Fe(3) bond lengths are 2.634(1) and 2.637(1) Å, larger than those for Fe(2)–Fe(3) (2.597(1) Å). The Fe(1)–S bond length is 2.203(1) Å, and the lengths of the two other bonds, Fe(2)–S and Fe(3)–S, are 2.186(1) and 2.170(1) Å, respectively.

The molecular geometry of II is very similar to that found in VII [5]. The average Fe–Fe bond length is 2.623 Å, slightly larger than the bond length found in $Fe_3(\mu_3\text{-}CO)(CO)_9(\mu_3\text{-}S)$ (2.606 Å) [2,10], but shorter than the average dimensions in tetrahedral $Fe_3(\mu_3\text{-}S)$ complexes: 2.657 Å in $Fe_3(CO)_9H(\mu_3\text{-}S\text{-}i\text{-}C_3H_7)$ [11] and 2.644 Å in $Fe_3(CO)_9H(\mu_3\text{-}S\text{-}c\text{-}C_6H_{11})$ [12]. The average Fe–S (2.186 Å) bond length dimension agreed with one in cluster VII.

As in bis(η^4-cyclohexa-1,3-diene)carbonyliron [13,14], the Fe–C distances to the end-capping atoms of the butadiene system are 2.155(5) and 2.156(5) Å, distances

Table 1

Atomic coordinates ($\times 10^4$) and their anisotropic temperature factors ($\times 10^3$) for compound II

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe(1)	1999(1)	2207(1)	2945(1)	29(1)	24(1)	26(1)	2(1)	8(1)	4(1)
Fe(2)	4026(1)	1832(1)	2167(1)	32(1)	36(1)	45(1)	5(1)	15(1)	10(1)
Fe(3)	2949(1)	4308(1)	1805(1)	42(1)	26(1)	35(1)	5(1)	15(1)	3(1)
S	3876(1)	3511(1)	3973(1)	35(1)	37(1)	32(1)	0(1)	5(1)	−3(1)
O(11)	−134(4)	3512(5)	877(5)	42(2)	61(2)	71(3)	25(2)	7(2)	9(2)
O(21)	1612(4)	−298(5)	504(5)	62(3)	59(3)	63(3)	−23(2)	27(2)	−8(2)
O(12)	4771(5)	−967(5)	3383(6)	102(3)	64(2)	87(3)	29(2)	38(3)	41(2)
O(22)	3576(5)	930(6)	−1121(5)	98(3)	77(3)	58(2)	9(2)	46(2)	16(3)
O(32)	6678(4)	3013(9)	2900(9)	47(2)	114(5)	211(7)	−11(5)	46(2)	5(3)
O(13)	5162(5)	5971(6)	1615(6)	101(3)	75(3)	90(3)	−2(3)	53(2)	−18(2)
O(23)	1884(3)	6983(5)	2771(7)	113(4)	45(2)	104(4)	8(2)	47(3)	24(2)
O(33)	1626(6)	3730(7)	−1545(5)	92(4)	104(4)	40(3)	11(3)	15(3)	27(3)
C(1)	514(5)	650(6)	3026(6)	48(3)	41(3)	46(3)	4(2)	23(2)	−6(2)
C(2)	1709(5)	619(6)	4249(6)	58(3)	44(3)	47(3)	16(2)	29(2)	4(2)
C(3)	2189(5)	2021(7)	5207(6)	47(3)	59(3)	30(2)	11(2)	16(2)	6(2)
C(4)	1423(5)	3218(6)	4786(6)	50(3)	47(3)	32(2)	−4(2)	16(2)	4(2)
C(5)	−21(5)	2980(8)	4333(7)	43(3)	73(4)	55(3)	−8(3)	26(2)	7(2)
C(6)	−543(5)	1467(8)	3312(7)	42(3)	68(4)	54(3)	0(3)	27(2)	−5(3)
C(11)	802(5)	3117(6)	1643(7)	43(3)	32(2)	45(3)	7(2)	10(2)	8(2)
C(21)	2059(5)	734(6)	1432(6)	40(3)	36(3)	38(3)	−2(2)	16(2)	2(2)
C(12)	4488(6)	121(7)	2937(7)	55(3)	52(3)	54(3)	11(3)	18(3)	23(2)
C(22)	3736(5)	1299(7)	150(7)	56(3)	48(3)	56(3)	14(2)	34(2)	13(2)
C(32)	5618(7)	2553(9)	2557(11)	46(3)	65(4)	112(6)	−8(4)	20(3)	0(3)
C(13)	4311(6)	5317(7)	1704(7)	56(3)	45(3)	58(3)	3(2)	29(3)	−9(3)
C(23)	2284(6)	5946(6)	2383(7)	65(4)	34(3)	54(3)	4(2)	28(3)	5(3)
C(33)	2112(6)	3954(7)	−261(7)	61(3)	48(3)	42(3)	13(2)	18(3)	17(3)

that are slightly larger than those to the central atoms, 2.075(5) and 2.082(5) Å; the C(1)–C(2), C(2)–C(3) and C(3)–C(4) bond lengths, coordinated by the Fe(1) atom, are 1.440(7), 1.425(7) and 1.422(7) Å, respectively. The cyclohexa-1,3-diene ligand

Table 2

Bond lengths (Å) for compound II

Fe(1)–Fe(2)	2.634(1)	Fe(3)–C(23)	1.795(5)
Fe(1)–Fe(3)	2.637(1)	Fe(3)–C(33)	1.818(6)
Fe(2)–Fe(3)	2.597(1)	Fe(3)–C(11)	2.538(5)
Fe(1)–S	2.203(1)	C(11)–O(11)	1.152(6)
Fe(2)–S	2.186(1)	C(21)–O(21)	1.156(6)
Fe(3)–S	2.170(1)	C(12)–O(12)	1.132(6)
Fe(1)–C(1)	2.156(5)	C(22)–O(22)	1.144(6)
Fe(1)–C(2)	2.075(5)	C(32)–O(32)	1.162(7)
Fe(1)–C(3)	2.082(5)	C(13)–O(13)	1.130(7)
Fe(1)–C(4)	2.155(5)	C(23)–O(23)	1.131(6)
Fe(1)–C(11)	1.788(5)	C(33)–O(33)	1.126(6)
Fe(1)–C(21)	1.842(5)	C(1)–C(2)	1.440(7)
Fe(2)–C(12)	1.809(6)	C(2)–C(3)	1.425(7)
Fe(2)–C(22)	1.801(5)	C(3)–C(4)	1.422(7)
Fe(2)–C(32)	1.769(6)	C(4)–C(5)	1.525(7)
Fe(2)–C(21)	2.217(5)	C(5)–C(6)	1.534(9)
Fe(3)–C(13)	1.776(6)	C(6)–C(1)	1.507(7)

Table 3

Bond angles (degrees) for compound II

Fe(2)-Fe(1)-Fe(3)	59.0(1)	S-Fe(2)-C(21)	97.0(1)
Fe(1)-Fe(2)-Fe(3)	60.6(1)	S-Fe(2)-C(22)	147.4(2)
Fe(1)-Fe(3)-Fe(2)	60.4(1)	S-Fe(2)-C(12)	109.8(2)
Fe(2)-Fe(1)-S	52.8(1)	S-Fe(2)-C(32)	90.3(3)
Fe(3)-Fe(1)-S	52.3(1)	S-Fe(3)-C(13)	97.6(2)
Fe(1)-Fe(2)-S	53.4(1)	S-Fe(3)-C(23)	102.4(2)
Fe(3)-Fe(2)-S	53.1(1)	S-Fe(3)-C(33)	150.7(2)
Fe(1)-Fe(3)-S	53.5(1)	S-Fe(3)-C(11)	91.0(1)
Fe(2)-Fe(3)-S	53.7(1)	C(21)-Fe(1)-C(11)	93.8(2)
Fe(1)-S-Fe(2)	73.7(1)	C(21)-Fe(2)-C(12)	84.6(2)
Fe(1)-S-Fe(3)	74.2(1)	C(21)-Fe(2)-C(22)	80.3(2)
Fe(2)-S-Fe(3)	73.2(1)	C(12)-Fe(2)-C(22)	102.4(2)
Fe(2)-Fe(1)-C(11)	114.0(2)	C(21)-Fe(2)-C(32)	172.7(3)
Fe(3)-Fe(1)-C(11)	66.8(2)	C(12)-Fe(2)-C(32)	93.6(3)
Fe(2)-Fe(1)-C(21)	56.1(1)	C(22)-Fe(2)-C(32)	93.2(3)
Fe(3)-Fe(1)-C(21)	92.3(1)	C(11)-Fe(3)-C(23)	80.6(2)
Fe(1)-Fe(2)-C(12)	99.8(2)	C(11)-Fe(3)-C(33)	78.5(2)
Fe(3)-Fe(2)-C(12)	158.7(2)	C(13)-Fe(3)-C(23)	94.7(3)
Fe(1)-Fe(2)-C(21)	43.6(1)	C(13)-Fe(3)-C(33)	95.2(3)
Fe(3)-Fe(2)-C(21)	85.4(1)	C(13)-Fe(3)-C(11)	170.9(2)
Fe(1)-Fe(2)-C(22)	116.3(2)	C(23)-Fe(3)-C(33)	102.6(2)
Fe(3)-Fe(2)-C(22)	94.4(2)	Fe(1)-C(11)-Fe(3)	72.8(2)
Fe(1)-Fe(2)-C(32)	143.7(3)	Fe(1)-C(21)-Fe(2)	80.3(2)
Fe(3)-Fe(2)-C(32)	98.6(2)	Fe(1)-C(11)-O(11)	166.2(4)
Fe(1)-Fe(3)-C(11)	40.4(1)	Fe(1)-C(21)-O(21)	152.3(4)
		Fe(2)-C(21)-O(21)	127.4(4)
Fe(2)-Fe(3)-C(11)	93.4(1)	Fe(2)-C(12)-O(12)	178.3(6)
Fe(1)-Fe(3)-C(13)	148.7(2)	Fe(2)-C(22)-O(22)	178.1(5)
Fe(2)-Fe(3)-C(13)	94.0(2)	Fe(2)-C(32)-O(32)	176.1(8)
Fe(1)-Fe(3)-C(23)	102.7(2)	Fe(3)-C(11)-O(11)	121.0(4)
Fe(2)-Fe(3)-C(23)	155.5(2)	Fe(3)-C(13)-O(13)	178.6(6)
Fe(1)-Fe(3)-C(33)	106.0(2)	Fe(3)-C(23)-O(23)	178.7(6)
Fe(2)-Fe(3)-C(33)	99.3(2)	Fe(3)-C(33)-O(33)	178.0(6)
S-Fe(1)-C(11)	114.6(2)	S-Fe(1)-C(21)	108.9(1)

has a half-chair conformation: the C(5) and C(6) atoms are on different sides of the plane comprising the four atoms of the ring at 0.89 and 0.90 Å, respectively. For terminal carbonyl groups the Fe–CO and C–O bond lengths vary from 1.766(6) to 1.842(5) and from 1.126(6) to 1.156(6) Å, respectively, and the Fe–C–O fragments are nearly linear (176.1–178.7°). The atomic coordinates and their anisotropic temperature factors, bond lengths and bond angles for compound II are listed in Tables 1–3.

Experimental

The IR spectrum was recorded in hexane on a UR-20 spectrophotometer. The mass spectrum was recorded on a Varian MAT-311A instrument with a direct inlet into the ion source at 80 °C and an ionization energy of 70 eV. The yields were determined relative to iron used for the reaction. An X-ray diffraction study was performed on a Syntex-P$\bar{1}$ diffractometer (λ(Mo-K_α), graphite monochromator,

$\theta/2\theta$ scanning, $3 \leqslant 2\theta \leqslant 51°$). Crystals of II are triclinic, a 11.203(6), b 9.061(5), c 9.355(5) Å, α 97.01(3), β 109.85(3), γ 92.69(3)°, V 880.6(9) Å^3, $Z = 2$, with space group $P\bar{1}$. The structure was solved by direct method and refined by the least-squares method in an anisotropic full-matrix approximation to $R = 0.047$ ($R_w = 0.050$) for 2983 reflections with $F^2 \geqslant 2\sigma$. Crystals of II were obtained from hexane at −5°C.

Synthesis of II

A mixture of 100 ml of cyclohexa-1,3-diene, sulfur (1.92 g, 0.06 g-at) and $Fe_3(CO)_{12}$ (5.04 g, 0.01 mol) was stirred for 10 h at 55°C under flowing Ar. Diene was removed under reduced pressure. The residue was extracted by hexane in a Soxhlet apparatus until the solvent became colourless. The hexane solution was evaporated to minimal volume and chromatographed on a silica gel column with hexane as eluent. Isolated: first fraction III; second fraction IV; third fraction I; fourth fraction VI; fifth fraction complex II, dark-brown crystals. Obtained: 0.4 g (8%) of III, 1.8 g (38%) of IV, 0.5 g (8%) of I, 0.06 g (1%) of VI, 0.15 g (3%) of II. For II: M.p. 115–117°C (dec.) (hexane). IR spectrum (ν, cm^{-1}): 2077, 2066, 2049, 2035, 2015, 1998 (C≡O), 1940, 1932, 1902, 1876 (C=O). Mass spectrum (m/z): 504, M^+; 476, $(M-CO)^+$: 448, $(M-2CO)^+$; 420, $(M-3CO)^+$; 392, $(M-4CO)^+$; 364, $(M-5CO)^+$; 336, $(M-6CO)^+$; 308, $(M-7CO)^+$; 280, $(M-8CO)^+$; 200,Fe_3S^+; 144, Fe_2S^+. Found: C, 33.50; H, 1.68; Fe, 33.40; S, 6.35. $C_{14}H_8Fe_3O_8S$ calcd.: C, 33.38; H, 1.60; Fe, 33.25; S, 6.36%.

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