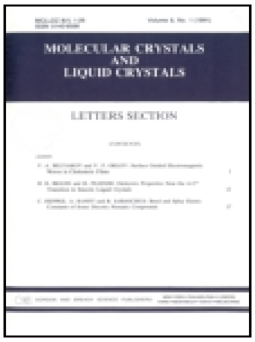

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X-Ray Structural Analysis of Diiron Complex with Tris(4-methoxyphenyl)phosphine

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The title complex was synthesized by the reaction of $(\mu\text{-}SCH_2CH_2CH_2S\text{-}\mu)Fe_2(CO)_6$ *with tris(4-methoxyphenyl)phosphine in the presence of the decarbonylating agent* $Me_3NO{\cdot}2H_2O$ *in* CH_2Cl_2*/MeCN solutions. The molecular structure was analyzed by X-ray diffraction analysis. The title complex contains a butterfly diiron dithiolate cluster with five terminal carbonyls and a tris(4-methoxyphenyl)phosphine. The phosphorus atom of tris(4-methoxyphenyl)phosphine resides in an apical position of the square-pyramidal geometry of the neighboring Fe2 atom. Intermolecular C—H. . . O hydrogen bonds between the phenyl and carbonyl groups stabilize the solid state in the crystal packing.*

Keywords Carbonyl substitution; crystal structure; diiron dithiolate; synthesis

Introduction

In recent years, diiron dithiolate complexes have received considerable attention because these complexes have the similar structures with the active site of [FeFe]-hydrogenases [1–8]. [FeFe]-hydrogenases is natural enzymes that can catalyze the proton to dihydrogen in microorganisms [9, 10]. Inspired by structural information, many derivatives have been prepared by a great variety of reactions, such as carbonyl substitution reactions [11–13]. Carbonyl substitution reactions of the parent complex with phosphines afforded monosubstituted or disubstituted derivatives [14–19]. In this paper, we present the diiron carbonyl complex with monosubstituted tris(4-methoxyphenyl)phosphine by carbonyl substitution. Fortunately, the molecular structure of the title complex was analyzed by X-ray crystallography.

Experimental

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

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

Empirical formula	$C_{14.50}H_{13.50}FeO_4P_{0.50}S$
Formula weight	355.15
Temperature (K)	113(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
a (Å)	10.759(2)
b (Å)	11.481(2)
c (Å)	13.031(3)
α (°)	87.74(3)
β (°)	86.33(3)
γ (°)	68.08(3)
V (Å^3)	1,490.1(5)
Z	4
D_{calc} (g·cm^{-3})	1.583
μ (mm^{-1})	1.217
F(000)	728
Crystal size (mm^3)	0.20 × 0.18 × 0.12
θ_{min}, θ_{max} (°)	1.57, 27.95
Reflections collected/unique	15,420/7,005
R_{int}	0.0350
hkl range	$-14 \le h \le 14$ $-15 \le k \le 15$ $-15 \le l \le 17$
Completeness to θ_{max} (%)	97.8
Data/restraints/parameters	7,005/106/392
Goodness of fit on F^2	1.039
$R1/wR2$ $(I>2\sigma(I))$	0.0297/0.0679
$R1/wR2$ (all data)	0.0440/0.0720
Largest diff peak and hole/e Å^{-3}	0.435/−0.492

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 [20]. The structure was solved by direct methods using the SHELXS-97 program [21] and refined by full-matrix least-squares techniques SHELXL-97 [22] 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 synthetic procedures of the title complex were disclosed in recent reported literature [23]. The molecular structure of the title complex was determined by single crystal X-ray diffraction analysis. While the ORTEP and packing views are shown in Figs. 1 and 2, selected bond lengths and angles are presented in Table 2, respectively. The title complex crystallizes in triclinic space group P-1 with four molecules in the unit cell and one molecule

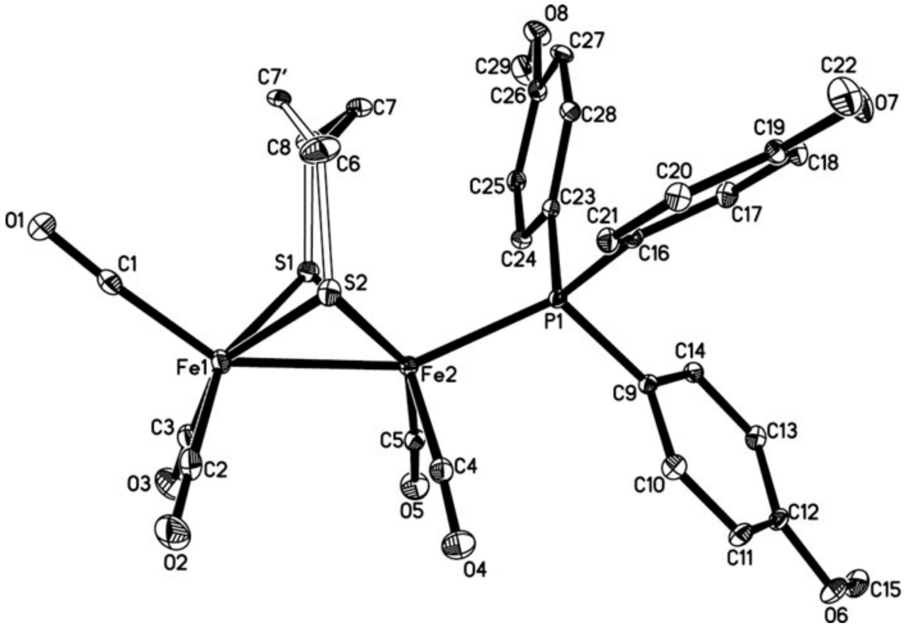

Figure 1. ORTEP view of the title complex with 30% probability level ellipsoids.

in the asymmetric unit. As shown in Fig. 1, the title complex contains a butterfly diiron dithiolate cluster with five terminal carbonyls and a tris(4-methoxyphenyl)phosphine. The phosphorus atom of tris(4-methoxyphenyl)phosphine resides in an apical position of the square-pyramidal geometry of the neighboring Fe2 atom, consistent with the analogous complexes [24]. The carbon atoms of the propylene (C6, C7, and C8) are in disordered state. The diiron propanedithiolate cluster has two fused six-membered rings, in which one six-membered ring Fe1S1C8C7C6S2 is a chair conformation and the other six-membered ring Fe2S1C8C7C6S2 is a boat conformation. The Fe1-Fe2 bond length [2.5089(7) Å] is shorter than the parent complex (μ-$SCH_2CH_2CH_2S$-μ)$Fe_2(CO)_6$ [2.5103(11) Å] [25], suggesting that the substitution of tris(4-methoxyphenyl)phosphine does not affect the

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

Fe(1)-C(3)	1.793 (2)	Fe(1)-C(1)	1.799 (2)
Fe(1)-C(2)	1.802 (2)	Fe(1)-S(2)	2.2531 (8)
Fe(1)-S(1)	2.2600 (8)	Fe(1)-Fe(2)	2.5089 (7)
Fe(2)-C(4)	1.760 (2)	Fe(2)-C(5)	1.765 (2)
Fe(2)-P(1)	2.2359 (7)	Fe(2)-S(1)	2.2575 (9)
Fe(2)-S(2)	2.2613 (8)	S(1)-C(8)	1.829 (2)
S(2)-Fe(1)-S(1)	84.75 (4)	S(2)-Fe(1)-Fe(2)	56.40 (2)
S(1)-Fe(1)-Fe(2)	56.22 (3)	P(1)-Fe(2)-S(1)	104.39 (3)
P(1)-Fe(2)-S(2)	109.77 (3)	S(1)-Fe(2)-S(2)	84.62 (4)
P(1)-Fe(2)-Fe(1)	154.39 (2)	S(1)-Fe(2)-Fe(1)	56.31 (2)
Fe(2)-S(1)-Fe(1)	67.47 (3)	C(6)-C(7)-C(8)	116.8 (2)

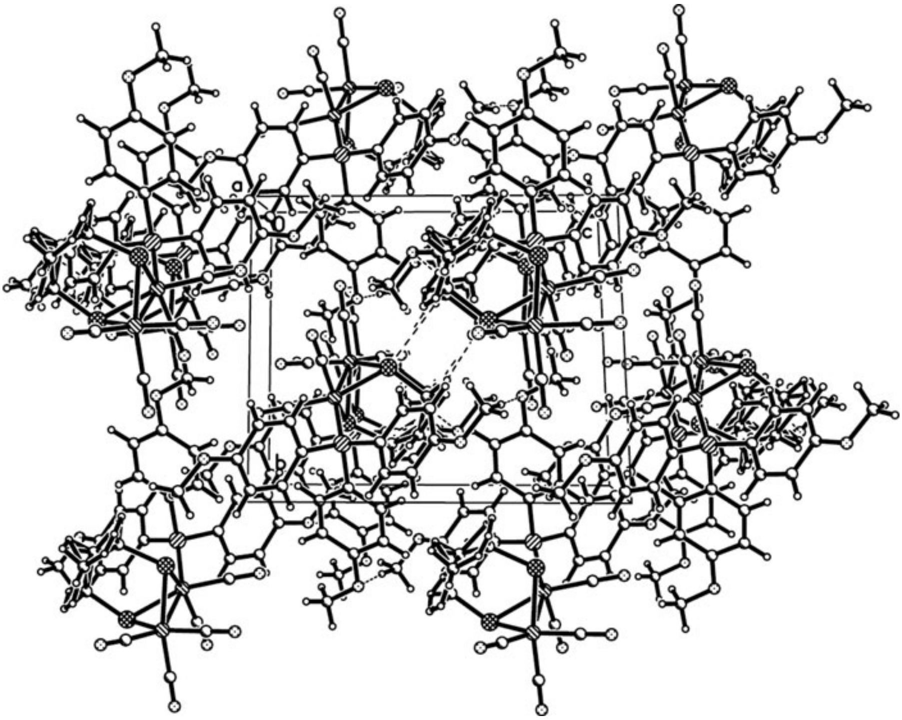

Figure 2. Crystal packing diagram of the title complex.

diiron bond distance. All carbon atoms of carbonyls are 1.60–1.80 Å apart from the iron atoms with some differences in apical and basal positions.

As shown in Fig. 2, the crystal packing diagram reveals that intermolecular C—H . . . O hydrogen bonds between the phenyl and carbonyl groups stabilize the solid state.

Conclusion

In summary, the molecular structure of the title complex was confirmed by X-ray crystallography.

Acknowledgments

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Supplementary Material

CCDC 1034493 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.

References

[1] Liu, X. F., & Xiao, X. W. (2011). *J. Organomet. Chem.*, *696*, 2767.
[2] Liu, X. F., & Gao, H. Q. (2014). *J. Clust. Sci.*, *25*, 367.
[3] Liu, X. F. (2011). *Inorg. Chim. Acta*, *378*, 338.
[4] Liu, X. F., & Gao, H. Q. (2014). *J. Clust. Sci.*, *25*, 495.
[5] Li, C. G., Li, Y. F., Shang, J. Y., & Lou, T. J. (2014). *Transition Met. Chem.*, *39*, 373.
[6] Liu X. F., Xiao, X. W., & Shen, L. J. (2011). *J. Coord. Chem.*, *64*, 1023
[7] Liu, X. F., Xiao, X. W., & Shen, L. J. (2011). *Transition Met. Chem.*, *36*, 465.
[8] Liu X. F., & Yin, B. S. (2010). *J. Coord. Chem.*, *63*, 4061
[9] Li, C. G., Xue, F., Cui, M. J., & Shang, J. Y. (2014). *J. Clust. Sci.*, *25*, 1641.
[10] Li, C. G., Xue, F., Cui, M. J., Shang, J. Y., & Lou, T. J. (2015). *Transition Met. Chem., 40,* 47.
[11] Liu, X. F., Jiang, Z. Q., & Jia, Z. J. (2012). *Polyhedron*, *33*, 166.
[12] Liu, X. F., & Yin, B. S. (2011). *Z. Anorg. Allg. Chem.*, *637*, 377.
[13] Li, C. G., Zhu, Y., Jiao, X. X., & Fu, X. Q. (2014). *Polyhedron*, *67*, 416.
[14] Liu, X. F., Yu, X. Y., & Gao, H. Q. (2014). *Mol. Cryst. Liq. Cryst.*, *592*, 229.
[15] Chen, M. Y., Liu, X. F., Yu, X. Y., & Gao, H. Q. (2014). *Mol. Cryst. Liq. Cryst., 605*, 119.
[16] Liu, X. F., & Gao, H. Q. (2013). *Polyhedron*, *65*, 1.
[17] Liu, X. F., Chen, M. Y., & Gao, H. Q. (2014). *J. Coord. Chem.*, *67*, 57.
[18] Liu, X. F., & Li, X. (2014). *J. Coord. Chem.*, *67*, 3226.
[19] Liu, X. F. (2014). *Polyhedron*, *72*, 66.
[20] CRYSTALCLEAR 1.3.6. (2005). *Rigaku and Rigaku/MSC*, The Woodlands: TX.
[21] Sheldrick, G. M. (1997). *SHELXS97, A Program for Crystal Structure Solution*, University of Göttingen: Germany.
[22] Sheldrick, G. M. (1997). *SHELXL97, A Program for Crystal Structure Refinement*, University of Göttingen: Germany.
[23] Zhao, P. H., Li, X. H., Liu, Y. F., & Liu, Y. Q. (2014). *J. Coord. Chem.*, *67*, 766.
[24] Huo, F., Hou, J., Chen, G., Guo, D., & Peng, X. (2010). *Eur. J. Inorg. Chem., 2010,* 3942.
[25] Lyon, E. J., Georgakaki, I. P., Reibenspies, J. H., & Darensbourg, M. Y. (1999). *Angew. Chem. Int. Ed.*, *38*, 3178.