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The crystal structure of pentakis(carbonyl)- $\{\mu$ -[2,3-bis(sulfanyl)propan-1-olato]-(triphenylphosphane)diiron ($Fe-Fe$)

$C_{26}H_{21}Fe_2O_6PS_2$

Table 1: Data collection and handling.

Crystal:	Red block
Size:	0.32 × 0.24 × 0.22 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.31 mm ⁻¹
Diffractometer, scan mode:	Bruker D8 QUEST, φ and ω
θ_{max} , completeness:	25.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	63350, 4837, 0.090
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 3418
$N(param)_{refined}$:	344
Programs:	Bruker [1], Olex2 [2], SHELX [3, 4]

Source of material

A mixture of complex $[Fe_2(CO)_6\{\mu-SCH_2CH(CH_2OH)\}]$ (1 mmol) and triphenylphosphine (1 mmol) was treated with $Me_3NO \cdot 2H_2O$ (1 mmol). The resulting solution was stirred at room temperature for 0.5 h. Afterwards, the solvent was reduced in vacuo and the residue was subjected to TLC separation using CH_2Cl_2 : petroleum ether = 1:3 (v/v) as eluent. The title complex was obtained from the main red band. Slow evaporation of CH_2Cl_2 /hexane solution at 4 °C afforded crystals suitable for X-ray diffraction analysis.

Experimental details

The structure was solved by direct method with the SHELXS program. Hydrogen atoms were positioned geometrically (C–H = 0.93–0.98 Å and O–H = 0.82 Å). Their U_{iso} values were set to 1.2 U_{eq} or 1.5 U_{eq} of the parent atoms. The hydroxy group features a disorder (see the figure).

Comment

Over the past decades, dithiolate-bridging diiron complexes have attracted great interest due to their structural resemblance with the active site of [FeFe]-hydrogenases [5–7]. [FeFe]-hydrogenases are natural metalloenzymes that can catalyze the reduction of protons to H_2 [8, 9]. The

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Abstract

$C_{26}H_{21}Fe_2O_6PS_2$, monoclinic, $P2_1/c$ (no. 14), $a = 9.0892(6)$ Å, $b = 27.6631(18)$ Å, $c = 11.3409(8)$ Å, $\beta = 106.409(2)^\circ$, $V = 2735.4(3)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0670$, $wR_{ref}(F^2) = 0.1620$, $T = 296(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
Fe1	0.15445 (10)	0.47736 (3)	0.78454 (10)	0.0539 (3)
Fe2	0.04267 (9)	0.39648 (3)	0.80761 (8)	0.0408 (2)
S1	0.0102 (2)	0.43417 (6)	0.62538 (18)	0.0630 (5)
S2	−0.0601 (2)	0.46758 (6)	0.8423 (2)	0.0666 (6)
P1	−0.14211 (17)	0.34028 (5)	0.77659 (14)	0.0377 (4)
O1	0.1284 (9)	0.5793 (2)	0.7129 (7)	0.116 (2)
O2	0.3498 (7)	0.4877 (3)	1.0349 (6)	0.095 (2)
O3	0.4231 (7)	0.4501 (3)	0.7076 (7)	0.110 (2)
O4	0.1733 (7)	0.3814 (2)	1.0694 (5)	0.0915 (19)
O5	0.2586 (6)	0.3345 (2)	0.7345 (5)	0.0789 (16)
O6 ^a	−0.3938 (18)	0.5321 (5)	0.5693 (15)	0.177 (9)
H6 ^a	−0.4199	0.5054	0.5395	0.265*
O6A ^b	−0.190 (2)	0.5637 (7)	0.673 (3)	0.181 (14)
H6A ^b	−0.1504	0.5572	0.6184	0.271*
C1	0.1361 (9)	0.5396 (3)	0.7370 (8)	0.076 (2)
C2	0.2699 (8)	0.4846 (3)	0.9364 (8)	0.064 (2)
C3	0.3178 (9)	0.4613 (3)	0.7375 (8)	0.071 (2)
C4	0.1203 (8)	0.3869 (3)	0.9665 (7)	0.0583 (18)
C5	0.1747 (7)	0.3581 (2)	0.7667 (6)	0.0493 (16)
C6	−0.1707 (10)	0.4643 (3)	0.5850 (9)	0.087 (3)
H6B	−0.1638	0.4937	0.5401	0.104*
H6C	−0.2476	0.4436	0.5319	0.104*
C7	−0.2161 (8)	0.4762 (3)	0.6950 (10)	0.083 (3)
H7	−0.2984	0.4537	0.6975	0.099*
C8	−0.2855 (14)	0.5268 (4)	0.6842 (11)	0.114 (4)
H8AA ^a	−0.3343	0.5318	0.7490	0.137*
H8AB ^a	−0.2052	0.5508	0.6935	0.137*
H8BC ^b	−0.3752	0.5274	0.6134	0.137*
H8BD ^b	−0.3199	0.5328	0.7564	0.137*
C9	−0.2793 (6)	0.34205 (19)	0.6247 (5)	0.0384 (13)
C10	−0.4319 (7)	0.3516 (2)	0.6067 (6)	0.0518 (16)
H10	−0.4697	0.3545	0.6745	0.062*
C11	−0.5296 (8)	0.3569 (3)	0.4918 (7)	0.069 (2)
H11	−0.6325	0.3638	0.4822	0.082*
C12	−0.4774 (10)	0.3522 (3)	0.3905 (7)	0.072 (2)
H12	−0.5449	0.3555	0.3123	0.087*
C13	−0.3266 (9)	0.3427 (2)	0.4041 (6)	0.0636 (19)
H13	−0.2912	0.3394	0.3352	0.076*
C14	−0.2258 (7)	0.3379 (2)	0.5203 (6)	0.0486 (15)
H14	−0.1225	0.3318	0.5294	0.058*
C15	−0.2676 (7)	0.3375 (2)	0.8774 (5)	0.0426 (14)
C16	−0.3450 (7)	0.2951 (3)	0.8861 (6)	0.0557 (17)
H16	−0.3301	0.2679	0.8429	0.067*
C17	−0.4441 (8)	0.2930 (3)	0.9585 (7)	0.069 (2)
H17	−0.4953	0.2643	0.9638	0.083*
C18	−0.4675 (8)	0.3328 (3)	1.0225 (7)	0.073 (2)
H18	−0.5352	0.3313	1.0704	0.088*
C19	−0.3904 (9)	0.3747 (3)	1.0156 (7)	0.076 (2)
H19	−0.4057	0.4018	1.0592	0.092*
C20	−0.2896 (8)	0.3769 (3)	0.9438 (6)	0.0584 (18)
H20	−0.2365	0.4054	0.9408	0.070*
C21	−0.0634 (6)	0.2792 (2)	0.7929 (5)	0.0399 (14)
C22	−0.1010 (8)	0.2444 (2)	0.7017 (6)	0.0532 (17)
H22	−0.1704	0.2518	0.6264	0.064*
C23	−0.0365 (9)	0.1987 (3)	0.7211 (7)	0.068 (2)

Table 2: (continued)

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
H23	−0.0637	0.1757	0.6591	0.081*
C24	0.0663 (9)	0.1872 (3)	0.8303 (8)	0.070 (2)
H24	0.1092	0.1565	0.8428	0.084*
C25	0.1060 (8)	0.2210 (3)	0.9210 (7)	0.067 (2)
H25	0.1764	0.2133	0.9956	0.081*
C26	0.0422 (8)	0.2668 (2)	0.9028 (7)	0.0588 (18)
H26	0.0708	0.2896	0.9655	0.071*

^aOccupancy: 0.589(16), ^bOccupancy: 0.411(16).

X-ray crystallographic structures of the active site of [FeFe]-hydrogenases have promoted chemists to produce a great number of diiron analogues as mimics for the active site of [FeFe]-hydrogenases [10–13]. In this study, we have successfully prepared a diiron analogue with a monophosphine ligand.

The asymmetric unit of the title complex consists of a butterfly diiron ethane-1,2-dithiolate dinuclear complex with five terminal carbonyls and a triphenylphosphine ligand, respectively. The phosphine ligand occupies an apical position of the distorted octahedral geometry of Fe2, in good agreement with monosubstituted analogues [14–16]. The Fe1–Fe2 bond length [2.5013(12) Å] is identical to that of the parent complex [Fe₂(CO)₆{μ-SCH₂CH(CH₂OH)}] [2.4998(6) Å] [17], but much shorter than those in diphosphine-substituted analogues [18–20] as well as in natural [FeFe]-hydrogenases [8, 9]. Note that the O6 atom is disordered over two sites with an occupancy of 0.589(16). The disorder suggests that it is unlikely that this OH···O hydrogen bond is present. Moreover, weak hydrogen bonds are also observed.

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