

Table 7. Some ligand-copper bond angles (°) and electronic spectra of [Cu(bpy)<sub>2</sub>Cl]<sub>2</sub>S<sub>5</sub>O<sub>6</sub>·6H<sub>2</sub>O and [Cu(bpy)<sub>2</sub>Cl]Cl·6H<sub>2</sub>O

	[Cu(bpy) <sub>2</sub> Cl] <sub>2</sub> S <sub>5</sub> O <sub>6</sub> ·6H <sub>2</sub> O	[Cu(bpy) <sub>2</sub> Cl]Cl·6H <sub>2</sub> O
Cl-Cu-N(2)	130.7	118.7
Cu-Cl-N(4)	122.0	118.6
N(2)-Cu-N(4)	107.3	122.7
Electronic reflectance (μm <sup>-1</sup> )	1.324, 1.047	1.28

more distorted [Cu(bpy)<sub>2</sub>Cl]<sub>2</sub>S<sub>5</sub>O<sub>6</sub>·6H<sub>2</sub>O involves two peaks with an energy difference of 0.277 μm<sup>-1</sup>. The significance of this difference in the electronic energies of the Cu<sup>II</sup> ion in these distorted trigonal-bipyramidal stereochemistries will be discussed elsewhere (Hathaway, Harrison & Kennedy, 1979).

The pyridine rings are reasonably planar in both (I) and (II); in (I) the pairs of pyridine rings in each 2,2'-bipyridyl ligand are inclined at angles of 5.29 and 4.88° and in (II) at angles of 2.31 and 2.31°, all of which are in reasonable agreement with previously reported values of 0.1–1.1° (Stephens, 1969, 1972).

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## The Crystal and Molecular Structure of Hexacarbonyl-[μ-(2,4-dimethyl-4-sulfido-2-penten-3-olato)-μ-O,μ-S]-diiron(Fe-Fe)

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#### Abstract

A crystal structure analysis has been carried out for the title compound with data from a crystal cooled to ca

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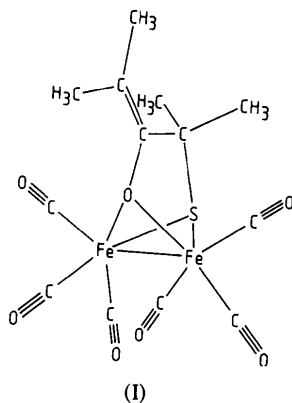
120 K. The space group is  $P2_1/c$  with  $Z = 4$ ,  $a = 8.492$  (1),  $b = 15.737$  (1),  $c = 15.499$  (1) Å,  $\beta = 125.129$  (5)°. The structure was refined with 6546 data ( $2\theta_{\max} = 70^\circ$ , Mo  $K\alpha$ ) to  $R = 0.037$  and  $R_w = 0.055$ . The crystalline complex displays a good approximation to the maximum allowed molecular symmetry,

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$C_s$ . The bonding geometry displays *trans* effects in the Fe—C carbonyl bonds opposite both coordinated atoms of the unique ligand. The effect is much greater *trans* to the Fe—O bond than *trans* to the Fe—S bond. The bond distances in the unique ligand are consistent with a nearly pure enolate structure.

### Introduction

The preparation of the title compound (I) from nonacarbonyldiiron and tetramethyl-3-thietanone, its spectroscopic characterization and partial results from this crystal structure analysis have been communicated (Czuderna, Jogun, Stezowski & Föhlich, 1976). It was pointed out that the valence electron structure of (I) is isoelectronic with a possible intermediate in the reductive rearrangement of  $\alpha, \alpha'$ -dibromoketones, a reaction of interest in synthetic organic chemistry. We now report the full results of the crystal structure determination of the formally Fe<sup>I</sup> complex [Fe<sub>2</sub>(C<sub>7</sub>H<sub>12</sub>OS)(CO)<sub>6</sub>].



### Experimental

Compound (I), crystallized by cooling a *n*-hexane solution to 195 K, displays space-group symmetry  $P2_1/c$  with  $Z = 4$ . All crystallographic data, from a  $0.5 \times 0.5 \times 0.3$  mm crystal in a thin-walled glass capillary, were collected with monochromatized Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å) on a Syntex  $P\bar{1}$  autodiffractometer equipped with a low-temperature device (Syntex LT-1) operating at *ca* 120 K. Lattice parameters:  $a = 8.492$  (1),  $b = 15.737$  (1),  $c = 15.499$  (1) Å,  $\beta = 125.129$  (5)° resulted from least-squares refinement (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) with automatically centered  $2\theta$  values for 81 reflections in the angular range  $41 < 2\theta < 66^\circ$ ;  $\rho_c = 1.662$  Mg  $m^{-3}$ . Diffraction intensities were measured in an  $\omega$ -scan mode in which the scan rate varied as a function of maximum peak intensity from 2.0 to 24.0°  $min^{-1}$ ; the scan range was 0.75° and background was counted on

each side of the reflection center ( $\Delta\omega = 1.0^\circ$ ) for one half the scan time. Three periodically monitored reference reflections displayed neither systematic nor significant variations from their initial intensities. 7250 unique reflections were measured to a resolution of  $2\theta = 70^\circ$ ; 6546 were classified as objectively observed under the criterion  $I \geq 2\sigma(I)$ . Data were corrected for Lorentz and polarization effects but not for absorption,  $\mu = 1.57$   $mm^{-1}$ .

Application of the heavy-atom technique yielded the crystallographic model for which all atomic coordinates were determined and refined by block-diagonal least-squares techniques. The following block structure was employed: scale factor; [Fe(1), Fe(2), S]; the atoms of each carbonyl group; [C(7), C(7M1), C(7M2) and atoms H(7M1–6)]; [C(9), C(9M1), C(9M2) and atoms H(9M1–6)]; and [C(8), O(7)]. 526 variables, including anisotropic temperature factors for all Fe, S, C and O atoms, isotropic temperature factors for H atoms, and all atomic coordinates, were so refined with 6546 data to give  $R = 0.037$  and  $R_w = 0.055$  for which  $w = [\sigma^2(F) + 0.0125|F| + 0.001|F|^2]^{-1}$ ; the e.s.d. of an observation of unit weight is 1.19.

Table 1. Fractional atomic coordinates ( $\times 10^4$ )

	<i>x</i>	<i>y</i>	<i>z</i>
Fe(1)	2958.4 (3)	3358.5 (1)	4888.1 (2)
Fe(2)	−454.6 (3)	3106.6 (1)	3965.5 (2)
S	1260.3 (5)	2605.7 (2)	3384.1 (3)
C(1)	5422 (2)	2997 (1)	5529 (1)
O(1)	6990 (2)	2802 (1)	5928 (1)
C(2)	3374 (3)	4023 (1)	5954 (1)
O(2)	3625 (3)	4453 (1)	6613 (1)
C(3)	3136 (2)	4250 (1)	4241 (1)
O(3)	3215 (2)	4822 (1)	3817 (1)
C(4)	−2522 (3)	2412 (1)	3468 (2)
O(4)	−3863 (2)	2011 (1)	3160 (2)
C(5)	−826 (3)	3762 (1)	4792 (2)
O(5)	−1064 (3)	4189 (1)	5301 (2)
C(6)	−1656 (3)	3835 (1)	2891 (1)
O(6)	−2400 (3)	4281 (1)	2182 (1)
C(7)	1751 (2)	1528 (1)	3962 (1)
C(7M1)	3602 (2)	1209 (1)	4114 (1)
C(7M2)	65 (2)	964 (1)	3152 (1)
C(8)	1925 (2)	1651 (1)	4991 (1)
O(7)	1675 (2)	2486 (1)	5184 (1)
C(9)	2297 (2)	1062 (1)	5711 (1)
C(9M1)	2431 (3)	1299 (1)	6688 (1)
C(9M2)	2621 (2)	132 (1)	5634 (1)
H(7M1)	3374 (43)	1235 (19)	3426 (23)
H(7M2)	4614 (42)	1561 (18)	4615 (22)
H(7M3)	3829 (41)	603 (20)	4358 (22)
H(7M4)	−37 (38)	1011 (17)	2498 (22)
H(7M5)	341 (40)	362 (18)	3389 (22)
H(7M6)	−996 (46)	1131 (21)	3034 (25)
H(9M1)	1554 (46)	1051 (21)	6763 (25)
H(9M2)	3619 (47)	1082 (21)	7328 (26)
H(9M3)	2465 (49)	1854 (24)	6836 (26)
H(9M4)	2463 (41)	−4 (20)	5043 (21)
H(9M5)	1715 (41)	−226 (19)	5638 (23)
H(9M6)	3842 (45)	−44 (22)	6267 (24)

## Results and discussion

Atomic coordinates are in Table 1. Temperature factors have been deposited.\* Bond distances, bond angles and selected dihedral angles are in Tables 2–4, respectively. A stereoscopic projection (Johnson, 1971) of (I), with atom labels, is presented in Fig. 1.

The maximum molecular symmetry allowed by the chemical structure of (I),  $C_s$ , is closely approximated in the solid state. Bonding parameters related by the local mirror symmetry have been tabulated on the same line in Tables 2 to 4. The appropriate bond distances differ by  $<0.008$  Å and bond angles by  $<3.4^\circ$ . Assessment of the approximation of the conformation to  $C_s$ ,

\* Lists of temperature factor coefficients and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34326 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances between Fe, S, C, and O atoms with *e.s.d.*'s (Å)

Bonds tabulated on the same line are related by the non-crystallographic mirror-symmetry operator.

Fe(1)–Fe(2)	2.4152 (4)	Fe(2)–S	2.2506 (6)
Fe(1)–S	2.2469 (5)	Fe(2)–O(7)	1.964 (2)
Fe(1)–O(7)	1.964 (2)	Fe(2)–C(4)	1.821 (2) 1.827
Fe(1)–C(1)	1.816 (2) 1.823†	Fe(2)–C(5)	1.808 (3) 1.816
Fe(1)–C(2)	1.810 (2) 1.817	Fe(2)–C(6)	1.782 (2) 1.789
Fe(1)–C(3)	1.781 (2) 1.783	C(4)–O(4)	1.139 (3) 1.145
C(1)–O(1)	1.141 (3) 1.147	C(5)–O(5)	1.140 (4) 1.146
C(2)–O(2)	1.139 (3) 1.143	C(6)–O(6)	1.141 (3) 1.146
C(3)–O(3)	1.139 (3) 1.144		
C(7)–S	1.850 (2)	C(7)–C(7M2)	1.533 (2)
C(7)–C(7M1)	1.534 (3)		
C(7)–C(8)	1.527 (3)		
C(8)–O(7)	1.390 (2)		
C(8)–C(9)	1.342 (2)		
C(9)–C(9M1)*	1.498 (3)	C(9)–C(9M2)*	1.506 (2)

\* Bonds that are chemically equivalent and contained in the local mirror plane.

† Bond distances corrected for riding motion (Busing & Levy, 1964; Busing, Martin & Levy, 1964). All corrections are with respect to riding on a central Fe atom.

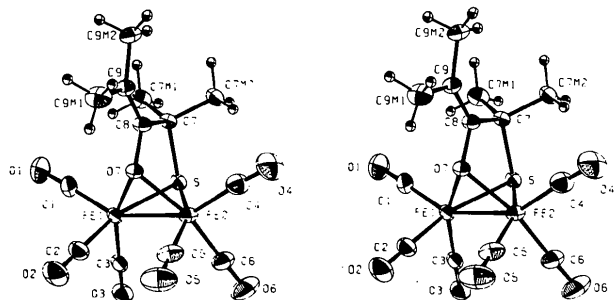


Fig. 1. Stereoscopic projection of (I) with atom labels.

Table 3. Bond angles between Fe, S, C, and O atoms with *e.s.d.*'s ( $^\circ$ )

Bond angles tabulated on the same line are related by the non-crystallographic mirror symmetry.

Fe(2)Fe(1)S	57.59 (2)	Fe(1)Fe(2)S	57.45 (1)
Fe(2)Fe(1)O(7)	52.07 (3)	Fe(1)Fe(2)O(7)	52.06 (4)
Fe(2)Fe(1)C(1)	152.26 (6)	Fe(1)Fe(2)C(4)	152.38 (6)
Fe(2)Fe(1)C(2)	99.96 (8)	Fe(1)Fe(2)C(5)	97.24 (7)
Fe(2)Fe(1)C(3)	104.94 (5)	Fe(1)Fe(2)C(6)	107.12 (7)
SFe(1)O(7)	76.24 (4)	SFe(2)O(7)	76.15 (5)
SFe(1)C(1)	104.60 (7)	SFe(2)C(4)	108.02 (9)
SFe(1)C(2)	157.42 (8)	SFe(2)C(5)	154.20 (7)
SFe(1)C(3)	92.47 (5)	SFe(2)C(6)	90.33 (9)
O(7)Fe(1)C(1)	105.83 (8)	O(7)Fe(2)C(4)	103.83 (7)
O(7)Fe(1)C(2)	91.99 (9)	O(7)Fe(2)C(5)	92.41 (7)
O(7)Fe(1)C(3)	156.98 (6)	O(7)Fe(2)C(6)	159.02 (9)
C(1)Fe(1)C(2)	97.08 (9)	C(4)Fe(2)C(5)	97.08 (12)
C(1)Fe(1)C(3)	96.35 (10)	C(4)Fe(2)C(6)	95.52 (9)
C(2)Fe(1)C(3)	92.32 (9)	C(5)Fe(2)C(6)	93.19 (10)
Fe(1)SFe(2)	64.96 (2)		
Fe(1)SC(7)	98.60 (5)	Fe(2)SC(7)	98.30 (7)
Fe(1)O(7)Fe(2)	75.87 (4)	Fe(2)O(7)C(8)	115.70 (8)
Fe(1)O(7)C(8)	115.91 (13)		
SC(7)C(8)	104.4 (1)	SC(7)C(7M2)	106.9 (1)
SC(7)C(7M1)	107.4 (1)	C(8)C(7)C(7M2)	114.4 (2)
C(8)C(7)C(7M1)	114.0 (1)		
C(7M1)C(7)C(7M2)	109.2 (1)		
C(7)C(8)O(7)	114.1 (1)		
C(7)C(8)C(9)	128.1 (1)		
O(7)C(8)C(9)	117.8 (2)		
C(8)C(9)C(9M1)	120.9 (2)	Fe(2)C(4)O(4)	176.7 (2)
C(8)C(9)C(9M2)	124.7 (2)	Fe(2)C(5)O(5)	178.6 (2)
C(9M1)C(9)C(9M2)	114.3 (2)	Fe(2)C(6)O(6)	177.0 (3)
Fe(1)C(1)O(1)	177.3 (2)		
Fe(1)C(2)O(2)	178.8 (2)		
Fe(1)C(3)O(3)	178.8 (2)		

Table 4. Selected dihedral angles with *e.s.d.*'s ( $^\circ$ )

Dihedral angles tabulated on the same line correspond to torsion angles about bonds related by the non-crystallographic mirror symmetry.

C(1)Fe(1)SC(7)	61.4 (1)	C(4)Fe(2)SC(7)	–58.2 (1)
C(1)Fe(1)O(7)C(8)	–49.0 (1)	C(4)Fe(2)O(7)C(8)	52.5 (2)
C(2)Fe(1)O(7)C(8)	–146.9 (1)	C(5)Fe(2)O(7)C(8)	150.4 (2)
C(2)Fe(1)SC(7)	–101.9 (2)	C(5)Fe(2)SC(7)	107.9 (2)
C(3)Fe(1)O(7)C(8)	115.0 (2)	C(6)Fe(2)O(7)C(8)	–104.2 (3)
C(3)Fe(1)SC(7)	158.7 (1)	C(6)Fe(2)SC(7)	–154.1 (1)
C(2)Fe(1)Fe(2)C(5)	2.7 (1)		
C(1)Fe(1)Fe(2)C(4)	9.1 (3)		
C(3)Fe(1)Fe(2)C(6)	4.1 (1)		
C(9M2)C(9)C(8)C(7)	–0.1 (2)		
C(9M1)C(9)C(8)O(7)	0.2 (2)		
O(7)C(8)C(7)S	0.2 (2)		
C(9)C(8)C(7)C(7M1)	–62.3 (2)	C(9)C(8)C(7)C(7M2)	64.2 (2)

symmetry is provided by the standard deviation,  $\sigma_{C_s}$ , calculated from

$$\sigma_{C_s} = \{[\sum (|\tau_1| - |\tau_2|)^2 + \sum \tau_3^2] / (n - 1)\}^{1/2} \quad (1)$$

where  $\tau_1$  and  $\tau_2$  are dihedral angles for bonds related by the local symmetry and  $\tau_3$  is for *cis* bonds contained in the operator. Application of (1) to the dihedral angles in Table 4 gives  $\sigma_{C_s} = 5.2^\circ$ , a value sufficiently near  $0^\circ$

Table 5. *Least-squares mean planes*

Plane	Atoms fit		E.s.d.
1	C(7), C(8), C(9), O(7), S		0.0042 Å
2	C(7), C(8), C(9), O(7), S, C(9M1), C(9M2)		0.0026
3	Fe(1), S, Fe(2)		—
4	Fe(1), O(7), Fe(2)		—

Equations for planes in direct space $Px + Qy + Rz = S$				
Plane	P	Q	R	S
1	7.3044	2.5690	-1.5447	1.0630
2	7.3149	2.6351	-1.6018	1.0475
3	1.1670	13.1877	-7.9192	0.9035
4	-3.9822	9.9250	12.0202	8.0309

Interplanar angles (°)			
	2	3	4
1	0.33 (10)	89.99 (10)	89.91 (10)
2		89.69 (10)	89.90 (10)
3			82.09 (10)

Distances of mirror-equivalent atoms from plane 2			
Fe(1)	1.219 (3) Å	Fe(2)	-1.197 (3) Å
C(1)	2.823 (4)	C(4)	-2.813 (5)
C(2)	1.528 (5)	C(5)	-1.428 (5)
C(3)	1.687 (4)	C(6)	-1.711 (5)
O(1)	3.854 (4)	O(4)	-3.852 (4)
O(2)	1.718 (4)	O(5)	-1.571 (5)
O(3)	1.964 (4)	O(6)	-2.025 (5)
C(7M1)	1.247 (4)	C(7M2)	-1.252 (4)

to justify characterization of crystalline (I) as displaying a good approximation to ideal molecular symmetry. This characterization is further supported by the selected mean planes (and their interplanar angles) presented in Table 5. These planes clearly demonstrate the coplanarity of the relevant atoms of the unique ligand and the appropriateness of the orientation of this plane as the mirror operator for  $C_s$  symmetry.

The coordination geometry of the formally  $Fe^I$  atoms is similar to that observed previously. Description of that geometry is frequently presented in terms of two base-edge-shared [the O(7)···S edge] tetragonal pyramids (Treichel, Dean & Calabrese, 1973, and references therein). The following description conforms to that model. The angles between the planes defined by Fe(1)O(7)S and Fe(2)O(7)S is  $85.5^\circ$ , which compares with  $75.8^\circ$  in hexacarbonyl- $\mu$ -hydroxo- $\mu$ -ditolylphosphido-diiron (II),  $Fe_2[P(p-C_6H_4CH_3)_2]OH(CO)_6$  (Treichel *et al.*, 1973), and  $93.2^\circ$  in *o*-aminothiophenolhexacarbonyldiiron (III),  $Fe_2(C_6H_4SNH)(CO)_6$  (Le Borgne & Grandjean, 1973). The displacement of each Fe atom from the respective plane fit to the basal atoms of the tetragonal pyramid, O(7)SC(2)C(3) and O(7)SC(5)C(6), is 0.36 Å; typical values range from 0.34 to 0.38 Å (Treichel *et al.*, 1973). (I) displays an Fe—Fe bond similar in length to that in (III), 2.415 and 2.411 Å, respectively.

The average Fe—S distance in (I), 2.249 Å, is shorter than its analog in (III), 2.283 Å; it is also shorter than that to the methylmercapto ligands in  $[CH_3SFe_2(CO)_6]_2S$  (IV) (Coleman, Wojcicki, Pollick & Dahl, 1967) but is similar to that of the tetrahedral-like S atom of (IV), respective Fe—S distances: 2.274 and 2.248 Å. The unique S atom of (IV) has been characterized as donating six electrons to four Fe atoms, which raises the possibility of some multibond character in the Fe—S bonds of (I). The average Fe—O(7) distance in (I), 1.964 Å, compares well with that in (II), 1.972 Å, in which the O atom is part of a nonorganic hydroxyl group. Thus the similarity in the Fe—O distances may be taken as evidence that the structure of the unique ligand in (I) is that of a nearly pure enolate. The observed C(8)—C(9) distance, 1.342 Å, is consistent with a typical C—C double-bond distance, 1.337 Å (Kennard, Watson, Allen, Isaacs, Motherwell, Pettersen & Town, 1972), which implies that C(8)—O(7), 1.390 Å, represents an enolic hydroxylate in contrast to a paraffinic hydroxyl C—O distance, 1.43 Å (Kennard *et al.*, 1972).

The presence of a unique ligand in the complex raises the possibility that non-equivalence, that is a *trans* effect, may be induced in the bonding between the Fe atoms and their carbonyl groups. The Fe—C distances for (I) in Table 2 demonstrate the presence of such an effect, particularly in the Fe—C bonds *trans* to O(7). A similar effect has been observed in the Fe—C bonds *trans* to the first-row atoms of the unique ligands in (II) and (III). The structure of (I) in the solid state displays an indication of a lesser, but probably still significant, effect opposite the S atom; the crystal structure determinations for (II) and (III) do not provide a consistent indication of this weaker *trans* effect, but the analyses were carried out neither with low-temperature data nor with data to as high a resolution as that of the present determination.

One aspect of the *trans* effect in (I) differs from that in the complex (V), between  $Cr(CO)_5$  and the parent ligand, 2,2,4,4-tetramethyl-3-thietanone (Jogun & Stezowski, 1979). The CO lengths in (I) do not show the corresponding lengthening that accompanies the *trans* effect in (V). We suspect that this difference reflects the ionization state of the central metal atoms in the two complexes  $Fe^I$  and  $Cr^0$ . It may be indicative that the *trans* effect in (I) arises from a polarization of the Fe atom opposite the more electronegative ligand atoms rather than from changes in the bond order in the FeC and CO bonds.

There is one relatively short intermolecular contact between C(7M2) and O(3), 3.243 Å, though it does not appear to affect the bonding geometry of either atom significantly.

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## The Crystal and Molecular Structure of Pentacarbonyl(2,2,4,4-tetramethyl-3-thietanone)chromium(0)

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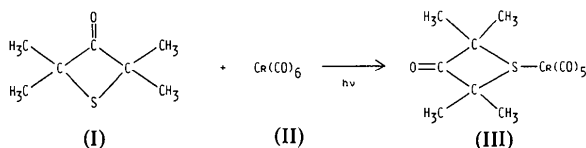
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### Abstract

The crystal structure of the title compound,  $C_{12}H_{12}CrO_6S$ ,  $Cr(C_4H_8OS)(CO)_5$ , has been determined at *ca* 120 K. The space group is  $P2_1/c$ ,  $Z = 4$ , with  $a = 13.154$  (2),  $b = 6.4534$  (6),  $c = 18.048$  (2) Å,  $\beta = 101.43$  (1)°. 9499 reflections ( $2\theta_{max} = 90^\circ$ ,  $\lambda = 0.71069$  Å) contributed to the refinement of 229 variables to give  $R = 0.049$  and  $R_w = 0.052$ . The complex displays approximate *m* molecular symmetry. The thietanone ligand, coordinated to the Cr through the S atom,  $Cr-S = 2.4241$  (5) Å, displays similarities with the bonding geometry of cyclobutanone but the endocyclic bond angle about the carbonyl C atom is *ca* 10° larger and that about the S atom *ca* 11° smaller than their analogs in cyclobutanone.

### Introduction

The title compound was prepared (Czauderna, 1976) by the following reaction:



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and the crystal structure determination was carried out to confirm that the product was indeed that of a substitution reaction rather than an oxidation–reduction reaction similar to that which gave rise to hexacarbonyl- $[\mu$ -(2,4-dimethyl-4-sulfido-2-penten-3-olato)- $\mu$ -O, $\mu$ -S]-diiron. The structure of the latter compound has been described previously (Jogun & Stezowski, 1979).

### Experimental

Crystals of (III) were obtained from hexane by warming a solution containing a large number of fine needles until only a trace of solid remained and then cooling slowly to *ca* 240 K. The resultant crystals were large but not well formed; examination with polarized light established their probable singularity. A fragment *ca* 0.5 × 0.5 × 0.5 mm was sealed in a capillary and used for all crystallographic measurements. The space group is  $P2_1/c$  with  $Z = 4$ ; lattice parameters (at *ca* 120 K):  $a = 13.154$  (2),  $b = 6.4534$  (6),  $c = 18.048$  (2) Å,  $\beta = 101.43$  (1)°, resulted from a least-squares refinement (Stewart, Kruger, Ammon, Dickinson & Hall, 1972)† with automatically centered  $2\theta$  values for 60 reflections in the angular range  $40.0 < 2\theta < 53.7^\circ$  (Mo  $K\alpha$  radiation,  $\lambda = 0.71069$  Å).

† Unless otherwise stated this program system was used for all 175°9 (1)

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