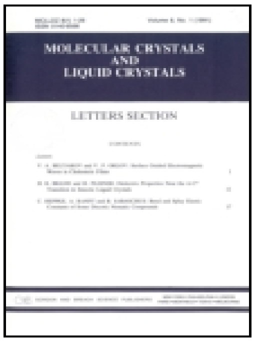

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Structural Analysis of Diiron Complex with Tris(*p*-tolyl)phosphine

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The title complex was obtained by the reaction of (μ-$SCH_2CH_2CH_2S$-μ)$Fe_2(CO)_6$ *with tris(p-tolyl)phosphine in the presence of the decarbonylating agent* $Me_3NO{\cdot}2H_2O$ *in* CH_2Cl_2/MeCN *solutions. The molecular structure was determined by X-ray diffraction analysis. The title complex contains a butterfly diiron dithiolate cluster with five terminal carbonyls and a tris(p-tolyl)phosphine. The phosphorus atom of tris(p-tolyl)phosphine occupies an apical position of the square-pyramidal coordination sphere of the Fe2 atom. The van der Waals' interactions stabilize the solid state in the crystal packing.*

Keywords Carbonyl substitution; crystal structure; diiron dithiolate; synthesis

Introduction

Diiron dithiolate complexes have attracted much interest in recent years, largely due to their structures close to the active site of [FeFe]-hydrogenases. [1, 2] [FeFe]-hydrogenases are a class of natural enzymes that can catalyze the production and consumption of H_2 in several microorganisms [3]. During 1998 [4] and 1999 [5], crystal structures of the [FeFe]-hydrogenases revealed that the active site contains a butterfly [2Fe2S] cluster with one of its iron atoms connected to a cubane-like [4Fe4S] cluster *via* the sulfur of a cysteinyl ligand. While the [2Fe2S] cluster is a catalytic center, the [4Fe4S] cluster is responsible for the electron transfer. The bridging dithiolate was supposed to be propanedithiolate [6] or azadithiolate [7]. A great number of [FeFe]-hydrogenases model complexes have been prepared. [8–16] Herein, we now report the crystal structure of diiron dithiolate complex with tris(*p*-tolyl)phosphine related to the active site of [FeFe]-hydrogenases.

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

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

Empirical formula	$C_{29}H_{27}Fe_2O_5PS_2$
Formula weight	662.30
Temperature (K)	113(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P2(1)/n
a (Å)	14.032(3)
b (Å)	12.637(3)
c (Å)	16.761(3)
α (°)	90
β (°)	107.53(3)
γ (°)	90
V ($Å^3$)	2,834.1(10)
Z	4
D_{calc} ($gȧcm^{-3}$)	1.552
μ (mm^{-1})	1.266
$F(000)$	1,360
Crystal size (mm^3)	0.20 × 0.18 × 0.12
θ_{min}, θ_{max} (°)	2.05, 27.95
Reflections collected/unique	28,527/6,788
R_{int}	0.0397
hkl range	$-18 \leq h \leq 18$
	$-14 \leq k \leq 16$
	$-20 \leq l \leq 22$
Completeness to θ_{max} (%)	99.6
Data/restraints/parameters	6,788/0/355
Goodness of fit on F^2	1.057
$R1/wR2$ ($I>2\sigma(I)$)	0.0310/0.0724
$R1/wR2$ (all data)	0.0388/0.0754
Largest diff peak and hole/e $Å^{-3}$	0.375/−0.642

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 [17]. The structure was solved by direct methods using the SHELXS-97 program [18] and refined by full-matrix least-squares techniques SHELXL-97 [19] 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 appeared in recent reported research paper [20]. The molecular structure of the title complex was characterized by X-ray diffraction analysis. While the ORTEP and packing views are shown in Figures 1 and 2, selected bond lengths and angles are presented in Table 2, respectively. The title complex crystallizes in monoclinic space group P2(1)/n with four molecules in the unit cell and one molecule in

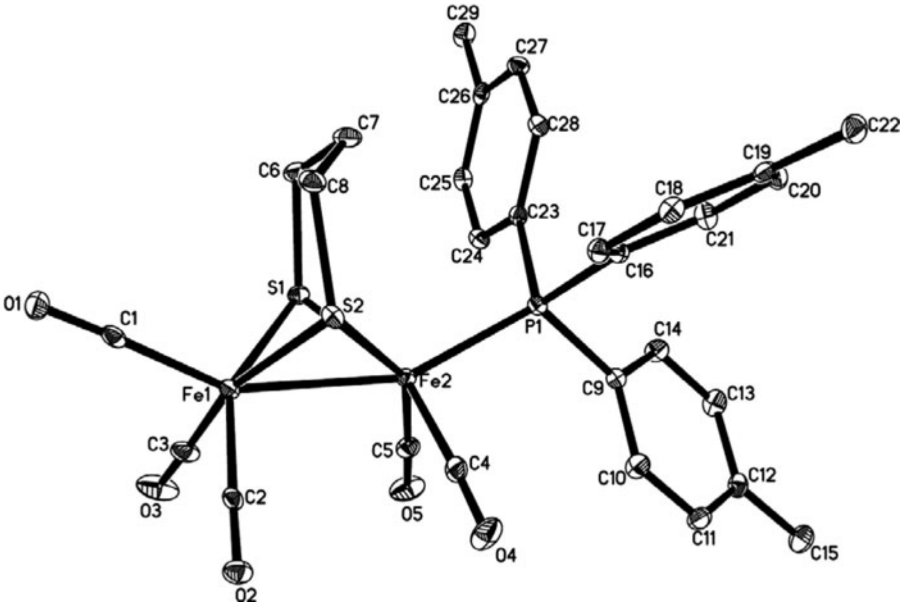

Figure 1. ORTEP view of the title complex with 30% probability level ellipsoids.

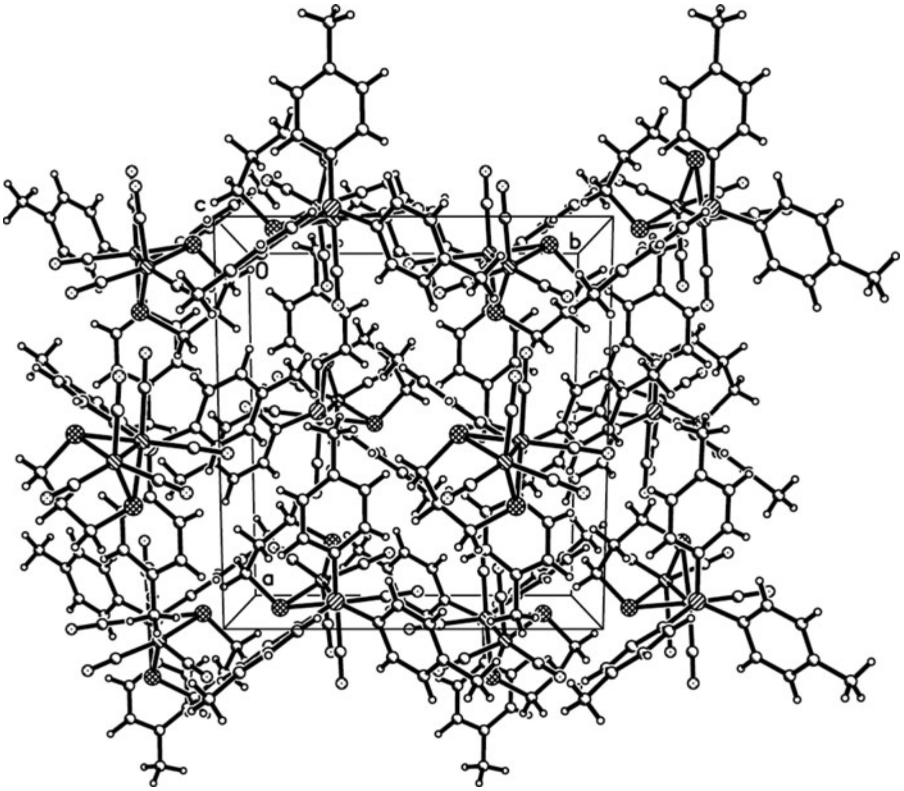

Figure 2. Crystal packing diagram of the title complex.

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

Fe(1)-C(2)	1.7956 (18)	Fe(1)-C(3)	1.800 (2)
Fe(1)-C(1)	1.8013 (19)	Fe(1)-S(2)	2.2589 (7)
Fe(1)-S(1)	2.2591 (7)	Fe(1)-Fe(2)	2.5156 (7)
Fe(2)-C(5)	1.765 (2)	Fe(2)-C(4)	1.7743 (19)
Fe(2)-P(1)	2.2380 (7)	Fe(2)-S(1)	2.2582 (9)
Fe(2)-S(2)	2.2811 (6)	P(1)-C(9)	1.8414 (18)
S(2)-Fe(1)-S(1)	84.76 (2)	S(2)-Fe(1)-Fe(2)	56.77 (2)
S(1)-Fe(1)-Fe(2)	56.14 (2)	P(1)-Fe(2)-S(1)	103.07 (3)
P(1)-Fe(2)-S(2)	113.538 (19)	S(1)-Fe(2)-S(2)	84.265 (19)
P(1)-Fe(2)-Fe(1)	155.297 (18)	S(1)-Fe(2)-Fe(1)	56.18 (3)
S(2)-Fe(2)-Fe(1)	55.930 (14)	Fe(2)-S(1)-Fe(1)	67.68 (2)

the asymmetric unit. As shown in Figure 1, the title complex consists of a [Fe_2S_2] cluster with a propylene, five terminal carbonyls and a tris(*p*-tolyl)phosphine. The phosphorus atom of tris(*p*-tolyl)phosphine is located in an apical position of the square-pyramidal geometry of the neighboring Fe2 atom, very similar to other diiron complexes [21]. The diiron propanedithiolate cluster contains two fused six-membered rings, in which one six-membered ring Fe1S1C6C7C8S2 is a chair conformation and the other six-membered ring Fe2S1C6C7C8S2 is a boat conformation. The Fe1-Fe2 bond length [2.5156(7) Å] is slightly longer than the corresponding bond distance in its parent complex (μ-$SCH_2CH_2CH_2S$-μ)$Fe_2(CO)_6$ [2.5103(11) Å][22] and other all-carbonyl diiron complexes [23]. All carbon atoms of carbonyls are 1.76-1.80 Å apart from the iron atoms with some differences in apical and basal positions.

As shown in Figure 2, the crystal packing diagram reveals that the van der Waals' interactions 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 1034494 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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