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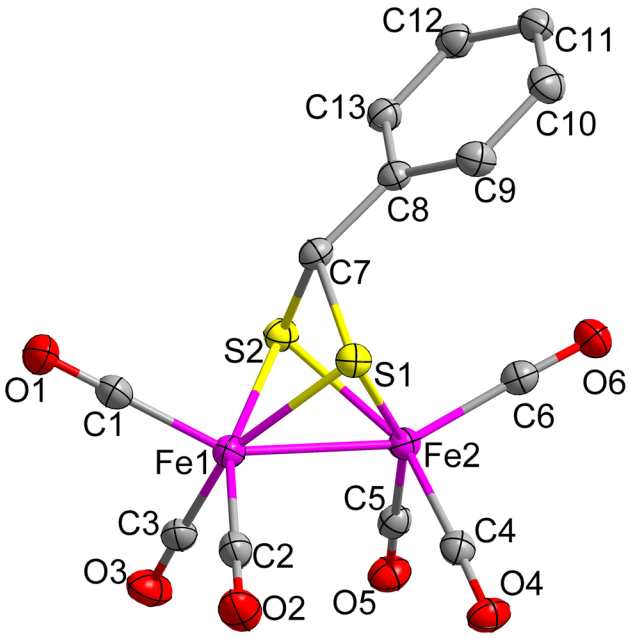
Crystal structure of hexacarbonyl-μ_2-[phenylmethanedithiolato-κ^4*S:S,S′:S′*]diiron (Fe–Fe) $C_{13}H_6Fe_2O_6S_2$



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Abstract

$C_{13}H_6Fe_2O_6S_2$, monoclinic, $P2_1/c$ (no. 14), a = 10.0181(3) Å, b = 6.4719(2) Å, c = 24.3922(6) Å, β = 94.630(1)°, V = 1576.34(8) Å^3, Z = 4, $R_{gt}(F)$ = 0.0245, w$R_{ref}(F^2)$ = 0.0566, T = 150(2) K.

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The molecular structure is shown in the figure. Table 1 contains the crystallographic data and the list of the atoms including atomic coordinates and displacement parameters can be found in the cif-file attached to this article.

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Table 1: Data collection and handling.

Crystal:	Red block
Size:	0.30 × 0.20 × 0.20 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	2.13 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω scans
θ_{max}, completeness:	26.4°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	28896, 3216, 0.042
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2594
$N(param)_{refined}$:	208
Programs:	Bruker,[1] SHELX,[2,3] Olex2[4]

1 Source of material

A mixture of 1-phenylmethanedithiol (0.156 g, 1.0 mmol) and triiron dodecacarbonyl (0.504 g, 1.0 mmol) was refluxed in THF (10 mL) under stirring for 2 h. After removal of the solvent under reduced pressure using a rotary evaporator, the residue was purified by preparative TLC with petroleum ether as the eluent. The main red band afforded the title complex as a red solid in 38 % yield. Single crystals were obtained by slow crystallization from a cold hexane solution.

2 Experimental details

The structure was solved by Direct Methods with the SHELXS program. Hydrogen atoms were positioned geometrically (C–H = 0.93–0.98 Å). Their U_{iso} values were set to 1.2U_{eq} or 1.5U_{eq} of the parent atoms.

3 Comment

The natural [FeFe]-hydrogenase exhibits exceptional catalytic efficiency in the reversible interconversion between protons and hydrogen gas, with turnover frequencies exceeding 10^{-4}s^{-1}, far surpassing most synthetic catalysts.[5] This remarkable capability establishes it as a paradigmatic model for investigating biological hydrogen production and hydrogen energy utilization mechanisms. $Fe_2(\mu\text{–}ER)_2(CO)_6$ complexes (E = S, Se, Te), which structurally mimic the $[2Fe]_H$ subcluster of the

native enzyme active site, serve as pivotal synthetic platforms to decipher structure-function relationships in hydrogenase-inspired catalysis.[6–12] Given these considerations, the investigation of such model compounds represents a strategic entry point for simulating the enzymatic active center. Herein, we report a biomimetic compound $C_{13}H_6Fe_2O_6S_2$ derived from 1-phenylmethanedithiol. The title complex features a butterfly-shaped [Fe_2S_2] cluster core coordinated with six terminal carbonyl ligands and a bridging phenylmethanedithiolate. The Fe1–Fe2 distance of 2.4881(4) Å is notably shorter than those reported for the natural [FeFe]-hydrogenases (2.55–2.60 Å).[13] The average Fe–C bond length (1.803 Å) and Fe–S bond distance (2.267 Å) fall within the normal range and align closely with values observed in analogous synthetic species.[14–19]

Conflict of interest: The authors declare no conflicts of interest regarding this article.

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