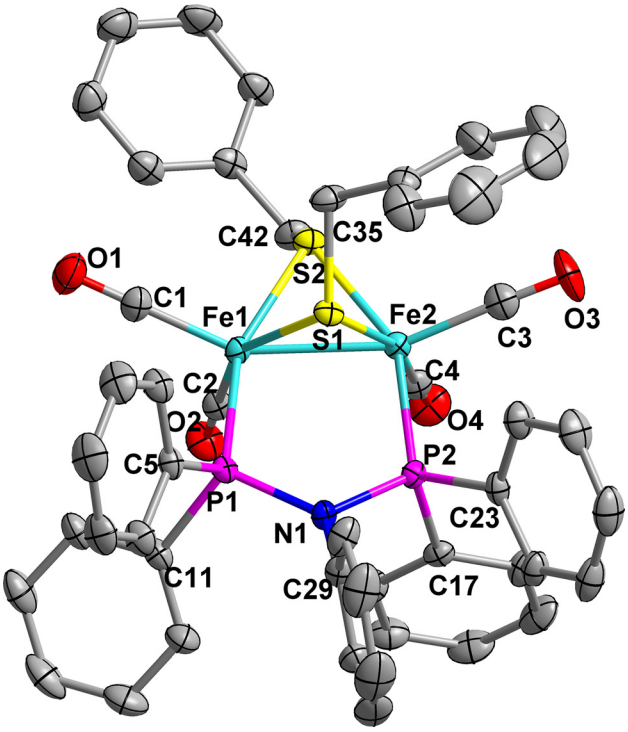
Xin-Ping Gao, Shuang Lü and Qian-Li Li*

Crystal structure of tetracarbonyl-{μ-[*N*-(diphenylphosphanyl)-*N*,*P*,*P*-triphenylphosphinous amide]}-bis[μ-(phenylmethanethiolato)]diiron (Fe–Fe), $C_{48}H_{39}Fe_2NO_4P_2S_2$



https://doi.org/10.1515/ncrs-2023-0115
Received March 13, 2023; accepted May 25, 2023;
published online June 6, 2023

Abstract

$C_{48}H_{39}Fe_2NO_4P_2S_2$, orthorhombic, $P2_1$ (no. 4), a = 11.4073(11) Å, b = 16.9013(14) Å, c = 11.8261(12) Å, α = 90°, β = 108.297(4)°, γ = 90°, V = 2164.8(4) Å^3, Z = 2, $R_{gt}(F)$ = 0.0355, w$R_{ref}(F^2)$ = 0.0740, T = 298(2) K.

CCDC no.: 2248002

***Corresponding author: Qian-Li Li**, Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252059, P.R. China, E-mail: liqianli1016@163.com. https://orcid.org/0000-0002-2191-1191
Xin-Ping Gao, Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252059, P.R. China
Shuang Lü, School of Pharmacy, Liaocheng University, Liaocheng 252059, P.R. China

Table 1: Data collection and handling.

Crystal:	Red block
Size	0.40 × 0.23 × 0.14 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.89 mm^{-1}
Diffractometer, scan mode:	φ and ω
θ_{max}, completeness:	25.0°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	10,927, 7335, 0.032
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 6467
$N(param)_{refined}$:	532
Programs:	Bruker [1], SHELX [2, 3], Olex2 [4]

1 Source of material

A mixture of solution of $[Fe_2(CO)_6(\mu\text{–}SCH_2C_6H_5)_2]$ (53 mg, 0.1 mmol) and $(Ph_2P)_2NC_6H_5$ (46 mg, 0.1 mmol) was dissolved in 10 ml of xylene. The reaction mixture was stirred at reflux for 1 h and the solvent was removed under vacuum. The title complex was obtained by preparative TLC separation using dichloromethane/pentane (1:2, v/v) as the eluent. The crystals were obtained from diffusion of dichloromethane solution into a hexane solution at room temperature.

2 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). Their U_{iso} values were set to 1.2 U_{eq} or 1.5 U_{eq} of the parent atoms.

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

Atom	x	y	z	U_{iso}*/U_{eq}
C1	0.2329 (5)	0.7461 (4)	0.7820 (5)	0.0416 (14)
C2	0.3808 (4)	0.8718 (3)	0.8665 (4)	0.0329 (12)
C3	0.1721 (5)	1.0262 (4)	0.5084 (5)	0.0426 (14)
C4	0.3671 (5)	1.0165 (3)	0.6998 (5)	0.0381 (13)
C5	0.0057 (4)	0.8303 (3)	0.8870 (5)	0.0328 (12)
C6	−0.0512 (5)	0.7777 (3)	0.7989 (5)	0.0420 (14)
H6	−0.020444	0.770072	0.735602	0.050*
C7	−0.1532 (5)	0.7360 (4)	0.8030 (6)	0.0573 (18)
H7	−0.191502	0.700891	0.742083	0.069*
C8	−0.1986 (5)	0.7460 (4)	0.8962 (6)	0.0612 (19)
H8	−0.267982	0.717970	0.898557	0.073*
C9	−0.1423 (5)	0.7967 (4)	0.9847 (6)	0.0536 (17)
H9	−0.173038	0.803119	1.048250	0.064*
C10	−0.0405 (5)	0.8388 (4)	0.9824 (5)	0.0442 (14)
H10	−0.002096	0.873051	1.044486	0.053*
C11	0.2272 (4)	0.8844 (3)	1.0422 (4)	0.0325 (12)
C12	0.2851 (5)	0.8144 (4)	1.0860 (5)	0.0453 (15)
H12	0.282736	0.772655	1.034045	0.054*
C13	0.3467 (5)	0.8053 (5)	1.2057 (6)	0.0593 (18)
H13	0.386658	0.758000	1.234486	0.071*
C14	0.3485 (5)	0.8665 (5)	1.2819 (5)	0.068 (2)
H14	0.388292	0.860455	1.363052	0.081*
C15	0.2925 (6)	0.9357 (5)	1.2395 (6)	0.066 (2)
H15	0.293999	0.977168	1.291608	0.079*
C16	0.2333 (5)	0.9450 (4)	1.1195 (5)	0.0487 (15)
H16	0.197104	0.993318	1.090842	0.058*
C17	0.2549 (4)	1.1067 (3)	0.8484 (5)	0.0319 (12)
C18	0.3418 (5)	1.0775 (4)	0.9499 (5)	0.0409 (14)
H18	0.332032	1.027039	0.977078	0.049*
C19	0.4430 (5)	1.1228 (4)	1.0113 (6)	0.0502 (16)
H19	0.500202	1.103252	1.080163	0.060*
C20	0.4582 (6)	1.1953 (4)	0.9706 (6)	0.0590 (18)
H20	0.526716	1.225349	1.011194	0.071*
C21	0.3737 (6)	1.2251 (4)	0.8701 (7)	0.0589 (18)
H21	0.384833	1.275431	0.843314	0.071*
C22	0.2723 (5)	1.1809 (3)	0.8086 (6)	0.0429 (14)
H22	0.215489	1.201223	0.740120	0.051*
C23	0.0079 (4)	1.0992 (3)	0.6849 (5)	0.0332 (12)
C24	−0.0731 (5)	1.0755 (4)	0.5774 (5)	0.0461 (14)
H24	−0.053440	1.032599	0.537501	0.055*
C25	−0.1841 (5)	1.1153 (4)	0.5281 (6)	0.0585 (18)
H25	−0.238619	1.099201	0.455346	0.070*
C26	−0.2122 (6)	1.1773 (4)	0.5864 (7)	0.0617 (19)
H26	−0.287762	1.202800	0.554763	0.074*
C27	−0.1313 (6)	1.2033 (4)	0.6913 (7)	0.0554 (18)
H27	−0.150802	1.247243	0.729304	0.066*
C28	−0.0213 (5)	1.1646 (3)	0.7408 (5)	0.0409 (14)
H28	0.033798	1.182536	0.812155	0.049*
C29	−0.0160 (4)	1.0127 (3)	0.8834 (5)	0.0327 (12)
C30	−0.1325 (5)	0.9890 (3)	0.8182 (6)	0.0456 (15)
H30	−0.143632	0.952354	0.757021	0.055*
C31	−0.2338 (6)	1.0201 (4)	0.8443 (8)	0.069 (2)
H31	−0.312919	1.003753	0.800633	0.083*
C32	−0.2187 (7)	1.0739 (5)	0.9327 (8)	0.075 (2)
H32	−0.286945	1.093414	0.950709	0.090*
C33	−0.1046 (8)	1.0988 (4)	0.9940 (7)	0.068 (2)
H33	−0.094846	1.137091	1.052806	0.082*
C34	−0.0020 (5)	1.0688 (3)	0.9716 (5)	0.0429 (14)
H34	0.076416	1.086284	1.015554	0.051*
C35	0.0212 (5)	0.8271 (3)	0.4858 (5)	0.0454 (14)
H35A	0.092354	0.819258	0.458890	0.055*
H35B	−0.008171	0.775683	0.501443	0.055*
C36	−0.0778 (5)	0.8690 (3)	0.3926 (5)	0.0413 (14)
C37	−0.1957 (5)	0.8712 (5)	0.3984 (6)	0.070 (2)
H37	−0.214757	0.844336	0.459026	0.084*
C38	−0.2863 (8)	0.9129 (7)	0.3154 (10)	0.113 (4)
H38	−0.365740	0.914746	0.321154	0.135*
C39	−0.2613 (13)	0.9507 (7)	0.2268 (10)	0.127 (5)
H39	−0.322843	0.978540	0.170367	0.152*
C40	−0.1443 (13)	0.9480 (6)	0.2199 (8)	0.114 (4)
H40	−0.126355	0.973897	0.157906	0.137*
C41	−0.0530 (8)	0.9077 (5)	0.3027 (6)	0.076 (2)
H41	0.026545	0.906922	0.297142	0.092*
C42	0.4791 (4)	0.8575 (3)	0.6447 (5)	0.0419 (13)
H42A	0.505599	0.896979	0.598284	0.050*
H42B	0.516544	0.869696	0.728464	0.050*
C43	0.5174 (4)	0.7766 (4)	0.6180 (5)	0.0369 (13)
C44	0.4998 (5)	0.7118 (4)	0.6788 (6)	0.0500 (16)
H44	0.468329	0.718359	0.741874	0.060*
C45	0.5271 (6)	0.6372 (4)	0.6498 (6)	0.0595 (18)
H45	0.514578	0.593810	0.692884	0.071*
C46	0.5730 (6)	0.6269 (5)	0.5569 (6)	0.068 (2)
H46	0.590377	0.576330	0.535469	0.081*
C47	0.5928 (6)	0.6906 (5)	0.4965 (6)	0.066 (2)
H47	0.624393	0.683903	0.433529	0.080*
C48	0.5666 (5)	0.7653 (4)	0.5277 (5)	0.0487 (15)
H48	0.582649	0.808882	0.486717	0.058*
Fe1	0.23891 (6)	0.84900 (4)	0.76262 (6)	0.02802 (17)
Fe2	0.22262 (6)	0.97013 (4)	0.64147 (6)	0.02851 (17)
N1	0.0889 (3)	0.9830 (2)	0.8533 (3)	0.0274 (9)
O1	0.2342 (4)	0.6793 (3)	0.7957 (4)	0.0678 (13)
O2	0.4747 (3)	0.8885 (3)	0.9345 (4)	0.0553 (11)
O3	0.1416 (4)	1.0638 (3)	0.4255 (4)	0.0739 (15)
O4	0.4618 (3)	1.0456 (3)	0.7328 (4)	0.0570 (12)
P1	0.14053 (11)	0.88789 (8)	0.88382 (11)	0.0271 (3)
P2	0.14185 (11)	1.03836 (8)	0.75573 (12)	0.0275 (3)
S1	0.06453 (10)	0.88645 (8)	0.62137 (11)	0.0302 (3)
S2	0.30959 (11)	0.85817 (8)	0.60588 (11)	0.0338 (3)

3 Comment

The butterfly diiron dithiolato complexes have received great interest, mainly owing to their rich chemistry and particularly their application as biomimetic models for the active sites of [FeFe]-hydrogenases [5–8]. Herein, we carried out the CO substitution reaction of $[Fe_2(CO)_6(\mu\text{–}SCH_2C_6H_5)_2]$ with a bisphosphine ligand $(Ph_2P)_2NC_6H_5$, and obtained the title complex. The title complex consists of a butterfly diiron dithiolato

core, ligated by four terminal carbonyls and a bisphosphine ligand. The Fe_2S_2 core is bridged by bisphosphine ligand *via* Fe1 and Fe2 with symmetrically cis-basal/basal coordination mode, and the two benzyl substituents are bonded to two S atoms in *anti*-positions, which is similar to the reported analogues [9, 10]. The Fe1–Fe2 bond length [2.4722(10) Å] is close to other phosphine-containing analogues [11–15].

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: This research was supported by Shandong Provincial Natural Science Foundation under Grant ZR2020MB019.

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

References

1. BRUKER. *SAINT*, *APEX2* and *SADABS*; Bruker AXS Inc.: Madison, Wisconsin, USA, 2009.
2. Sheldrick G. M. A short history of SHELX. *Acta Crystallogr.* 2008, *A64*, 112–122.
3. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
4. Dolomanov O. V., Bourhis L. J., Gildea R. J., Howard J. A. K., Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* 2009, *42*, 339–341.
5. Frey M. Hydrogenases: hydrogen-activating enzymes. *ChemBioChem* 2002, *3*, 153–160.
6. Lubitz W., Ogata H., Rdiger O., Reijerse E. Hydrogenases. *Chem. Rev.* 2014, *3*, 4081–4148.
7. Li Y., Rauchfuss T. B. Synthesis of diiron(I) dithiolato carbonyl complexes. *Chem. Rev.* 2016, *116*, 7043–7077.
8. Kleinhaus J. T., Wittkamp F., Yadav S., Siegmund D., Apfel U.-P. [FeFe]–Hydrogenases: maturation and reactivity of enzymatic systems and overview of biomimetic models. *Chem. Rev.* 2021, *50*, 1668–1784.
9. Lü S., Gong S., Qin C.-R., Li Q.-L. PNP bridged diiron carbonyls containing Fe/E (E = S and Se) cluster core related to the active site of [FeFe]–H_2ases. *J. Organomet. Chem.* 2020, *929*, 121581.
10. Gao X.-P., Bai S.-F., Guo Y.-N., Li Q.-L., Lü S. Synthesis, characterization and electrochemical properties of aminophosphine monodentate, -chelate, and -bridge diiron bis(monothiolate) carbonyls. *Z. Anorg. Allg. Chem.* 2023, *649*, e202200296.
11. Ghosh S., Hogarth G., Hollingsworth N., Holt K. B., Richards I., Richmond M. G., Sanchez B. E., Unwin D. Models of the iron-only hydrogenase: a comparison of chelate and bridge isomers of $Fe_2(CO)_4\{Ph_2PN(R)PPh_2\}$-(μ-pdt) as proton-reduction catalysts. *Dalton Trans.* 2013, *42*, 6775–6792.
12. Song L.-C., Wang Y.-X., Xing X.-K., Ding S.-D., Zhang L.-D., Wang X.-Y., Zhang H.-T. Hydrophilic quaternary ammonium-group-containing FeFe-hydrogenase models: synthesis, structures, and electrocatalytic hydrogen production. *Chem. Eur. J.* 2016, *22*, 16304–16314.
13. Song L.-C., Feng L., Guo Y.-Q. Hydrophilic quaternary ammonium-group- containing [FeFe]H_2ase models prepared by quaternization of the pyridyl N atoms in pyridylazadiphosphine- and pyridylmethylazadiphosphine-bridged diiron complexes with various electrophiles. *Dalton Trans.* 2019, *48*, 1443–1453.
14. Hu M. Y., Zhao P. H., Li J. R., Gu X. L., Jing X. B., Liu X. F. Synthesis, structures, and electrocatalytic properties of phosphine- monodentate, -chelate, and -bridge diiron 2,2-dimethylpropanedithiolate complexes related to [FeFe]-hydrogenases. *Appl. Organomet. Chem.* 2020, *34*, e5523.
15. Zhao P.-H., Ma Z.-Y., Hu M.-Y., He J., Wang Y.-Z., Jing X.-B., Chen H.-Y., Wang Z., Li Y.-L. PNP-chelated and -bridged diiron dithiolate complexes Fe_2 (μ-pdt)$(CO)_4\{(Ph_2P)_2NR\}$ together with related monophosphine complexes for the 2Fe(H) subsite of FeFe-hydrogenases: preparation, structure, and electrocatalysis. *Organometallics* 2018, *37*, 1280–1290.