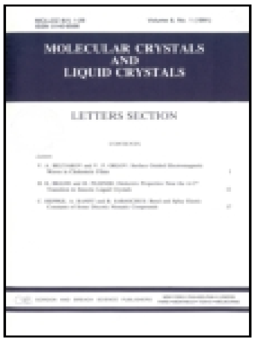

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LETTERS SECTION

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Synthesis and structural analysis of $(\mu\text{-}SCH_2CH_2CH_2S\text{-}\mu)Fe_2(CO)_5(2\text{-}C_5H_4NPPh_2)$

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ABSTRACT
Treatment of $(\mu\text{-}SCH_2CH_2CH_2S\text{-}\mu)Fe_2(CO)_6$ with equimolar $2\text{-}C_5H_4NPPh_2$ in the presence of $Me_3NO{\cdot}2H_2O$ in CH_2Cl_2/MeCN solutions gave the title complex $(\mu\text{-}SCH_2CH_2CH_2S\text{-}\mu)Fe_2(CO)_5(2\text{-}C_5H_4NPPh_2)$ in 76% yield. The title complex was characterized by spectroscopy as well as by single crystal X-ray diffraction analysis. The molecular structure consists of a butterfly $[Fe_2S_2]$ cluster with propane, five carbonyls, and $2\text{-}C_5H_4NPPh_2$. In the crystal packing diagram, intermolecular C–H···O hydrogen bonds between phenyl and carbonyl groups stabilize the solid state.

KEYWORDS
Carbonyl substitution; crystal structure; diiron dithiolate; synthesis

Introduction

In recent years, diiron dithiolate complexes have received special interest due to their potential applications in a great number of catalytic reactions [1–5]. On the other hand, these complexes have the similar structure as the active site of [FeFe]-hydrogenases which catalyze the proton reduction in microorganism [6–8]. Our previous studies have shown that numerous derivatives could be prepared by the carbonyl substitution reactions [9–11] of the all-carbonyl diiron complex of the type $(\mu\text{-}SRS\text{-}\mu)Fe_2(CO)_6$ with various monophosphine or diphosphine ligands [12–15]. In recent study, pyridyl-containing derivative $(\mu\text{-}SCH_2CH_2CH_2S\text{-}\mu)Fe_2(CO)_5(2\text{-}C_5H_4NPPh_2)$ has been synthesized by carbonyl substitution and its structure has been fully characterized.

Experimental

Synthesis of the title complex

To a solution of $(\mu\text{-}SCH_2CH_2CH_2S\text{-}\mu)Fe_2(CO)_6$ (0.077 g, 0.2 mmol) and $2\text{-}C_5H_4NPPh_2$ (0.053 g, 0.2 mmol) in CH_2Cl_2 (10 mL) was added a solution of $Me_3NO{\cdot}2H_2O$ (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 TLC separation using CH_2Cl_2/petroleum ether (v/v = 1:1) as eluent. From the main red band afforded 0.095 g (76%) of the title complex as a red solid. IR (KBr disk, cm^{-1}): $\nu_{C\equiv O}$ 2039 (vs), 2001 (vs), 1955 (vs), 1921 (vs). ^1H NMR (500 MHz, $CDCl_3$): 8.80 (*d*, $J = 3.5$ Hz, 1H, Py*H*), 7.80 (*t*, $J = 8.2$ Hz,

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

Empirical formula	$C_{25}H_{20}Fe_2NO_5PS_2$
Formula weight	621.21
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2(1)/c$
a (Å)	9.5711(19)
b (Å)	10.048(2)
c (Å)	27.771(6)
α (°)	90
β (°)	91.84(3)
γ (°)	90
V (Å^3)	2669.4(9)
Z	4
D_{calc} (g·cm^{-3})	1.546
μ (mm^{-1})	1.339
F(000)	1264
Crystal size (mm^3)	0.20 × 0.18 × 0.12
θ_{min}, θ_{max} (°)	2.13, 27.93
Reflections collected/unique	24,886/6,375
R_{int}	0.0389
hkl range	$-12 \leq h \leq 12$ $-12 \leq k \leq 13$ $-32 \leq l \leq 36$
Completeness to θ_{max} (%)	99.3
Data/restraints/parameters	6,375/24/326
Goodness of fit on F^2	1.081
$R1/wR2$ ($I>2\sigma(I)$)	0.0414/0.1023
$R1/wR2$ (all data)	0.0533/0.1109
Largest diff peak and hole/e Å^{-3}	0.370/−0.449

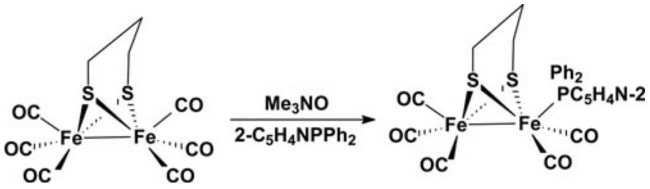
4H, Ph*H*), 7.66 (*s*, 1H, Py*H*), 7.45 (*s*, 6H, Ph*H*), 7.26 (s, 2H, Py*H*), 1.75 (*t*, $J = 9.2$ Hz, 2H, $CH_2CH_2CH_2$), 1.51 (s, 4H, $2SCH_2$) ppm. $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$, 85% H_3PO_4): 66.55 (s) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): 213.23 (*d*, $J_{P\text{-}C} = 9.7$ Hz, PFeCO), 209.68 (FeCO), 161.72 (*d*, $J_{P\text{-}C} = 63.5$ Hz, 2-Py*C*), 150.16 (*d*, $J_{P\text{-}C} = 15.6$ Hz, 6-Py*C*), 135.76 (*d*, $J_{P\text{-}C} = 6.5$ Hz, 4-Py*C*), 134.75 (*d*, $J_{P\text{-}C} = 37.9$ Hz, *i*-Ph*C*), 134.07 (*d*, $J_{P\text{-}C} = 10.7$ Hz, *o*-Ph*C*), 130.35 (*s*, *p*-Ph*C*), 128.47 (*d*, $J_{P\text{-}C} = 9.4$ Hz, *m*-Ph*C*), 127.26 (*d*, $J_{P\text{-}C} = 19.7$ Hz, 3-Py*C*), 123.43 (*s*, 5-Py*C*), 30.03 (SCH_2), 22.09 ($CH_2CH_2CH_2$) ppm.

X-ray structure determination

Single crystals of the title complex suitable for X-ray diffraction analysis were grown by slow evaporation of CH_2Cl_2/hexane solutions at 4°C. 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 Kα radiation ($\lambda = 0.71073$ Å) in the ω-ϕ scanning mode. Data collection, reduction, and absorption correction were performed by *CRYSTALCLEAR* program [16]. The structure was solved by direct methods using the SHELXS-97 program [17] and refined by full-matrix least-squares techniques SHELXL-97 [18] 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

The route of synthesis is shown in Scheme 1. The parent complex (μ-$SCH_2CH_2CH_2S$-μ)$Fe_2(CO)_6$ reacted with 2-$C_5H_4NPPh_2$ and $Me_3NO{\cdot}2H_2O$ resulting in the formation of the



Scheme 1. Route of synthesis.

title complex in 76% yield. The title complex is air-stable red solids, which has been characterized by IR and NMR spectroscopy.

The IR spectra of the title complex showed four absorption bands in the region of 2039–1921 cm^{-1} for the terminal carbonyls. The values of IR are shifted toward lower frequencies with respect to the parent complex (2072, 2033, and 1993 cm^{-1}) [19] because the monophosphine 2-$C_5H_4NPPh_2$ is stronger electron-donating than CO. The ^{1}H NMR spectra of the title complex displayed a doublet at δ 8.80 ppm and two singlets at δ 7.66 and 7.26 ppm for the pyridyl protons. The ^{13}C{^{1}H} NMR spectra of the title complex exhibited seven doublets and two singlets in the region of δ 161.72–123.43 ppm for the pyridyl and phenyl carbons which is consistent with analogous complexes [20].

The molecular structure of the title complex was further confirmed by X-ray diffraction analysis. The molecular structure and packing view are shown in Figs. 1 and 2. The selected bond lengths and angles are presented in Table 1. The title complex crystallizes in monoclinic space group $P2(1)/c$ with four molecules in the unit cell and one molecule in the asymmetric unit. As shown in Fig. 1, the molecular structure consists of a butterfly [Fe_2S_2] cluster with propane, five carbonyls, and 2-$C_5H_4NPPh_2$. The diiron propanedithiolate contains two fused six-membered rings, in which one six-membered ring Fe1S1C6C7C8S2 is chair conformation and the other six-membered ring Fe2S1C6C7C8S2 is boat conformation. The phosphorus atom of 2-$C_5H_4NPPh_2$ attached to Fe2 atom resides in an apical position of the square-pyramidal geometry, very close to the most monophosphine substituted derivatives [21–25]. The Fe1-Fe2 bond length [2.5060(7) Å] is slightly shorter than the corresponding value in the

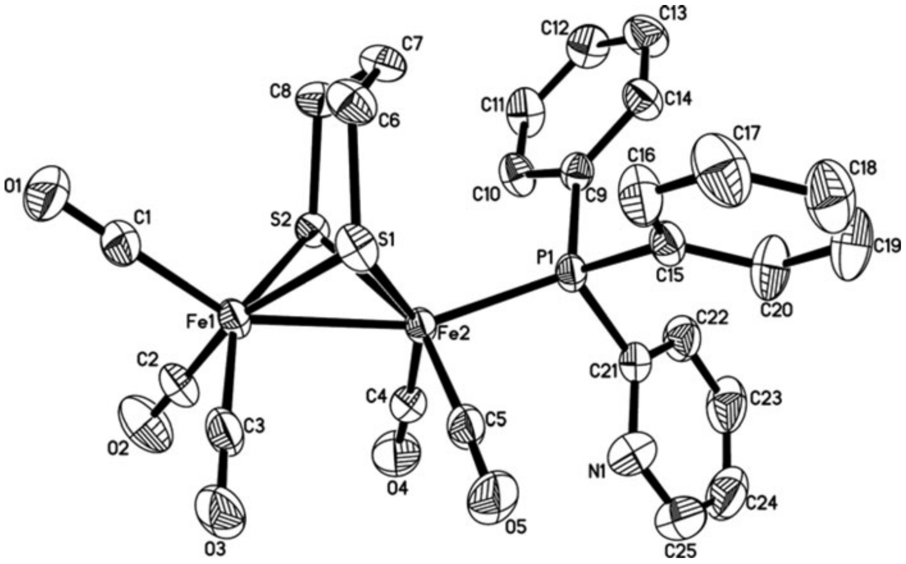


Figure 1. Molecular structure of the title complex.

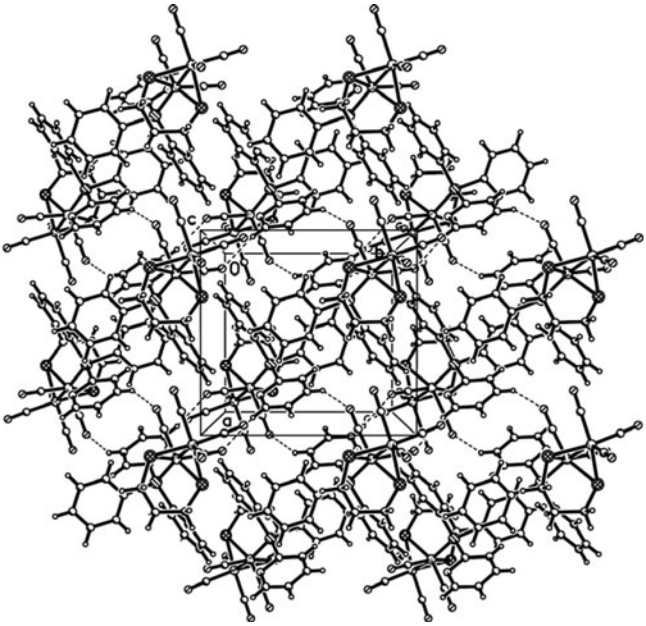


Figure 2. Packing diagram of the title complex.

Table 2. Selected bond lengths (Å) and bond angles (°).

Bond lengths			
Fe(1)-S(2)	2.2559(7)	Fe(1)–S(1)	2.2639(9)
Fe(1)-Fe(2)	2.5060(7)	Fe(2)–P(1)	2.2348(8)
Fe(2)-S(2)	2.2600(7)	Fe(2)–S(1)	2.2718(9)
S(1)-C(6)	1.823(3)	S(2)–C(8)	1.820(3)
Bond angles			
S(2)-Fe(1)-S(1)	84.40(2)	S(2)–Fe(1)–Fe(2)	56.372(17)
S(1)-Fe(1)-Fe(2)	56.61(3)	P(1)–Fe(2)–S(2)	108.13(3)
S(2)-Fe(2)-S(1)	84.13(3)	S(2)–Fe(2)–Fe(1)	56.22(2)
S(1)-Fe(2)-Fe(1)	56.31(2)	Fe(1)–S(1)–Fe(2)	67.08(3)
Fe(1)-S(2)-Fe(2)	67.41(2)	C(8)–C(7)–C(6)	114.3(2)

parent complex [2.5103(11) Å] [19], indicating that carbonyl substitution did not affect the Fe-Fe bond.

As shown in Fig. 2, intermolecular C–H···O hydrogen bonds between phenyl and carbonyl groups existing in the crystal structure to stabilize the solid state of the title complex.

Acknowledgments

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Supplementary Material

CCDC 1038834 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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