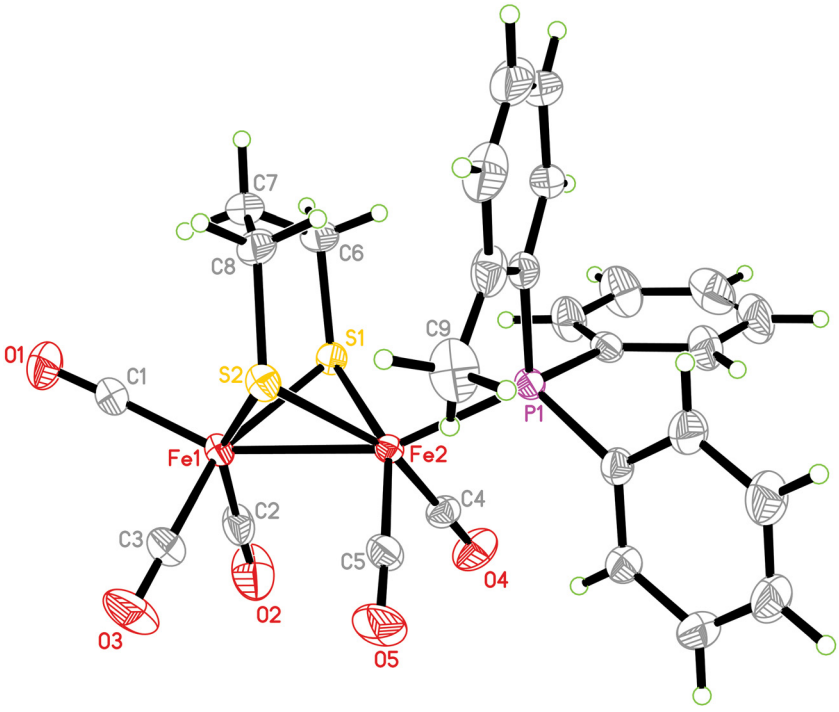
Lu-Yan Bi and Xu-Feng Liu*

# Crystal structure of pentacarbonyl-($\mu_2$-propane-1,3-dithiolato-$\kappa^4$*S:S,S′:S′*)-(diphenyl(o-tolyl) phosphine-$\kappa^1$*P*)diiron (Fe-Fe), $C_{27}H_{23}Fe_2O_5PS_2$




https://doi.org/10.1515/ncrs-2022-0268
Received May 25, 2022; accepted June 28, 2022;
published online July 14, 2022

**Abstract**

$C_{27}H_{23}Fe_2O_5PS_2$, monoclinic, $P2_1/c$ (no. 14), $a$ = 15.4423(7) Å, $b$ = 9.8615(5) Å, $c$ = 18.0727(8) Å, $\beta$ = 90.0380(10)°, $V$ = 2752.2(2) Å$^3$, $Z$ = 4, $R_{gt}(F)$ = 0.0296, $wR_{ref}(F^2)$ = 0.0703, T = 296(2) K.

**CCDC no.:** 2182454

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.

**Table 1:** Data collection and handling.

| | |
|---|---|
| Crystal: | Red block |
| Size: | 0.38 × 0.36 × 0.32 mm |
| Wavelength: | Mo *Kα* radiation (0.71073 Å) |
| $\mu$: | 1.30 mm$^{-1}$ |
| Diffractometer, scan mode: | BRUKER D8 QUEST, $\omega$ |
| $\theta_{max}$, completeness: | 25.1°, >99% |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$, $R_{int}$: | 54,372, 4885, 0.073 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs}$ > 2 σ($I_{obs}$), 4140 |
| $N(param)_{refined}$: | 335 |
| Programs: | Bruker [1], Olex2 [2], SHELX [3, 4] |

## Source of material

To a solution of the complex [$Fe_2(CO)_6$(μ-$SCH_2CH_2CH_2S$)] (1 mmol) and diphenyl(*o*-tolyl)phosphine (1 mmol) in

***Corresponding author: Xu-Feng Liu**, School of Materials and Chemical Engineering, Ningbo University of Technology, Ningbo, Zhejiang 315211, China, E-mail: nkxfliu@126.com. https://orcid.org/0000-0002-9717-5645
**Lu-Yan Bi,** School of Materials and Chemical Engineering, Ningbo University of Technology, Ningbo, Zhejiang 315211, China

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

| Atom | x | y | z | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Fe1 | 0.43816 (2) | 0.09396 (3) | 0.31662 (2) | 0.03461 (10) |
| Fe2 | 0.28985 (2) | 0.17386 (3) | 0.35269 (2) | 0.02898 (9) |
| S1 | 0.37835 (4) | 0.05643 (6) | 0.42936 (3) | 0.03509 (14) |
| S2 | 0.40624 (4) | 0.31378 (6) | 0.34043 (3) | 0.03888 (15) |
| P1 | 0.19035 (4) | 0.28463 (6) | 0.42070 (3) | 0.03157 (14) |
| O1 | 0.62517 (12) | 0.0545 (2) | 0.33748 (12) | 0.0740 (6) |
| O2 | 0.38477 (16) | −0.1782 (2) | 0.27402 (16) | 0.0949 (9) |
| O3 | 0.44544 (18) | 0.1700 (3) | 0.16077 (11) | 0.0883 (8) |
| O4 | 0.18868 (13) | −0.07373 (19) | 0.34371 (12) | 0.0655 (5) |
| O5 | 0.23554 (15) | 0.2630 (3) | 0.20651 (10) | 0.0838 (7) |
| C1 | 0.55300 (17) | 0.0710 (3) | 0.33058 (14) | 0.0467 (6) |
| C2 | 0.40779 (17) | −0.0733 (3) | 0.29155 (16) | 0.0542 (7) |
| C3 | 0.44286 (18) | 0.1400 (3) | 0.22161 (15) | 0.0516 (7) |
| C4 | 0.22737 (15) | 0.0250 (3) | 0.34688 (13) | 0.0404 (6) |
| C5 | 0.25572 (16) | 0.2310 (3) | 0.26472 (13) | 0.0460 (6) |
| C6 | 0.42621 (17) | 0.1603 (3) | 0.50225 (13) | 0.0496 (6) |
| H6A | 0.3798 | 0.2060 | 0.5284 | 0.060* |
| H6B | 0.4545 | 0.1004 | 0.5373 | 0.060* |
| C7 | 0.48955 (18) | 0.2635 (3) | 0.47824 (15) | 0.0576 (7) |
| H7A | 0.5369 | 0.2179 | 0.4532 | 0.069* |
| H7B | 0.5133 | 0.3072 | 0.5218 | 0.069* |
| C8 | 0.45398 (17) | 0.3711 (3) | 0.42763 (15) | 0.0515 (7) |
| H8A | 0.5004 | 0.4338 | 0.4161 | 0.062* |
| H8B | 0.4102 | 0.4214 | 0.4546 | 0.062* |
| C9 | 0.2452 (2) | 0.5714 (3) | 0.34870 (19) | 0.0713 (9) |
| H9A | 0.2349 | 0.4844 | 0.3265 | 0.107* |
| H9B | 0.2990 | 0.6074 | 0.3308 | 0.107* |
| H9C | 0.1989 | 0.6321 | 0.3360 | 0.107* |
| C10 | 0.22727 (14) | 0.4369 (2) | 0.46970 (14) | 0.0407 (6) |
| C11 | 0.24957 (16) | 0.5562 (3) | 0.43145 (17) | 0.0541 (7) |
| C12 | 0.2779 (2) | 0.6663 (3) | 0.4736 (3) | 0.0761 (11) |
| H12 | 0.2917 | 0.7470 | 0.4498 | 0.091* |
| C13 | 0.2859 (2) | 0.6588 (4) | 0.5486 (3) | 0.0879 (13) |
| H13 | 0.3045 | 0.7344 | 0.5749 | 0.105* |
| C14 | 0.26700 (19) | 0.5411 (4) | 0.5858 (2) | 0.0745 (10) |
| H14 | 0.2742 | 0.5356 | 0.6368 | 0.089* |
| C15 | 0.23715 (16) | 0.4310 (3) | 0.54613 (15) | 0.0522 (7) |
| H15 | 0.2234 | 0.3513 | 0.5710 | 0.063* |
| C16 | 0.09313 (15) | 0.3427 (2) | 0.37106 (13) | 0.0397 (6) |
| C17 | 0.04935 (17) | 0.4597 (3) | 0.39124 (16) | 0.0566 (7) |
| H17 | 0.0724 | 0.5162 | 0.4275 | 0.068* |
| C18 | −0.02828 (19) | 0.4930 (3) | 0.35794 (19) | 0.0701 (9) |
| H18 | −0.0570 | 0.5720 | 0.3715 | 0.084* |
| C19 | −0.06290 (19) | 0.4103 (4) | 0.30515 (18) | 0.0700 (9) |
| H19 | −0.1156 | 0.4326 | 0.2834 | 0.084* |
| C20 | −0.02054 (18) | 0.2948 (3) | 0.28389 (16) | 0.0618 (8) |
| H20 | −0.0441 | 0.2391 | 0.2475 | 0.074* |
| C21 | 0.05768 (16) | 0.2613 (3) | 0.31690 (14) | 0.0464 (6) |
| H21 | 0.0866 | 0.1830 | 0.3023 | 0.056* |
| C22 | 0.13853 (15) | 0.1834 (2) | 0.49418 (12) | 0.0379 (5) |
| C23 | 0.18226 (19) | 0.0808 (3) | 0.52900 (15) | 0.0591 (7) |
| H23 | 0.2382 | 0.0596 | 0.5139 | 0.071* |
| C24 | 0.1452 (2) | 0.0082 (4) | 0.58600 (18) | 0.0765 (10) |
| H24 | 0.1764 | −0.0602 | 0.6094 | 0.092* |
| C25 | 0.0626 (2) | 0.0371 (4) | 0.60806 (18) | 0.0770 (10) |
| H25 | 0.0375 | −0.0113 | 0.6467 | 0.092* |
| C26 | 0.0173 (2) | 0.1365 (4) | 0.57353 (19) | 0.0754 (10) |
| H26 | −0.0391 | 0.1554 | 0.5883 | 0.090* |
| C27 | 0.05411 (18) | 0.2098 (3) | 0.51657 (16) | 0.0578 (7) |
| H27 | 0.0222 | 0.2773 | 0.4931 | 0.069* |

$CH_2Cl_2$ (10 mL) was added a solution of $Me_3NO \cdot 2H_2O$ (1 mmol) in $CH_3CN$ (10 mL). The mixture was stirred for 1 h and the solvent was reduced by rotary evaporator. The brown residue was subjected to TLC separation to collect the main red band. Slow evaporation of $CH_2Cl_2$/isopropanol solution at 4° 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). Their $U_{iso}$ values were set to $1.2U_{eq}$ or $1.5U_{eq}$ of the parent atoms.

## Comment

Carbonyl substitution of a diiron propanedithiolate complex [$Fe_2(CO)_6$(μ-$SCH_2CH_2CH_2S$)] with phosphine ligands has received great interest in recent years [5–8]. A great number of crystal structures of these complexes have been reported.

The asymmetric unit of the title complex is composed of a diiron propanedithiolate moiety ligated by five terminal carbonyls and a phosphine ligand (see the figure). The diiron propanedithiolate fragment contains two six-membered metallocycles, in which the six-membered metallocycle Fe1S1C6C7C8S2 is a boat-conformation and the other six-membered metallocycle Fe2S1C6C7C8S2 is a chair-conformation. The position of the phosphine ligand is apical of the pseudo-octahedral geometry of the Fe2 atom, in accord with other analogues containing mono-substituted ligands [9]. The Fe1–Fe2 bond length [2.5085(4) Å] is slightly shorter than that of the diiron hexacarbonyl complex [$Fe_2(CO)_6$(μ-$SCH_2CH_2CH_2S$)] [2.5103(11) Å] [10], indicating that the phosphine ligand does not affect the Fe–Fe bond length. Moreover, the Fe1–Fe2 bond length is close to those of hexacarbonyl analogues [11], but much shorter than those of diphosphine-containing analogues [12].

**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 Zhejiang Provincial Natural Science Foundation of China under Grant LY19B020002.

**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. 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.
3. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
4. Sheldrick G. M. A short history of *SHELX*. *Acta Crystallogr.* 2008, *A64*, 112–122.
5. Sheng Y. D., Yu X. Y., Liu X. F., Li Y. L. 2-(Diphenylphosphino) benzaldehyde or isopropyldiphenylphosphine substituted diiron dithiolate complexes. *Polyhedron* 2017, *137*, 134–139.
6. Wang Z., Jiang W., Liu J., Jiang W., Wang Y., Åkermark B., Sun L. Pendant bases as proton transfer relays in diiron dithiolate complexes inspired by [Fe–Fe] hydrogenase active site. *J. Organomet. Chem.* 2008, *693*, 2828–2834.
7. Pandey I. K., Natarajan M., Hemlata, Hussain F., Kaur–Ghumaan S. Diiron complexes $[Fe_2(CO)_5(\mu\text{-pdt/Mebdt})(L)]$ containing a chelating diphosphine ligand L=(oxydi-2,1-phenylene) bis(diphenylphosphine): bioinspired [FeFe] hydrogenase model complexes. *ChemistrySelect* 2016, *1*, 5671–5678.
8. Li P., Wang M., He C., Li G., Liu X., Chen C., Åkermark B., Sun L. Influence of tertiary phosphanes on the coordination configurations and electrochemical properties of iron hydrogenase model complexes: crystal structures of $[(\mu\text{-}S_2C_3H_6)Fe_2(CO)_{6-n}L_n]$ (L = PMe2Ph, n = 1, 2; $PPh_3$, $P(OEt)_3$, n = 1). *Eur. J. Inorg. Chem.* 2005, *2005*, 2506–2513.
9. Yan L., Hu K., Liu X. F., Li Y. L., Liu X. H., Jiang Z. Q. Diiron ethane-1,2-dithiolate complexes with 1,2,3-thiadiazole moiety: synthesis, X-ray crystal structures, electrochemistry, and fungicidal activity. *Appl. Organomet. Chem.* 2021, *35*, e6084.
10. Lyon E. J., Georgakaki I. P., Reibenspies J. H., Darensbourg M. Y. Carbon monoxide and cyanide ligands in a classical organometallic complex model for Fe-only hydrogenase. *Angew. Chem. Int. Ed.* 1999, *38*, 3178–3180.
11. Lian M., He J., Yu X. Y., Mu C., Liu X. F., Li Y. L., Jiang Z. Q. Diiron ethanedithiolate complexes with acetate ester: synthesis, characterization and electrochemical properties. *J. Organomet. Chem.* 2018, *870*, 90–96.
12. Zhao P. H., Hu M. Y., Li J. R., Wang Y. Z., Lu B. P., Han H. F., Liu X. F. Impacts of coordination modes (chelate versus bridge) of PNP-diphosphine ligands on the redox and electrocatalytic properties of diiron oxadithiolate complexes for proton reduction. *Electrochim. Acta* 2020, *353*, 136615.