Acta Cryst. (1980). B**36**, 2434–2436

μ-{1–2-*η*-[Hydroseleno-1-cyclohexene-1-carbaldehydato(2−)]-*μ*-*Se*}-bis(tricarbonyliron)(*Fe*–*Fe*)

BY ROGER C. PETTERSEN*

Department of Chemistry, Texas A & M University, College Station, Texas 77843, *USA*

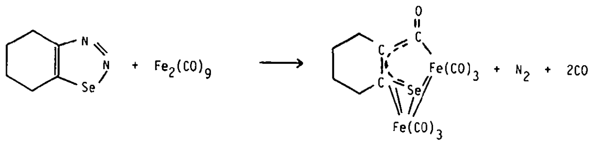
AND KEITH H. PANNELL AND ARMIN J. MAYR

Department of Chemistry, University of Texas at El Paso, El Paso, Texas 79968, *USA*

(*Received* 21 *November* 1979; *accepted* 18 *June* 1980)

Abstract. $C_{13}H_8Fe_2O_7Se$, M_r = 466·86, monoclinic, $P2_1/c$, a = 7·399 (2), b = 12·509 (4), c = 18·429 (6) Å, β = 114·83 (2)°, V = 1548·0 (9) Å^3, Z = 4, D_m = 2·02 ± 0·02, D_c = 2·003 Mg m^{-3}, μ =4·195 mm^{-1} (Mo $K\alpha$ radiation); crystal shape: rectangular block, crystal size: 0·09 × 0·29 × 0·53 mm. Diffractometer data, 2017 reflections measured, 1734 classed as significant, R = 0·064. The molecule contains a ferrole-type ring incorporating a Se atom and a carbonyl C atom at the positions adjacent to iron. The ring is completed by double-bonded C atoms of a cyclohexene moiety. A second Fe atom of a Fe(CO)$_3$ group is complexed to Fe, Se and olefinic C atoms of the ferrole ring. The Fe–Fe distance is 2·631 (2) Å; Fe(ferrole)–Se = 2·327 (1) Å and Fe–Se = 2·353 (1) Å.

Introduction. The title compound (3) was synthesized from cyclohexeno-1,2,3-selenadiazole (1) and nonacarbonyldiiron (2) as starting materials.



(1) (2) (3)

Deep-red crystals of (3) were grown from a pentane solution. Accurate unit-cell constants were determined by a least-squares refinement of carefully measured 2θ values for 43 independent reflections. These measurements and subsequent intensity data were obtained with a General Electric XRD-7 quarter-circle manual diffractometer using Mo $K\alpha$ radiation (λ = 0·71069 Å). A total of 2017 independent reflection intensities was measured using the stationary-crystal/stationary-counter method with balanced Zr and Y filters [$2\theta_{\max}$ = 45·00°, $(\sin\theta/\lambda)_{\max}$ = 0·5383 Å^{-1}]. Five reflections were monitored during data collection and no significant variation in intensity was noted. A background correction for the scattered Mo $K\alpha$ radiation was determined as a function of 2θ using the Zr filter and added directly to the Y filter measurements. Reflections were classed to be significantly above background using the criteria $[I_{\rm Zr} - 2\sigma(I_{\rm Zr})] - [I_{\rm Y} + 2\sigma(I_{\rm Y})] \geq 50$ counts, where $I_{\rm Zr}$ is the measured count for the Zr filter and $I_{\rm Y}$ is the measured count for the Y filter corrected for $K\alpha$ scatter; $\sigma(I_{\rm Zr})$ and $\sigma(I_{\rm Y})$ are the usual standard deviations from the counting statistics. 1731 reflections were classed as significant. A weight w was assigned to each reflection where $w = 1{\cdot}0/\sigma^2(F_o)$ and $\sigma(F_o) = \frac{1}{2}\{({\rm Lp})^{-1}[(I_{\rm Zr} + I_{\rm Y})/(I_{\rm Zr} - I_{\rm Y})]\}^{1/2}$ and Lp is the Lorentz–polarization factor. The data were reduced to F_o and $\sigma(F_o)$ values by the program *INCON* (Davis, 1965). An absorption correction was made as a function of the diffractometer angle φ and ranged from 1·00 to 1·90 as applied to the intensities. Scattering factors not incorporated in the *SHELX* system [iron(0) and selenium(0)] were taken from *International Tables for X-ray Crystallography* (1974). Real and imaginary anomalous-dispersion corrections were respectively f' = 0·301, f'' = 0·845 for Fe and f' = −0·178, f'' = 2·223 for Se.

The structure was solved by the centrosymmetric direct-phasing method segment of the *SHELX* program system (Sheldrick, 1976). All non-hydrogen atoms were refined with anisotropic thermal parameters. The coordinates of the eight H atoms varied with those of the bonded C atom in such a way as to maintain idealized geometry (C–H = 1·08 Å). An overall isotropic temperature factor for the H atoms was allowed to refine independently to a final value of U = 0·07 Å^2. The weights w were refined in the final least-squares calculations to minimize the variation of $w\sum|F_o - |F_c||^2$ as a function of F. Here $w = K/[\sigma^2(F_o) + gF_o^2]$ where K is a scale factor applied to

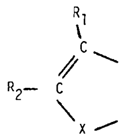
---

* Present address: Forest Products Laboratory, PO Box 5130, Madison, Wisconsin 53705, USA.

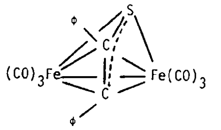
0567-7408/80/102434-03$01.00

the weights and g is the refined variable. The final cycle had $K = 1{\cdot}17$ and $g = 0{\cdot}008$. The final R value defined as $\sum|F_o - |F_c||/\sum F_o$ is 0·064 and the weighted R_w defined as $[\sum w|F_o - |F_c||^2/\sum F_o^2]^{1/2}$ is 0·070. All parameter shifts in the last cycle were less than $0{\cdot}11\sigma$. Three peaks on a difference Fourier map had densities of about 1 e Å^{-3} and all were located near the Fe and Se atoms. The parameters were refined in two cycles including all measured reflections (2014). The agreement factors were $R = 0{\cdot}075$ and $R_w = 0{\cdot}085$ with no significant change in the structure.*

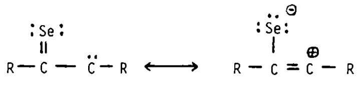
Discussion. Nonacarbonyldiiron is known to catalyze the elimination of N from 1,2,3-thiadiazoles (4) and 1,2,3-selenadiazoles (5) (Gilchrist, Mente & Rees, 1972). A product obtained using (4) as starting material with $R_1 = R_2$ = phenyl has physical properties identical to the product obtained using the 1,4-dimethyl derivative of bis(*cis*-stilbenedithiolato)nickel(II) and $Fe(CO)_5$ as starting materials and has been shown by X-ray structure analysis to be (6) (Schrauzer, Rabinowitz, Frank & Paul, 1970). (6) contains a phenylthiobenzoylcarbene moiety and has been useful in the study of 1,3 dipoles (7).†



(4) X = S
(5) X = Se



(6)



(7)

The title compound (3) was a product of the reaction of a 1,2,3-selenadiazole and $Fe_2(CO)_9$, and was expected to be similar to the derivative (6). The structure analysis of (3) indicates retention of one bridge carbonyl from $Fe_2(CO)_9$ which now bonds to an Fe atom and to a delocalized sp^2 C atom of the cyclohexene ring.

Table 1. *Fractional coordinates* (×10⁴) *and* U_{eq} *values*

Estimated standard deviations are given in parentheses.

	x	y	z	U_{eq}/U_{iso} (Å^2)*
Se	4376·0 (1·1)	3934·4 (0·7)	3529·1 (0·5)	0·042
Fe(1)	1957·5 (1·8)	3662·7 (1·0)	4006·3 (0·7)	0·043
Fe(2)	2435·9 (1·6)	2412·1 (0·9)	2952·4 (0·7)	0·039
C(1)	−61 (11)	3994 (6)	2908 (5)	0·039
O(1)	−1759 (9)	4283 (6)	2732 (4)	0·065
C(2)	621 (13)	3786 (6)	2277 (5)	0·039
C(3)	2601 (12)	3912 (6)	2433 (5)	0·038
C(4)	−919 (13)	3742 (8)	1412 (5)	0·051
H(1)	−1277 (13)	2915 (8)	1245 (5)	0·073
H(2)	−2241 (13)	4158 (8)	1366 (5)	0·073
C(5)	−186 (14)	4253 (9)	831 (6)	0·064
H(3)	−119 (14)	5109 (9)	915 (6)	0·073
H(4)	−1223 (14)	4064 (9)	227 (6)	0·073
C(6)	1824 (17)	3860 (8)	961 (6)	0·068
H(5)	1761 (17)	3004 (8)	879 (6)	0·073
H(6)	2259 (17)	4233 (8)	530 (6)	0·073
C(7)	3395 (13)	4126 (7)	1814 (5)	0·049
H(7)	3793 (13)	4960 (7)	1838 (5)	0·073
H(8)	4699 (13)	3639 (7)	1945 (5)	0·073
C(8)	3915 (14)	3260 (9)	4971 (6)	0·058
O(8)	5041 (13)	3009 (8)	5570 (5)	0·093
C(9)	12 (15)	2888 (8)	4105 (6)	0·055
O(9)	−1217 (11)	2413 (6)	4137 (5)	0·085
C(10)	1488 (15)	4927 (9)	4305 (5)	0·060
O(10)	1071 (13)	5743 (7)	4476 (5)	0·102
C(11)	3323 (14)	1746 (8)	2298 (6)	0·058
O(11)	3858 (14)	1289 (6)	1900 (5)	0·095
C(12)	3743 (15)	1545 (8)	3759 (6)	0·062
O(12)	4618 (12)	983 (6)	4279 (5)	0·087
C(13)	69 (15)	1736 (7)	2633 (6)	0·051
O(13)	−1438 (11)	1342 (6)	2440 (5)	0·079

* $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\bar{a}_i\bar{a}_j$. U_{iso} for H atoms is explained in the text.

Table 1 lists the fractional atomic coordinates for all atoms. Table 2 presents interatomic distances and angles for all non-hydrogen atoms. A perspective view of the molecule generated by the *ORTEP* program is given in Fig. 1 (Johnson, 1965). The selenaferrole ring has an envelope form with C(1) and O(1) tilting up out of the plane containing Fe(1), Se, C(2) and C(3) by 0·44 and 0·94 Å respectively. Fe(2) is out of this same plane by 1·77 Å in the opposite direction. If the C(1)—O(1) carbonyl is one of the three bridging carbonyls from $Fe_2(CO)_9$, then the present complex can be considered as an intermediate in the formation of a selenoketocarbene moiety similar to that in (6).

The molecule contains two Fe—Se bonds of 2·327 (1) and 2·353 (1) Å, significantly different from each other, with the shorter distance within the selenaferrole ring. There is some delocalization of the π electrons in the selenaferrole ring. C(1)—C(2) is 1·472 (12) Å and C(2)—C(3) is 1·378 (12) Å. The Se—C(3) bond is 1·891 (9) Å, longer than the Se=C double bond of 1·83 (2) Å in 2-pyridinecarbaldehyde selenosemicarbazone (Conde, López-Castro & Márquez, 1972), but shorter than the Se—C single-bond distance of 1·991 (15) Å determined for 1*H*,4*H*-

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35379 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† We have recently completed an X-ray structure determination of a compound similar to (6) with the S replaced by Se. Details will be published in *Crystal Structure Communications* (1980).

Table 2. *Interatomic distances* (Å) *and angles* (°)

Fe(1)–Fe(2)	2·631 (2)	Fe(2)–Se	2·353 (1)
Fe(1)–Se	2·327 (1)	Fe(2)–C(2)	2·214 (8)
Se–C(3)	1·891 (9)	Fe(2)–C(3)	2·132 (7)
Fe(1)–C(1)	1·990 (8)	Fe(2)–C(11)	1·804 (9)
C(1)–O(1)	1·213 (9)	C(11)–O(11)	1·121 (11)
Fe(1)–C(8)	1·830 (11)	Fe(2)–C(12)	1·765 (11)
C(8)–O(8)	1·113 (12)	C(12)–O(12)	1·144 (12)
Fe(1)–C(9)	1·807 (10)	Fe(2)–C(13)	1·806 (10)
C(9)–O(9)	1·108 (11)	C(13)–O(13)	1·131 (11)
Fe(1)–C(10)	1·756 (10)	C(4)–C(5)	1·528 (13)
C(10)–O(10)	1·149 (12)	C(5)–C(6)	1·486 (14)
C(1)–C(2)	1·472 (12)	C(6)–C(7)	1·548 (13)
C(2)–C(3)	1·378 (12)	C(3)–C(7)	1·511 (11)
C(2)–C(4)	1·522 (12)		

Se–Fe(1)–Fe(2)	56·3 (1)	Se–Fe(2)–Fe(1)	55·3 (1)
Se–Fe(1)–C(1)	87·3 (2)	Se–Fe(2)–C(2)	74·7 (2)
Se–Fe(1)–C(8)	89·2 (2)	Se–Fe(2)–C(3)	49·6 (2)
Se–Fe(1)–C(9)	152·6 (3)	Se–Fe(2)–C(11)	110·8 (8)
Se–Fe(1)–C(10)	105·8 (3)	Se–Fe(2)–C(12)	95·9 (3)
Fe(2)–Fe(1)–C(1)	69·5 (2)	Se–Fe(2)–C(13)	148·2 (3)
Fe(2)–Fe(1)–C(8)	104·8 (3)	Fe(1)–Fe(2)–C(2)	73·5 (2)
Fe(2)–Fe(1)–C(9)	96·6 (3)	Fe(1)–Fe(2)–C(3)	81·9 (2)
Fe(2)–Fe(1)–C(10)	150·7 (3)	Fe(1)–Fe(2)–C(11)	165·9 (3)
C(1)–Fe(1)–C(8)	174·3 (4)	Fe(1)–Fe(2)–C(12)	86·5 (3)
C(1)–Fe(1)–C(9)	85·7 (4)	Fe(1)–Fe(2)–C(13)	96·1 (3)
C(1)–Fe(1)–C(10)	88·2 (4)	C(2)–Fe(2)–C(3)	36·9 (3)
C(8)–Fe(1)–C(9)	95·4 (4)	C(2)–Fe(2)–C(11)	106·9 (4)
C(8)–Fe(1)–C(10)	97·1 (5)	C(2)–Fe(2)–C(12)	159·9 (4)
C(9)–Fe(1)–C(10)	100·4 (4)	C(2)–Fe(2)–C(13)	84·5 (3)
Fe(1)–Se–Fe(2)	68·4 (1)	C(3)–Fe(2)–C(11)	106·9 (4)
Fe(1)–Se–C(3)	95·9 (2)	C(3)–Fe(2)–C(12)	143·5 (4)
Fe(2)–Se–C(3)	59·1 (2)	C(3)–Fe(2)–C(13)	119·7 (3)
Fe(1)–C(1)–C(2)	114·0 (5)	C(11)–Fe(2)–C(12)	93·0 (5)
Fe(1)–C(1)–O(1)	125·8 (6)	C(11)–Fe(2)–C(13)	98·0 (4)
C(2)–C(1)–O(1)	120·1 (8)	C(12)–Fe(2)–C(13)	95·8 (4)
C(1)–C(2)–C(3)	120·1 (8)	Se–C(3)–Fe(2)	71·3 (3)
C(1)–C(2)–C(4)	118·7 (8)	Se–C(3)–C(2)	115·2 (6)
C(1)–C(2)–Fe(2)	91·2 (5)	Se–C(3)–C(7)	119·2 (6)
C(3)–C(2)–C(4)	119·1 (8)	C(2)–C(3)–C(7)	125·3 (8)
C(3)–C(2)–Fe(2)	68·3 (5)	C(2)–C(3)–Fe(2)	74·8 (4)
C(4)–C(2)–Fe(2)	124·8 (6)	C(7)–C(3)–Fe(2)	127·5 (6)
C(2)–C(4)–C(5)	112·9 (7)	Fe(1)–C(9)–O(9)	177·6 (9)
C(4)–C(5)–C(6)	112·0 (8)	Fe(1)–C(10)–O(10)	176·3 (10)
C(5)–C(6)–C(7)	111·5 (8)	Fe(2)–C(11)–O(11)	177·5 (9)
C(6)–C(7)–C(3)	111·4 (7)	Fe(2)–C(12)–O(12)	178·8 (10)
Fe(1)–C(8)–O(8)	176·8 (8)	Fe(2)–C(13)–O(13)	177·7 (8)

naphtho[1,8]diselenepine (Aleby, 1972).* A Se–C(aromatic) bond distance of 1·899 (5) Å was measured for dibenzoselenophene (Hope, Knobler & McCullough, 1970), in good agreement with our distance. Thus, the selenaferrole ring of (3) can be considered to bond as a π complex to the out-of-plane Fe atom [Fe(2)]. It follows that the longer of the two Se–Fe distances in (3) is from the ring to Fe(2). We have not found any structures in the literature with comparable examples of Fe–Se bonds. The Fe–Fe distance of 2·631 (2) Å is longer than the usual distance of about 2·50 Å found for most structures containing the $Fe_2(CO)_6$ moiety. This lengthening is probably due to the large covalent radius of the Se atom.

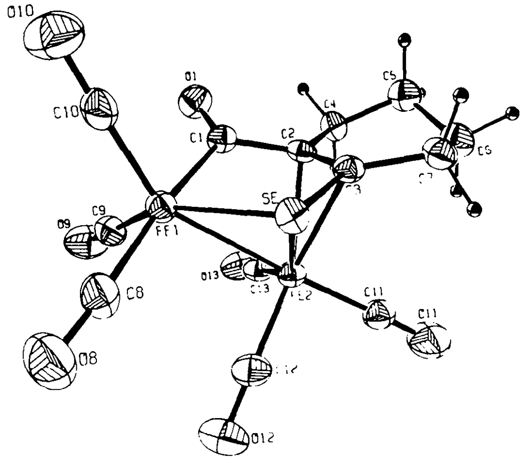


Fig. 1. A perspective view of $C_{13}H_8Fe_2O_7Se$.

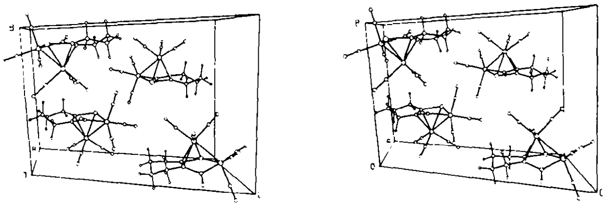


Fig. 2. A stereographic packing diagram showing the contents of one unit cell of $C_{13}H_8Fe_2O_7Se$.

A stereographic view of the unit-cell contents is presented in Fig. 2. There are no unusually short intermolecular contacts. The shortest O···O contact is 3·057 Å between O(11) and O(8) related by the symmetry operation $x, \frac{1}{2} - y, -\frac{1}{2} + z$.

Financial support from The Robert A. Welch Foundation of Houston, Texas, is gratefully acknowledged.

---

* Aleby lists 24 different structures with distances for Se–C bonds.

References

Aleby, S. (1972). *Acta Cryst.* B**28**, 1509–1518.
Conde, A., López-Castro, A. & Márquez, R. (1972). *Acta Cryst.* B**28**, 3464–3469.
Davis, R. E. (1965). *INCON* 2. A Fortran IV program for *I* to *F* conversion. Unpublished.
Gilchrist, T. L., Mente, P. G. & Rees, C. W. (1972). *J. Chem. Soc. Perkin Trans.* 1, pp. 2165–2170.
Hope, H., Knobler, C. & McCullough, J. D. (1970). *Acta Cryst.* B**26**, 628–640.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
Schrauzer, B. N., Rabinowitz, H. N., Frank, J. K. & Paul, I. C. (1970). *J. Am. Chem. Soc.* **92**, 212–214.
Sheldrick, G. M. (1976). *SHELX* 76. Program for crystal structure determination. Univ. of Cambridge, England.