



Synthesis and Crystal Structure of Complex $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_4(\text{PPh}_3)_2$

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The title complex $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_4(\text{PPh}_3)_2$ was prepared by reaction of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ and PPh_3 at reflux in toluene. Its structure was determined by single crystal X-ray diffraction analysis. The crystals are monoclinic, space group $C2/c$ with $a = 19.203(7)$, $b = 10.199(3)$, $c = 19.403(7)$ Å, $\alpha = 90.00$, $\beta = 102.386(5)$, $\gamma = 90.00^\circ$, $V = 3712(2)$ Å³, $Z = 4$, $F_{(000)} = 1664$, $D_c = 1.454$ g/cm³, $\mu = 1.021$ cm⁻¹, the final $R = 0.0395$ and $wR = 0.0944$. A total of 18901 reflections were collected, of which 4437 were independent ($R_{\text{int}} = 0.0545$).

Key Words: Diiron complex, PPh_3 , Synthesis, Crystal structure.

INTRODUCTION

Heterocycles and heteroatom compounds had received considerable attentions in industrial field¹. In recent years, diiron dithiolate complexes have been received much attention because their structures are close to the active site of $[\text{FeFe}]$ -hydrogenases². Those diiron complexes bearing PPh_3 ligand were prepared by the substitution of carbonyl with PPh_3 in the presence of $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ in MeCN or at reflux in toluene³.

Recently, we have successfully prepared the title complex bearing PPh_3 ligands by substitution reaction. In this paper, we report the synthesis and crystal structure of complex $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_4(\text{PPh}_3)_2$.

EXPERIMENTAL

Crystal structure determination: The crystal of title compound with dimensions of 0.20 mm \times 0.18 mm \times 0.10 mm was mounted on a Rigaku Saturn CCD area-detector diffractometer with a graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) by using a phi and scan modes at 113(2) K in the range of $2.15^\circ \leq \theta \leq 27.88^\circ$. The crystal belongs to monoclinic system with space group $C2/c$ and crystal parameters of $a = 19.203(7)$, $b = 10.199(3)$, $c = 19.403(7)$ Å, $\alpha = 90.00$, $\beta = 102.386(5)$, $\gamma = 90.00^\circ$, $V = 3712(2)$ Å³, $D_c = 1.454$ g/cm³, the absorption coefficient $\mu = 1.021$ mm⁻¹ and $Z = 4$. The structure was solved by direct methods with SHELXS-97⁴ and refined by the full-matrix least squares method on F^2 data using SHELXL-97⁵. The empirical absorption corrections were applied to all intensity data. H atom of N-H was initially located in a difference Fourier map and were refined with the restraint $\text{Uiso}(\text{H}) = 1.2\text{Ueq}(\text{N})$. Other H atoms were positioned

geometrically and refined using a riding model, with $d(\text{C-H}) = 0.93\text{-}0.97$ Å and $\text{Uiso}(\text{H}) = 1.2\text{Ueq}(\text{C})$ or $1.5\text{Ueq}(\text{C-methyl})$. The final full-matrix least squares refinement gave $R = 0.0395$ and $wR = 0.0944$.

Synthesis: A solution of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ (0.2 mmol) and PPh_3 (0.4 mmol) in toluene (10 mL) was refluxed for 1 h. The solvent was reduced *in vacuo*. The residue was crystallized in CH_2Cl_2 /hexane at 4 °C and the red crystals were obtained after several days.

RESULTS AND DISCUSSION

Reaction of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_6$ and PPh_3 in toluene at reflux afforded the title complex. Slow evaporation of the title complex in CH_2Cl_2 /hexane gave red crystals.

Structure of the title complex: The title complex was confirmed by single crystal X-ray diffraction analysis. Crystallographic and refinement parameters are given in Table-1. The selected bond lengths and bond angles are listed in Tables 2-4, respectively. The structure was solved by direct methods. Anisotropic displacement parameters were applied to all nonhydrogen atoms in full-matrix least-square refinements based on F^2 . The hydrogen atoms were set in calculated positions with a common fixed isotropic thermal parameter.

The molecular structure and the packing view of the title complex are shown in Figs. 1 and 2, respectively.

The title complex crystallizes in the monoclinic space group $C2/c$. The unit cell contains one molecule of $(\mu\text{-S}_2)\text{Fe}_2(\text{CO})_4(\text{PPh}_3)_2$. As can be seen in Fig. 1, the molecular structure of the title complex consists of a butterfly $[\text{2Fe}_2\text{S}]$ cluster with four carbonyls and two PPh_3 ligands. Generally,

TABLE-1
CRYSTAL DATA AND STRUCTURE
REFINEMENT FOR THE TITLE COMPLEX

Items	Values
Empirical formula	C ₄₀ H ₃₀ O ₄ P ₂ S ₂ Fe ₂
Formula weight	812.40
Crystal system	Monoclinic
Unit cell dimensions	
a (Å)	19.203(7)
b (Å)	10.199(3)
c (Å)	19.403(7)
Unit cell angles (°)	
α	90
β	102.386(5)
γ	90
Volume (Å ³)	3712(2)
Z	4
Temperature (K)	113(2)
Space group	C2/c
Wavelength (Å)	0.71073
Calculated density (g/cm ³)	1.454
Absorption coefficient (mm ⁻¹)	1.021
F ₍₀₀₀₎	1664
Crystal size (mm)	0.20 × 0.18 × 0.10
θ range for data collection (°)	2.15–27.88
Reflections collected	18901
Independent reflections	4437 [R _(int) = 0.0545]
Final R indices [I > 2σ(I)]	R ₁ = 0.0395, wR ₂ = 0.0944

TABLE-2
SELECTED BOND LENGTHS [Å] FOR THE TITLE COMPLEX

Bond lengths	X-Ray crystal	Bond lengths	X-Ray crystal
Fe(1)-C(1)	1.750(2)	Fe(1)-Fe(1)#1	2.5551(9)
Fe(1)-C(2)	1.753(2)	S(1)-S(1)#1	2.0318(12)
Fe(1)-P(1)	2.2202(7)	S(1)-Fe(1)#1	2.2380(8)
Fe(1)-S(1)#1	2.2379(8)	P(1)-C(9)	1.825(2)
Fe(1)-S(1)	2.2569(8)	P(1)-C(15)	1.831(2)

TABLE-3
SELECTED BOND ANGLES [°] FOR THE TITLE COMPLEX

Bond angles	X-Ray crystal	Bond angles	X-Ray crystal
C(1)-Fe(1)-C(2)	92.62(10)	C(2)-Fe(1)-S(1)#1	101.01(7)
C(1)-Fe(1)-P(1)	100.25(8)	P(1)-Fe(1)-S(1)#1	104.97(3)
C(2)-Fe(1)-P(1)	97.69(7)	P(1)-Fe(1)-S(1)	95.65(3)
C(1)-Fe(1)-S(1)#1	149.27(8)	S(1)#1-Fe(1)-S(1)	53.74(3)

TABLE-4
SELECTED BOND ANGLES [°] TORSIONAL
ANGLES (°) FOR THE TITLE COMPLEX

Bond angles	X-Ray crystal
C(1)-Fe(1)-P(1)-C(9)	-78.44(11)
C(2)-Fe(1)-P(1)-C(9)	15.64(10)
S(1)#1-Fe(1)-P(1)-C(9)	119.27(8)
S(1)-Fe(1)-P(1)-C(9)	173.21(8)
Fe(1)#1-Fe(1)-P(1)-C(9)	164.27(8)
C(1)-Fe(1)-P(1)-C(15)	159.80(11)
C(2)-Fe(1)-P(1)-C(15)	-106.12(10)
S(1)#1-Fe(1)-P(1)-C(15)	-2.49(8)

the average bond lengths and bond angles of phenyl ring and carbonyl group are normal ranges⁶. Two PPh₃ both reside in an apical position of the square-pyramidal coordination sphere of the Fe1 and Fe1A atoms. The Fe1-Fe1A bond length [2.5551(9) Å] is very close to parent complex (μ-S₂)Fe₂(CO)₆ [2.552(2) Å]⁷. The phenyl rings (C3, C4, C5, C6, C7, C8),

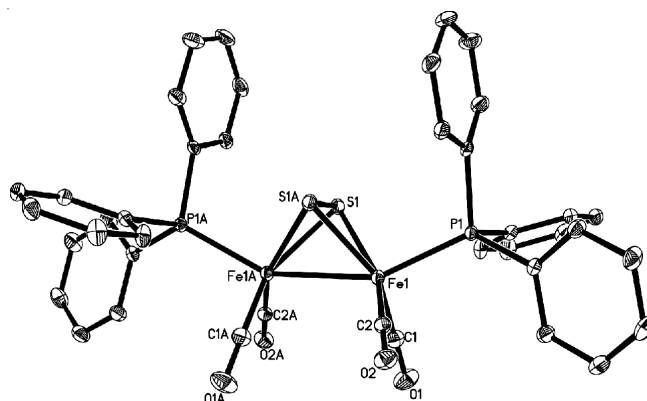


Fig. 1. Molecular structure of the title complex

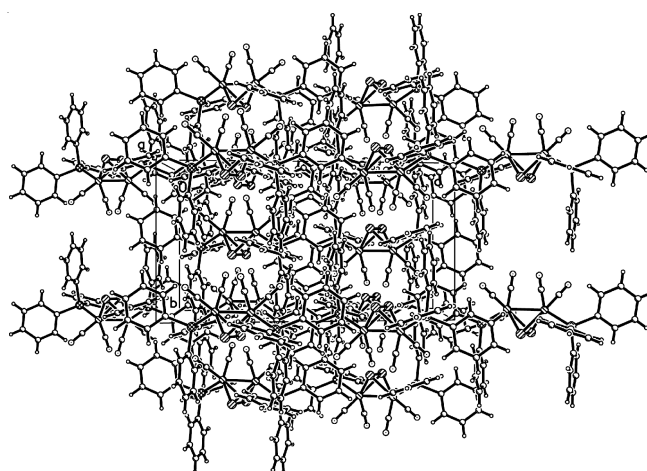


Fig. 2. Crystal packing for the title complex

(C9, C10, C11, C12, C13, C14) and (C15, C16, C17, C18, C19, C20) are fairly planar with plane equation $-1.615x + 9.629y + (-5.688)z = -2.0666$, $18.915x + 1.753y + (-3.829)z = 0.7734$ and $5.840x + 0.722y + 16.738z = 7.4868$, respectively. The largest deviation from the least squares plane is 0.0023 Å.

As shown in Fig. 2, van der Waals' interactions stabilize the solid state of the crystal structure in the crystal packing.

Supplementary material

CCDC 923236 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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REFERENCES

- (a) X.H. Liu, C.X. Tan and J.Q. Weng, *Asian J. Chem.*, **23**, 4064 (2011); (b) X.H. Liu, J.Q. Weng, C.X. Tan, L. Pan, B.L. Wang and Z.M. Li, *Asian J. Chem.*, **23**, 4031 (2011); (c) X.H. Liu, C.X. Tan and J.Q. Weng, *Phosphorus Sulfur Silicon Rel. Elem.*, **186**, 552 (2011); (d) C.X. Tan,

- Y.X. Shi, J.Q. Weng, X. H. Liu, B.J. Li and W.G. Zhao, *Lett. Drug Des. Discov.*, **9**, 431 (2012); (e) C.X. Tan, Y.X. Shi, J.Q. Weng, X.H. Liu, B.J. Li and W.G. Zhao, *J. Heterocycl. Chem.*, doi: 10.1002/jhet.1656; (f) J.Y. Tong, Y.X. Shi, X.H. Liu, N.B. Sun and B.J. Li, *Chin. J. Org. Chem.*, **32**, 2373 (2012); (g) X.H. Liu, W.G. Zhao, B.L. Wang and Z.M. Li, *Res. Chem. Intermed.*, **38**, 1999 (2012); (h) N.N. Su, Y. Li, S.J. Yu, X. Zhang, X.H. Liu and W.G. Zhao, *Res. Chem. Intermed.*, **39**, 759 (2012); (i) X.H. Liu, L. Pan, Y. Ma, J.Q. Weng, C.X. Tan, Y.H. Li, Y.X. Shi, B.J. Li, Z.M. Li and Y.G. Zhang, *Chem. Biol. Drug Des.*, **78**, 689 (2011).
2. (a) X.F. Liu and X.W. Xiao, *J. Organomet. Chem.*, **696**, 2767 (2011); (b) X.F. Liu, Z.Q. Jiang and Z.J. Jia, *Polyhedron*, **33**, 166 (2011); (c) B.S. Yin, T.B. Li and M.S. Yang, *J. Coord. Chem.*, **64**, 2066 (2011).
3. (a) X.F. Liu, X.W. Xiao, L.J. Shen, J.H. Fang, J.R. Wang, H.Q. Gao and X.H. Liu, *Chin. J. Struct. Chem.*, **30**, 1016 (2011); (b) X.F. Liu, X.W. Xiao and L.J. Shen, *Trans. Met. Chem.*, **36**, 465 (2011); (c) B.S. Yin, T.B. Li and M.S. Yang, *Acta Crystallogr.*, **E67**, m1502 (2011).
4. G.M. Sheldrick, SHELXS97, A Program for Crystal Structure Solution; University of Göttingen: Germany (1997).
5. G.M. Sheldrick, SHELXL97, A Program for Crystal Structure Refinement; University of Göttingen: Germany (1997).
6. (a) Y.L. Xue, Y.G. Zhang and X.H. Liu, *Asian J. Chem.*, **24**, 3016 (2012); (b) P.Q. Chen, C.X. Tan, J.Q. Weng and X.H. Liu, *Asian J. Chem.*, **24**, 2808 (2012); (c) Y.L. Xue, Y.G. Zhang and X.H. Liu, *Asian J. Chem.*, **24**, 1571 (2012); (d) Y.L. Xue, Y.G. Zhang and X.H. Liu, *Asian J. Chem.*, **24**, 5087 (2012); (e) X.F. Liu and X.H. Liu, *Acta Crystallogr.*, **E67**, o202 (2011); (f) X.H. Liu, L. Pan, C.X. Tan, J.Q. Weng, B.L. Wang and Z.M. Li, *Pestic. Biochem. Physiol.*, **101**, 143 (2011); (g) X.H. Liu, J.Q. Weng, C.X. Tan and H.J. Liu, *Acta Crystallogr.*, **E67**, o1940 (2011); (h) H.J. Liu, J.Q. Weng, C.X. Tan and X.H. Liu, *Acta Crystallogr.*, **E67**, o1940 (2011); (i) X.H. Liu, C.X. Tan and J.Q. Weng, *Phosphorus Sulfur Silicon Rel. Elem.*, **186**, 558 (2011); (j) C.X. Tan, J.Q. Weng, Z.X. Liu, X.H. Liu and W.G. Zhao, *Phosphorus Sulfur Silicon Rel. Elem.*, **187**, 990 (2012); (k) J.Q. Weng, L. Wang, X.H. Liu, *J. Chem. Soc. Pakistan*, **34**, 1248 (2012); (l) X.H. Liu, L. Pan, J.Q. Weng, C.X. Tan, Y.H. Li, B.L. Wang and Z.M. Li, *Mol. Divers.*, **16**, 251 (2012); (m) R. Wu, C. Zhu, X.J. Du, L.X. Xiong, S.J. Yu, X.H. Liu, Z.M. Li and W.G. Zhao, *Chem. Cent. J.*, **6**, 99 (2012); (n) X.H. Liu, J.Q. Weng, C.X. Tan, *J. Chem.*, **Article ID 306361** (2013); (o) X.F. Liu, X.W. Xiao and X.H. Liu, *Chin. J. Struct. Chem.*, **30**, 1437 (2011).
7. C.H. Wei and L.F. Dahl, *Inorg. Chem.*, **4**, 1 (1965).