Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1161). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The First μ_4-Se Spiro-Type Fe_4Se_3 Cluster: $[(\mu\text{-}4\text{-}CH_3\text{-}C_6H_4Se)Fe_2(CO)_6]_2(\mu_4\text{-}Se)$

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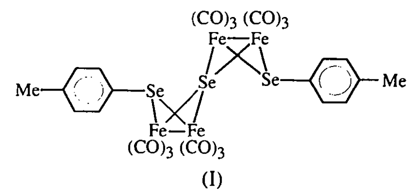
Abstract

In the molecule of the title cluster compound, μ_4-selenido-bis[μ-(4-tolylselenido)-hexacarbonyldiiron], two identical $(\mu\text{-}4\text{-}CH_3C_6H_4Se)Fe_2(CO)_6$ moieties are joined by a spiro-type four-coordinate Se atom, μ_4-Se. The four Se—Fe bond lengths around the central Se atom are 2.353 (3), 2.353 (3), 2.347 (3) and 2.358 (3) Å. The average (2.353 Å) is shorter than that (2.392 Å) of Se—Fe bond lengths formed between Fe atoms and the 4-tolylselenido ligands. In each diiron subcluster core, the 4-tolylselenido ligand is bridged between two Fe atoms.

Comment

In the course of our study on the reactions of alkylselenido-bridged anions $(\mu\text{-}R\text{Se})(\mu\text{-Se}^-)Fe_2(CO)_6$ (Song, Yan, Hu, Wang & Wang, 1995) with SO_2Cl_2, the title cluster, $[(\mu\text{-}4\text{-}CH_3C_6H_4Se)Fe_2(CO)_6]_2(\mu_4\text{-Se})$, (I), was isolated, which is the first spiro-type μ_4-Se cluster complex with an Fe_4Se_3 core.



(I)

The crystal of the title cluster is monoclinic and consists of discrete molecules. There are two crystallographically independent molecules in the asymmetric unit. However, only one set of bond lengths and angles are listed (Table 2) since those of the two independent molecules are essentially the same, the slight differences between them being considered as experimental error.

The molecule consists of two identical subclusters, $(\mu\text{-}4\text{-}CH_3C_6H_4Se)Fe_2(CO)_6$, joined together by a spiro-type four-coordinate Se atom, μ_4-Se, which is situated on the center of a distorted tetrahedron constructed by four Fe atoms; the 4-tolylselenido ligand (μ-$SeC_6H_4CH_3$-4) bridges two Fe atoms in each subcluster core. The structure is very similar to that of its sulfur analogs, $[(\mu\text{-}RS)Fe_2(CO)_6]_2(\mu_4\text{-S})$ (R = CH_3, C_2H_5) (Coleman, Wojcicki, Pollick & Dahl, 1967; Song, Kadiata, Wang, Wang & Wang, 1988).

In this cluster compound, the bond distances between the μ_4-Se atom and the four Fe atoms are almost the same [Se(1)—Fe(1) 2.353 (3), Se(1)—Fe(2) 2.353 (3), Se(1)—Fe(3) 2.347 (3), Se(1)—Fe(4) 2.358 (3) Å], but slightly shorter than those between the Fe atoms and the bridging Se atoms attached to the tolyl groups [Se(2)—Fe(1) 2.392 (3) and Se(2)—Fe(2) 2.390 (4) Å; Se(3)—Fe(3) 2.386 (3) and Se(3)—Fe(4) 2.400 (4) Å]. This may mean that the bonds formed between Fe and μ_4-Se atoms are stronger than those formed between Fe and μ_2-Se atoms. The two Fe—Fe bond distances in

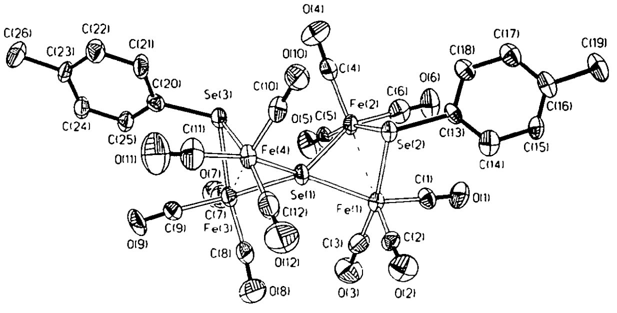


Fig. 1. Molecular structure of the title cluster showing 35% probability displacement ellipsoids. H atoms are omitted for clarity.

this molecule are very similar [Fe(1)—Fe(2) 2.601 (4), Fe(3)—Fe(4) 2.575 (4) Å] and slightly longer than the Fe—Fe bond distance in another hexacarbonyldiiron cluster with Se atoms bridging Fe atoms, namely [μ-Se(Ph)CC(H)Se-μ]$Fe_2(CO)_6$ (2.534 Å; Mathur, Hossain, Das & Sinha, 1993). The coordination geometry around each Fe atom is distorted tetragonal bipyramidal with two carbonyl groups and two Se atoms at the equatorial positions, and the other carbonyl and Fe atom at the axial positions. Each 4-tolyl group is attached to its bridging μ_2-Se atom by an e-type of bond, as seen intuitively from Fig. 1.

Experimental

The title compound was prepared through reaction of $[(\mu\text{-}4\text{-}CH_3C_6H_4Se)(\mu\text{-}Se)Fe_2(CO)_6]^-$ with SO_2Cl_2 in thf. The dark red crystals were obtained by recrystallization from CH_2Cl_2–hexane at 255 K.

Crystal data

$[Fe_4Se(C_7H_7Se)_2(CO)_{12}]$
$M_r = 978.64$
Monoclinic
$P2_1/n$
$a = 11.059\ (2)$ Å
$b = 32.367\ (6)$ Å
$c = 18.933\ (3)$ Å
$\beta = 97.14\ (3)°$
$V = 6720\ (2)$ Å^3
$Z = 8$
$D_x = 1.934$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 23 reflections
$\theta = 7–15°$
$\mu = 5.00$ mm^{-1}
$T = 294$ K
Block
0.40 × 0.40 × 0.20 mm
Dark red

Data collection

Siemens *P4/PC* four-circle diffractometer
ω scans
Absorption correction: ψ scans
$T_{min} = 0.173$, $T_{max} = 0.373$
8904 measured reflections
8195 independent reflections
3509 observed reflections $[F_o \geq 4\sigma(F_o)]$

$R_{int} = 0.023$
$\theta_{max} = 22°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 34$
$l = -19 \rightarrow 19$
3 standard reflections monitored every 100 reflections intensity decay: 5.0%

Refinement

Refinement on F
$R = 0.060$
$wR = 0.053$
$S = 1.19$
3509 reflections
811 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(|F_o|) + 0.0003|F_o|^2]$

$(\Delta/\sigma)_{max} = 0.32$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.72$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

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

	x	y	z	U_{eq}
Se(1)	0.9447 (2)	0.0927 (1)	0.8115 (1)	0.048 (1)
Se(2)	0.7236 (2)	0.0390 (1)	0.8177 (1)	0.046 (1)
Se(3)	1.1861 (2)	0.0640 (1)	0.8846 (1)	0.048 (1)
Fe(1)	0.7508 (3)	0.0976 (1)	0.7444 (2)	0.043 (1)
Fe(2)	0.8873 (3)	0.0320 (1)	0.7475 (2)	0.048 (1)
Fe(3)	1.1284 (3)	0.1296 (1)	0.8339 (2)	0.049 (1)
Fe(4)	1.0213 (3)	0.0972 (1)	0.9334 (2)	0.050 (1)
O(1)	0.5802 (12)	0.0660 (4)	0.6278 (7)	0.077 (3)
O(2)	0.5867 (14)	0.1536 (4)	0.8070 (7)	0.084 (3)
O(3)	0.8317 (14)	0.1618 (5)	0.6516 (8)	0.098 (3)
O(4)	1.0123 (15)	−0.0374 (5)	0.8277 (9)	0.111 (3)
O(5)	1.0674 (13)	0.0496 (5)	0.6527 (8)	0.089 (3)
O(6)	0.7370 (12)	−0.0146 (4)	0.6353 (8)	0.086 (3)
O(7)	1.2742 (15)	0.1236 (5)	0.7156 (9)	0.101 (3)
O(8)	1.0122 (14)	0.2067 (5)	0.7842 (10)	0.112 (3)
O(9)	1.2886 (14)	0.1776 (4)	0.9396 (8)	0.092 (3)
O(10)	0.8999 (13)	0.0268 (4)	0.9903 (8)	0.083 (3)
O(11)	1.1691 (17)	0.1217 (6)	1.0655 (9)	0.134 (3)
O(12)	0.8433 (16)	0.1599 (5)	0.9529 (10)	0.127 (3)
C(1)	0.6478 (18)	0.0791 (6)	0.6733 (10)	0.052 (3)
C(2)	0.6548 (17)	0.1323 (5)	0.7826 (10)	0.045 (3)
C(3)	0.8032 (18)	0.1359 (6)	0.6847 (11)	0.065 (3)
C(4)	0.9663 (18)	−0.0103 (6)	0.7970 (11)	0.062 (3)
C(5)	0.9973 (18)	0.0432 (6)	0.6893 (11)	0.053 (3)
C(6)	0.7957 (18)	0.0032 (7)	0.6806 (11)	0.063 (3)
C(7)	1.2159 (19)	0.1271 (7)	0.7609 (12)	0.071 (3)
C(8)	1.0527 (17)	0.1755 (6)	0.8047 (11)	0.060 (3)
C(9)	1.2290 (17)	0.1577 (6)	0.8993 (11)	0.055 (3)
C(10)	0.9470 (17)	0.0547 (7)	0.9668 (10)	0.057 (3)
C(11)	1.1143 (21)	0.1116 (8)	1.0131 (13)	0.092 (3)
C(12)	0.9130 (20)	0.1351 (7)	0.9436 (12)	0.079 (3)
C(13)	0.5816 (16)	0.0080 (5)	0.7785 (9)	0.040 (3)
C(14)	0.4694 (18)	0.0262 (7)	0.7645 (10)	0.062 (3)
C(15)	0.3663 (16)	0.0027 (6)	0.7411 (9)	0.047 (3)
C(16)	0.3723 (18)	−0.0387 (6)	0.7325 (10)	0.059 (3)
C(17)	0.4843 (19)	−0.0574 (6)	0.7479 (10)	0.062 (3)
C(18)	0.5871 (17)	−0.0346 (6)	0.7698 (9)	0.050 (3)
C(19)	0.2587 (17)	−0.0646 (6)	0.7094 (10)	0.077 (3)
C(20)	1.3364 (16)	0.0679 (5)	0.9472 (10)	0.042 (3)
C(21)	1.3532 (17)	0.0442 (6)	1.0075 (10)	0.059 (3)
C(22)	1.4650 (18)	0.0433 (6)	1.0496 (11)	0.063 (3)
C(23)	1.5634 (16)	0.0648 (6)	1.0328 (10)	0.046 (3)
C(24)	1.5466 (17)	0.0887 (6)	0.9711 (10)	0.054 (3)
C(25)	1.4344 (16)	0.0890 (5)	0.9285 (10)	0.050 (3)
C(26)	1.6833 (17)	0.0633 (6)	1.0802 (10)	0.077 (3)
Se(4)	1.1501 (2)	0.1894 (1)	0.4165 (1)	0.055 (1)
Se(5)	0.9155 (2)	0.1665 (1)	0.3272 (1)	0.055 (1)
Se(6)	1.3757 (2)	0.1394 (1)	0.4142 (1)	0.050 (1)
Fe(5)	1.0931 (3)	0.1996 (1)	0.2929 (2)	0.061 (1)
Fe(6)	0.9723 (3)	0.2287 (1)	0.3900 (2)	0.050 (1)
Fe(7)	1.2011 (3)	0.1262 (1)	0.4735 (2)	0.044 (1)
Fe(8)	1.3321 (3)	0.1916 (1)	0.4960 (2)	0.052 (1)
O(13)	0.9749 (15)	0.2355 (5)	0.1618 (10)	0.120 (3)
O(14)	1.2746 (15)	0.2630 (6)	0.2985 (11)	0.142 (3)
O(15)	1.2031 (17)	0.1289 (5)	0.2317 (9)	0.124 (3)
O(16)	0.8108 (15)	0.2193 (5)	0.5002 (9)	0.110 (3)
O(17)	1.0978 (13)	0.3010 (4)	0.4520 (9)	0.090 (3)
O(18)	0.8244 (13)	0.2789 (4)	0.2871 (9)	0.089 (3)
O(19)	1.0350 (16)	0.1444 (5)	0.5752 (9)	0.114 (3)
O(20)	1.3228 (12)	0.0656 (4)	0.5743 (8)	0.081 (3)
O(21)	1.0544 (13)	0.0688 (4)	0.3793 (8)	0.091 (3)
O(22)	1.5001 (13)	0.1605 (4)	0.6152 (8)	0.090 (3)
O(23)	1.4883 (16)	0.2570 (5)	0.4508 (10)	0.138 (3)
O(24)	1.1977 (15)	0.2349 (5)	0.5961 (9)	0.110 (3)
C(27)	1.0194 (20)	0.2201 (7)	0.2163 (13)	0.085 (3)
C(28)	1.2037 (21)	0.2376 (6)	0.2940 (12)	0.073 (3)
C(29)	1.1646 (21)	0.1562 (7)	0.2565 (12)	0.087 (3)
C(30)	0.8733 (19)	0.2225 (6)	0.4565 (12)	0.068 (3)
C(31)	1.0514 (17)	0.2724 (6)	0.4270 (10)	0.053 (3)
C(32)	0.8763 (20)	0.2587 (7)	0.3278 (12)	0.078 (3)
C(33)	1.0978 (21)	0.1380 (7)	0.5316 (13)	0.085 (3)

C(34)	1.2787 (18)	0.0900 (6)	0.5332 (11)	0.053 (3)
C(35)	1.1118 (17)	0.0914 (6)	0.4155 (10)	0.052 (3)
C(36)	1.4325 (19)	0.1723 (6)	0.5681 (11)	0.061 (3)
C(37)	1.4245 (21)	0.2320 (7)	0.4700 (13)	0.091 (3)
C(38)	1.2552 (21)	0.2192 (7)	0.5546 (13)	0.088 (3)
C(39)	0.7690 (17)	0.1750 (5)	0.2591 (10)	0.049 (3)
C(40)	0.7667 (19)	0.1656 (6)	0.1889 (10)	0.064 (3)
C(41)	0.6546 (21)	0.1681 (7)	0.1467 (12)	0.084 (3)
C(42)	0.5535 (22)	0.1810 (7)	0.1724 (14)	0.090 (3)
C(43)	0.5538 (22)	0.1909 (7)	0.2415 (14)	0.106 (3)
C(44)	0.6633 (18)	0.1880 (6)	0.2880 (11)	0.067 (3)
C(45)	0.4345 (19)	0.1844 (7)	0.1216 (11)	0.117 (3)
C(46)	1.5152 (16)	0.1076 (5)	0.4489 (9)	0.041 (3)
C(47)	1.5137 (17)	0.0649 (6)	0.4447 (10)	0.055 (3)
C(48)	1.6139 (16)	0.0412 (6)	0.4587 (9)	0.045 (3)
C(49)	1.7291 (18)	0.0608 (7)	0.4771 (10)	0.060 (3)
C(50)	1.7294 (19)	0.1028 (7)	0.4861 (11)	0.072 (3)
C(51)	1.6233 (17)	0.1268 (6)	0.4699 (10)	0.056 (3)
C(52)	1.8445 (17)	0.0338 (6)	0.4933 (11)	0.081 (3)

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

Se(1)—Fe(1)	2.353 (3)	Se(1)—Fe(2)	2.353 (3)
Se(1)—Fe(3)	2.347 (3)	Se(1)—Fe(4)	2.358 (3)
Se(2)—Fe(1)	2.392 (3)	Se(2)—Fe(2)	2.390 (4)
Se(2)—C(13)	1.93 (2)	Se(3)—Fe(3)	2.386 (3)
Se(3)—Fe(4)	2.400 (4)	Se(3)—C(20)	1.92 (2)
Fe(1)—Fe(2)	2.601 (4)	Fe(3)—Fe(4)	2.575 (4)
Fe(1)—Se(1)—Fe(2)	67.1 (1)	Fe(1)—Se(1)—Fe(3)	140.4 (1)
Fe(2)—Se(1)—Fe(3)	133.4 (1)	Fe(1)—Se(1)—Fe(4)	135.4 (1)
Fe(2)—Se(1)—Fe(4)	126.4 (1)	Fe(3)—Se(1)—Fe(4)	66.4 (1)
Fe(1)—Se(2)—Fe(2)	65.9 (1)	Fe(3)—Se(3)—Fe(4)	65.1 (1)
Se(1)—Fe(1)—Se(2)	78.9 (1)	Se(1)—Fe(2)—Se(2)	78.9 (1)
Se(1)—Fe(3)—Se(3)	78.4 (1)	Se(1)—Fe(4)—Se(3)	77.9 (1)

The structure was solved by Patterson superposition and successive difference Fourier syntheses. The non-H atoms were subjected to anisotropic refinement. All H atoms were generated geometrically (C—H = 0.96 Å), allowed to ride on their respective parent C atom, assigned the same isotropic displacement parameters (U = 0.08 Å^2) and included in the structure-factor calculations. Computations were performed using a PC 486 computer.

Data collection: Seimens software. Cell refinement: Seimens software. Data reduction: Seimens software. Program(s) used to solve structure: *XS* in *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *XLS* in *SHELXTL/PC*. Molecular graphics: *XP* in *SHELXTL/PC*. Software used to prepare material for publication: *XPUBL* in *SHELXTL/PC*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1209). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). **C52**, 1359–1362

Bis{[3-(diphenylphosphino)propyl]trimethylphosphonium-*P*}[(2,3,5,6-*η*)norbornadiene]rhodium(I) Tris(tetrafluoroborate)

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Abstract

The title complex, $[Rh(C_{18}H_{25}P_2)_2(C_7H_8)](BF_4)_3$, is representative of a family of excellent biphasic olefin hydrogenation catalysts. The cation exhibits essentially square-planar geometry around the Rh^I ion, with the two PPh_2 groups and the two norbornadiene C=C double bonds forming the inner coordination sphere; Rh—P 2.3082 (11) and 2.3332 (12), and Rh—C 2.180 (5)–2.204 (5) Å.

Comment

The chemistry and catalytic activity of rhodium(I) complexes containing two coordinated [3-(diphenylphosphino)propyl]trimethylphosphonium (henceforth III-phophos) ions and higher homologues have been of particular interest because of the ease with which the catalysts can be heterogenized. Thus, bis(phophos)–rhodium(I) complexes are active for the hydrogenation of olefins both in aqueous solution and when supported, *via* the phosphonium ion end groups, on a cationic exchange resin (Renaud, Russell, Fortier, Brown & Baird, 1991; Renaud & Baird, 1992, 1993). We have reported the crystal and molecular structure of the mono(II-phophos) cationic complex $[(NBD)RhCl(II\text{-}phophos)]PF_6$ {where NBD is norbornadiene and II-phophos is [2-(diphenylphosphino)ethyl]trimethylphosphonium} (Renaud, Russell, Fortier, Brown & Baird, 1991) and now report the crystal and molecular structure of the analogous bis(III-phophos) complex $[(NBD)Rh(III\text{-}phophos)_2](BF_4)_3$, (I), which is of interest both because it is the direct precursor of the III-phophos