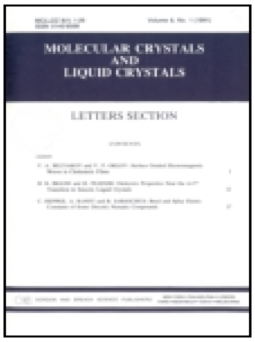

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Tetrairon ethanedithiolate complex with intermolecularly bridging bis(diphenylphosphino)acetylene

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ABSTRACT
In this article, a tetrairon ethanedithiolate complex [(μ-SCH_2CH_2S-μ)$Fe_2(CO)_5]_2(Ph_2PC{\equiv}CPPh_2)$ was reported. The title complex could be easily prepared by ligand exchange reaction of the starting material (μ-SCH_2CH_2S-μ)$Fe_2(CO)_6$ with $Ph_2PC{\equiv}CPPh_2$ and $Me_3NO{\cdot}2H_2O$ in CH_2Cl_2/MeCN solutions at ambient temperature. The title complex was new and structurally characterized by NMR spectroscopy and X-ray diffraction analysis. Its molecular structure reveals that it consists of two butterfly diiron ethanedithiolate units linked together through $Ph_2PC{\equiv}CPPh_2$. In addition, intermolecular C-H ...O hydrogen bonds and π-π stacking interactions stabilize the solid state in the crystal packing diagram.

KEYWORDS
Carbonyl substitution; crystal structure; diiron ethanedithiolate; diphosphine ligand; synthesis

Introduction

The parent complex (μ-SCH_2CH_2S-μ)$Fe_2(CO)_6$ could be synthesized either by the heating reaction of $Fe_3(CO)_{12}$ with $HSCH_2CH_2SH$ [1] or by the in situ reaction of (μ-$LiS)_2Fe_2(CO)_6$ with $BrCH_2CH_2Br$ [2]. After 20 years later, since (μ-SCH_2CH_2S-μ)$Fe_2(CO)_6$ was first reported, the studies on (μ-SCH_2CH_2S-μ)$Fe_2(CO)_6$ and derivatives have been attracted great interests by chemists because the active site of [Fe-Fe]-hydrogenases consists of a butterfly diiron dithiolate cluster with terminal carbonyls, cyanide, and other ligands in microorganism [3–10]. On the basis of our studies on the diiron ethanedithiolate complexes [11], we started to investigate the carbonyl substitution reaction of (μ-SCH_2CH_2S-μ)$Fe_2(CO)_6$ with a diphosphine ligand bis(diphenylphosphino)acetylene by using the decarbonylating agent $Me_3NO{\cdot}2H_2O$. In this article, we describe the synthesis, spectral characterization, and X-ray crystal structure of the tetrairon ethanedithiolate complex with bridging $Ph_2PC{\equiv}CPPh_2$.

Experimental

$Ph_2PC{\equiv}CPPh_2$ and $Me_3NO{\cdot}2H_2O$ were available commercially and used as received. Complex (μ-SCH_2CH_2S-μ)$Fe_2(CO)_6$ [1] was prepared according to literature procedures. NMR spectra were obtained on a Bruker Avance 500 MHz spectrometer.

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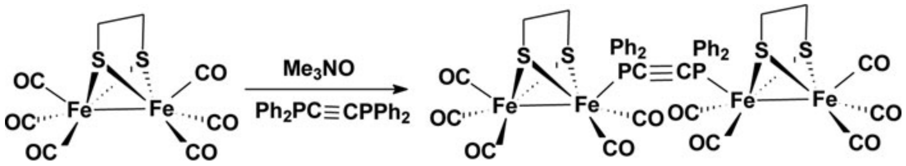

Scheme 1. Synthesis of the title complex.

Synthesis of the title complex

To a solution of (μ-SCH$_2$CH$_2$S-μ)Fe$_2$(CO)$_6$ (0.074 g, 0.2 mmol) and Ph$_2$PC≡CPPh$_2$ (0.040 g, 0.1 mmol) in CH$_2$Cl$_2$ (10 mL) was added a solution of Me$_3$NO·2H$_2$O (0.022 g, 0.2 mmol) in MeCN. The mixture was stirred at room temperature for 1 hr and then the solvent was reduced in vacuo and the residue was subjected to thin layer chromatography separation using CH$_2$Cl$_2$/petroleum ether ($v/v = 1:2$) as eluent. From the main red band afforded 0.060 g (56%) of the title complex as a red solid. ^{1}H NMR (500 MHz, C*D*Cl$_3$): 7.84–7.80 (m, 4H, PhH), 7.46–7.42 (m, 6H, PhH), 1.94 (q, $J = 4.5$ Hz, 2H, SCH$_2$), and 1.63 (q, $J = 4.0$ Hz, 2H, SCH$_2$) ppm. ^{31}P{^{1}H} NMR (200 MHz, CDCl$_3$, 85% H$_3$PO$_4$): 39.04 (s) ppm. ^{13}C{^{1}H} NMR (125 MHz, C*D*Cl$_3$): 213.74 (d, $J_{\text{P-C}} = 7.6$ Hz, PFeCO), 209.62 (FeCO), 134.49 (d, $J_{\text{P-C}} = 47.1$ Hz, *i*-PhC), 131.52 (d, $J_{\text{P-C}} = 13$ Hz, *o*-PhC), 130.89 (s, *p*-PhC), 129.05 (d, $J_{\text{P-C}} = 10.7$ Hz, *m*-PhC), 105.91 (d, $J_{\text{P-C}} = 54.7$ Hz, C≡C), and 35.05 (d, $J_{\text{P-C}} = 3.7$ Hz, SCH$_2$) ppm.

X-ray structure determination

A single crystal of the title complex was mounted on a Rigaku MM-007 CCD diffractometer. Data were collected at 113 K by using a graphite monochromator with Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) in the ω-ϕ scanning mode. Data collection, reduction and absorption correction were performed by CRYSTALCLEAR program [12]. The structure was solved by direct methods using the SHELXS-97 program [13] and refined by full-matrix least-squares techniques SHELXL-97 [14] on F^2. Hydrogen atoms were located using the geometric method. Details of crystal data, data collections, and structure refinement are summarized in Table 1.

Results and discussion

Spectral characterization

As shown in Scheme 1, the synthetic procedures for the title complex reveal that carbonyl substitution reaction of (μ-SCH$_2$CH$_2$S-μ)Fe$_2$(CO)$_6$ with 0.5 equivalent of Ph$_2$PC≡CPPh$_2$ and equimolar of Me$_3$NO·2H$_2$O in CH$_2$Cl$_2$/MeCN solutions afforded the title complex in 56% yield. The title complex is an air-stable red solid, which has been characterized by NMR spectroscopy. The ^{1}H NMR spectra show two multiplets in the region of $\delta = 7.84$–7.42 ppm for phenyl protons and two quadruplets at $\delta = 1.94$ and 1.63 ppm for the methylene protons. The ^{31}P{^{1}H} NMR spectra display a singlet at $\delta = 39.04$ ppm for the two phosphorus atoms of Ph$_2$PC≡CPPh$_2$, each coordinated to the iron atoms of the diiron subsite. The ^{13}C{^{1}H} NMR spectra demonstrate a doublet at $\delta = 213.74$ ppm and a singlet at $\delta = 209.62$ ppm for the terminal carbonyls and a singlet at $\delta = 105.91$ ppm with a coupling constant $J_{\text{P-C}} = 54.7$ Hz for acetylene carbons. The NMR data are consistent with its structure.

Table 1. Crystal data and structure refinements details for the title complex.

Empirical formula	$C_{40}H_{28}Fe_4O_{10}P_2S_4$
Formula weight	1082.20
Temperature (K)	113(2)
Wavelength (SÅ)	0.71073
Crystal system	Tetragonal
Space group	P4(2)/n
a (SÅ)	23.084(3)
b (SÅ)	23.084(3)
c (SÅ)	8.7317(17)
α (°)	90
β (°)	90
γ (°)	90
V ($SÅ^3$)	4653.0(13)
Z	4
D_{calc} ($g\cdot cm^{-3}$)	1.545
μ (mm^{-1})	1.523
F(000)	2184
Crystal size (mm^3)	0.20 × 0.18 × 0.12
θ_{min}, θ_{max} (°)	1.76, 25.02
Reflections collected/unique	36,694/4128
R_{int}	0.1256
hkl range	$-27 \leq h \leq 25$
	$-27 \leq k \leq 22$
	$-10 \leq l \leq 10$
Completeness to θ_{max} (%)	100.0
Data/restraints/parameters	4128/0/271
Goodness of fit on F^2	1.137
$R1/wR2$ ($I > 2\sigma(I)$)	0.0682/0.1825
$R1/wR2$ (all data)	0.0897/0.2009
Largest diff peak and hole/e $Å^{-3}$	1.573/−0.736

X-ray crystal structure

The molecular structure of the title complex has been characterized by X-ray diffraction analysis. The ORTEP and packing views are shown in Figs. 1 and 2, respectively. The selected bond distances and bond angles are presented in Table 2. The title complex crystallizes in tetragonal

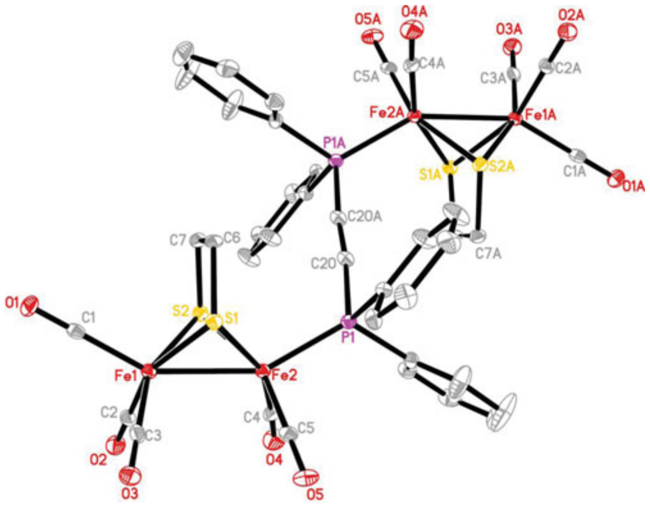

Figure 1. ORTEP view of the title complex with 30% probability level ellipsoids.

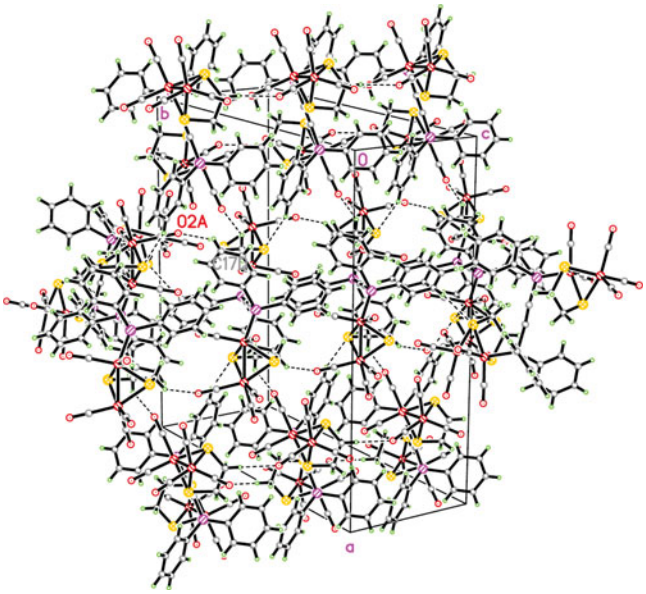

Figure 2. Crystal packing diagram of the title complex.

space group P2(1)/*n* with four molecules in the unit cell and one molecule in the asymmetric unit. As shown in Fig. 1, the molecular structure consists of two butterfly diiron ethanedithiolate clusters joined together through two phosphorus atoms of $Ph_2PC{\equiv}CPPh_2$. The molecule is centrosymmetric with the midpoint of C20-C20A as the inversion center, in accord with other diiron ethanedithiolate complexes, such as $[(\mu\text{-}SCH_2CH_2S\text{-}\mu)Fe_2(CO)_5]_2[(\eta^5\text{-}Ph_2PC_5H_4)_2Fe]$, $[(\mu\text{-}SCH_2CH_2S\text{-}\mu)Fe_2(CO)_5]_2(Ph_2PCH_2CH_2PPh_2)$, and $[(\mu\text{-}SCH_2CH_2S\text{-}\mu)Fe_2(CO)_5]_2(Ph_2PCH{=}CHPPh_2)$ [11]. The bis(diphenylphosphino)acetylene resides in an apical position of the square-pyramidal coordination sphere of Fe2 and Fe2A, consistent with monosubstituted diiron complexes [15–18]. The Fe1-Fe2 bond distance [2.5100(12) Å] is slightly longer than that of $(\mu\text{-}SCH_2CH_2S\text{-}\mu)Fe_2(CO)_6$ [2.5103(11) Å] [19], but shorter than those in *Clostrium pasteurianum* and *Desulfovibrio desulfuricans* (2.55—2.62 Å) [20,21].

As shown in Fig. 2, the crystal packing of the title complex is stabilized by weak intermolecular C-H …O hydrogen bonds between the methylene groups and carbonyl groups as well as by π-π stacking interactions and other noncovalent associations. For example, the O2A atom of carbonyl has a short nonbonded contact with the H atom of methylene group between the adjacent molecules.

Table 2. Selected bond lengths (*SÅ*) and angles (°) for the title complex.

Fe(1)-S(2)	2.2508(17)	Fe(1)-S(1)	2.2526(18)
Fe(1)-Fe(2)	2.5100(12)	Fe(2)-P(1)	2.1930(17)
Fe(2)-S(2)	2.2497(17)	Fe(2)-S(1)	2.2518(17)
C(6)-C(7)	1.538(9)	C(20)-C(20)A	1.227(12)
S(2)-Fe(1)-S(1)	80.22(6)	S(2)-Fe(1)-Fe(2)	56.08(5)
S(1)-Fe(1)-Fe(2)	56.12(5)	P(1)-Fe(2)-S(2)	105.31(6)
P(1)-Fe(2)-Fe(1)	149.34(6)	S(2)-Fe(2)-Fe(1)	56.12(5)
S(1)-Fe(2)-Fe(1)	56.15(5)	Fe(2)-S(1)-Fe(1)	67.73(5)
Fe(2)-S(2)-Fe(1)	67.80(5)	C(20)A-C(20)-P(1)	174.2(7)

Conclusion

In summary, the title complex $[(\mu\text{-SCH}_2\text{CH}_2\text{S-}\mu)\text{Fe}_2(\text{CO})_5]_2(\text{Ph}_2\text{PC}{\equiv}\text{CPPh}_2)$ has been prepared by the carbonyl substitution reaction of the parent complex with a diphosphine ligand and the decarbonylating agent and structurally characterized by NMR spectroscopy. In addition, the molecular structure of the title complex was determined by X-ray diffraction analysis, indicating that it consists of two diiron dithiolate moieties linked together through $\text{Ph}_2\text{PC}{\equiv}\text{CPPh}_2$. Intermolecular C-H …O hydrogen bonds and π-π stacking interactions were observed in the crystal packing diagram.

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