Crystal structure of hexacarbonyl-bis(μ_2 -4-chlorophenylthiolato-S,S)-diiron(I) diethyl ether hemisolvate, $\text{Fe}_2(\text{CO})_6(\text{ClC}_6\text{H}_4\text{S})_2 \cdot \frac{1}{2}(\text{C}_2\text{H}_5)_2\text{O}$

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Abstract

$\text{C}_{20}\text{H}_{13}\text{Cl}_2\text{Fe}_2\text{O}_{6.50}\text{S}_2$, monoclinic, $C12/c1$ (no. 15), $a = 18.4439(8)$ Å, $b = 11.0999(5)$ Å, $c = 25.183(1)$ Å, $\beta = 97.037(1)^\circ$, $V = 5116.8$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.055$, $wR_{\text{ref}}(F^2) = 0.172$, $T = 298$ K.

Source of material

All operations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. A solution of dodecacarbonyl triiron (0.50 g, 1 mmol) and 4-chlorothiophenol (0.29 g, 2 mmol) in toluene (50 mL) was refluxed for 2 h, during which time the solution turned from green to red. Removal of solvent under vacuum resulted in a dark red solid, which was dissolved in a minimum amount of hexane (ca. 15 mL), which upon layering with diethyl ether yielded red crystals of the title compound.

Experimental details

All H atoms were located in idealized positions and treated as riding atoms, with C—H distances of 0.93 Å, 0.96 Å and 0.97 Å for $\text{CH}_{\text{aromatic}}$, CH_3 and CH_2 , respectively, and with $U_{\text{iso}}(\text{H})$ defined as $1.2U_{\text{eq}}(\text{C}_{\text{parent}})$, and $U_{\text{iso}}(\text{H}_{\text{diethyl ether}})$ fixed at 0.05 Å². The diethyl ether solvent is disordered over a crystallographic inversion centre, and refined with the bond distance restraints. The very large U_{ani} values of O7, C19 and C20 atoms correspond with the disorder of the solvent molecule.

Discussion

The dinuclear hexacarbonyls of the general formula $[\text{Fe}_2(\mu\text{-SR})_2(\text{CO})_6]$ $R = \text{alkyl}$ are of interest, due to their application in organic synthesis and their framework similarity to the di-iron active site of the Fe-only hydrogenase as well as their stereochemical features associated with the bridging mercaptide group. Hitherto, three thiophenol-based complexes, $[\text{Fe}_2(\mu\text{-SPh})_2(\text{CO})_6]$ [1], $[\text{Fe}_2(\mu\text{-SPh-2,4,6-}^i\text{Pr}_3)_2(\text{CO})_6]$ [2], and $[\text{Fe}_2(\mu\text{-SPh-4-OH})_2(\text{CO})_6]$ [3], have been reported.

The title structure consists of a neutral $[\text{Fe}_2(\mu\text{-SPhCl})_2(\text{CO})_6]$ unit (SPhCl = 4-chlorophenylthiolate) and the diethyl ether solvent molecule in 2:1 ratio. The dinuclear $[\text{Fe}_2(\mu\text{-SPhCl})_2(\text{CO})_6]$ cluster lies on a general position in the unit cell, in which the Fe—Fe bond is almost symmetrically bridged by two S atoms of thiolate ligands. The Fe—S distances [Fe1—S: 2.260(2) Å and 2.275(2) Å; Fe2—S: 2.268(1) Å and 2.280(2) Å] agree well with the corresponding distances observed in other related complexes. The Fe_2S_2 core displays the well-known butterfly-like arrangement, with a dihedral angle of $99.1(2)^\circ$ between the Fe_2S planes. The Fe—Fe bond distance of $2.503(1)$ Å is somewhat shorter than those reported in $[\text{Fe}_2(\mu\text{-SPh})_2(\text{CO})_6]$ ($2.515(2)$ Å) [1] and $[\text{Fe}_2(\mu\text{-SPh-4-OH})_2(\text{CO})_6]$ ($2.522(1)$ Å) [3], but larger than that found in $[\text{Fe}_2(\mu\text{-SPh-2,4,6-}^i\text{Pr}_3)_2(\text{CO})_6]$ ($2.466(2)$ Å) [2]. One of two organic 4-chlorophenyl groups attached to the bridging S atoms is axial to the Fe_2S_2 core, while the other is equatorial [4], resulting in the orientation of the two groups *anti* to each other. An octahedral arrangement around each Fe center is completed through the additional coordination of three terminal carbonyl groups (one axial and two equatorial), with the Fe—C bond distances averaging $1.787(4)$ Å, and the octahedra are highly distorted, as indicated by the *cis* angles varying from $78.68(5)^\circ$ to $105.8(2)^\circ$. The individual Fe—C—O angles do not deviate significantly from the linearity. The oxygen atom of diethyl ether solvent molecule is located on a center of symmetry, over which the solvent molecule is disordered, resulting in an unexpected C—O—C angle of 180° . The case has been encountered in other known complexes, e.g. in $[\text{Au}_2(\text{S}_2\text{CC}(\text{CN})_2)(\text{Ph}_3\text{P})_2] \cdot \frac{1}{2}\text{Et}_2\text{O}$ [5].

Table 1. Data collection and handling.

Crystal:	red prism, size $0.43 \times 0.44 \times 0.56$ mm
Wavelength:	Mo K_{α} radiation (0.71073 Å)
μ :	15.40 cm^{-1}
Diffractometer, scan mode:	Siemens SMART CCD, ϕ/ω
$2\theta_{\text{max}}$:	50.12°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	8300, 4476
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 3443
$N(\text{param})_{\text{refined}}$:	295
Programs:	SHELXS-97 [6], SHELXL-97 [7]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U _{iso}
H(8A)	8f	0.4388	−0.5921	0.5135	0.083
H(9A)	8f	0.4108	−0.6378	0.4231	0.096
H(11A)	8f	0.2220	−0.4649	0.4195	0.096
H(12A)	8f	0.2498	−0.4140	0.5098	0.084
H(14A)	8f	0.5285	−0.3746	0.6741	0.073
H(15A)	8f	0.5860	−0.1916	0.6651	0.085
H(17A)	8f	0.4009	−0.0187	0.6842	0.098

Table 2. Continued.

Atom	Site	x	y	z	U _{iso}
H(18A)	8f	0.3446	−0.2022	0.6946	0.092
H(19A)	8f	0.0641	−0.4551	0.4534	0.050
H(19B)	8f	0.1000	−0.4888	0.5106	0.050
H(20A)	8f	0.1222	−0.2974	0.5179	0.050
H(20B)	8f	0.0414	−0.2866	0.5306	0.050
H(20C)	8f	0.0597	−0.2636	0.4723	0.050

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Fe(1)	8f	0.40508(4)	−0.60075(7)	0.64745(3)	0.0678(5)	0.0522(4)	0.0532(4)	−0.0020(3)	0.0079(3)	0.0024(3)
Fe(2)	8f	0.28796(4)	−0.48576(7)	0.64482(3)	0.0578(4)	0.0648(5)	0.0563(5)	−0.0068(3)	0.0137(3)	0.0021(3)
Cl(1)	8f	0.2922(1)	−0.5937(2)	0.34674(6)	0.159(2)	0.136(2)	0.0479(8)	−0.029(2)	−0.002(1)	−0.013(1)
Cl(2)	8f	0.5418(1)	0.0484(2)	0.6666(1)	0.137(2)	0.072(1)	0.142(2)	−0.040(1)	0.013(1)	−0.016(1)
S(1)	8f	0.37224(7)	−0.4520(1)	0.58806(5)	0.0625(7)	0.0554(7)	0.0434(6)	−0.0072(6)	0.0086(5)	−0.0014(5)
S(2)	8f	0.38924(8)	−0.4445(1)	0.70335(5)	0.0740(8)	0.0669(8)	0.0435(6)	−0.0089(7)	0.0128(6)	−0.0011(6)
O(1)	8f	0.3577(3)	−0.7948(5)	0.5731(2)	0.143(5)	0.081(3)	0.101(4)	−0.028(3)	0.018(3)	−0.028(3)
O(2)	8f	0.5638(3)	−0.6237(5)	0.6464(3)	0.071(3)	0.110(4)	0.192(6)	0.012(3)	0.020(4)	0.008(4)
O(3)	8f	0.3883(4)	−0.7647(6)	0.7359(2)	0.224(7)	0.095(4)	0.097(4)	−0.001(4)	0.022(4)	0.047(4)
O(4)	8f	0.2240(4)	−0.5952(7)	0.7334(2)	0.127(5)	0.212(7)	0.093(4)	−0.065(5)	0.043(3)	0.028(4)
O(5)	8f	0.2033(3)	−0.2611(6)	0.6369(3)	0.108(4)	0.099(4)	0.209(7)	0.034(4)	0.018(4)	0.002(5)
O(6)	8f	0.1937(3)	−0.6333(5)	0.5700(2)	0.106(4)	0.107(4)	0.104(4)	−0.043(3)	−0.008(3)	0.000(3)
O(7)	4b	0	−½	½	0.10(1)	1.4(2)	0.49(5)	0.02(3)	0.03(2)	−0.34(7)
C(1)	8f	0.3768(3)	−0.7180(6)	0.6015(2)	0.086(4)	0.068(4)	0.063(3)	−0.004(3)	0.015(3)	0.005(3)
C(2)	8f	0.5022(4)	−0.6134(6)	0.6463(3)	0.084(5)	0.061(4)	0.092(5)	−0.004(3)	0.007(3)	−0.007(3)
C(3)	8f	0.3963(4)	−0.7003(7)	0.7018(3)	0.120(6)	0.075(4)	0.072(4)	0.004(4)	0.000(4)	0.007(4)
C(4)	8f	0.2489(4)	−0.5516(8)	0.6992(3)	0.083(4)	0.120(6)	0.072(4)	−0.026(4)	0.024(3)	0.008(4)
C(5)	8f	0.2362(4)	−0.3475(7)	0.6401(3)	0.072(4)	0.089(5)	0.106(5)	0.006(4)	0.021(4)	0.002(4)
C(6)	8f	0.2310(4)	−0.5749(6)	0.5982(3)	0.072(4)	0.078(4)	0.075(4)	−0.016(3)	0.006(3)	0.014(3)
C(7)	8f	0.3469(3)	−0.5003(5)	0.5204(2)	0.074(3)	0.051(3)	0.044(3)	−0.011(2)	0.011(2)	0.000(2)
C(8)	8f	0.3950(3)	−0.5660(6)	0.4949(2)	0.079(4)	0.074(4)	0.055(3)	−0.004(3)	0.008(3)	0.001(3)
C(9)	8f	0.3781(4)	−0.5937(6)	0.4407(2)	0.103(5)	0.089(5)	0.050(3)	−0.004(4)	0.019(3)	−0.010(3)
C(10)	8f	0.3140(4)	−0.5562(6)	0.4139(2)	0.104(5)	0.081(4)	0.037(3)	−0.030(4)	0.006(3)	0.003(3)
C(11)	8f	0.2657(4)	−0.4901(6)	0.4386(2)	0.088(4)	0.090(5)	0.056(3)	−0.014(4)	−0.011(3)	0.008(3)
C(12)	8f	0.2821(3)	−0.4602(6)	0.4927(2)	0.075(4)	0.081(4)	0.054(3)	−0.003(3)	0.004(3)	0.005(3)
C(13)	8f	0.4310(3)	−0.3061(5)	0.6862(2)	0.066(3)	0.060(3)	0.042(2)	−0.008(2)	0.007(2)	−0.010(2)
C(14)	8f	0.5029(3)	−0.3031(5)	0.6766(2)	0.059(3)	0.062(3)	0.059(3)	0.000(2)	0.000(2)	−0.009(3)
C(15)	8f	0.5371(3)	−0.1940(6)	0.6708(2)	0.064(3)	0.072(4)	0.076(4)	−0.015(3)	0.003(3)	−0.013(3)
C(16)	8f	0.4986(4)	−0.0901(6)	0.6734(2)	0.092(4)	0.064(4)	0.059(3)	−0.019(3)	0.001(3)	−0.010(3)
C(17)	8f	0.4266(4)	−0.0904(6)	0.6824(3)	0.099(5)	0.058(4)	0.089(4)	−0.003(3)	0.017(4)	−0.024(3)
C(18)	8f	0.3934(4)	−0.2001(6)	0.6886(3)	0.082(4)	0.067(4)	0.084(4)	0.001(3)	0.024(3)	−0.022(3)
C(19)	8f	0.0596(9)	−0.445(2)	0.491(1)	0.7(1)	1.6(2)	0.30(4)	1.0(1)	−0.26(6)	−0.38(8)
C(20)	8f	0.0719(8)	−0.311(1)	0.5042(7)	0.19(2)	0.22(2)	0.51(4)	0.04(1)	0.13(2)	0.15(2)

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