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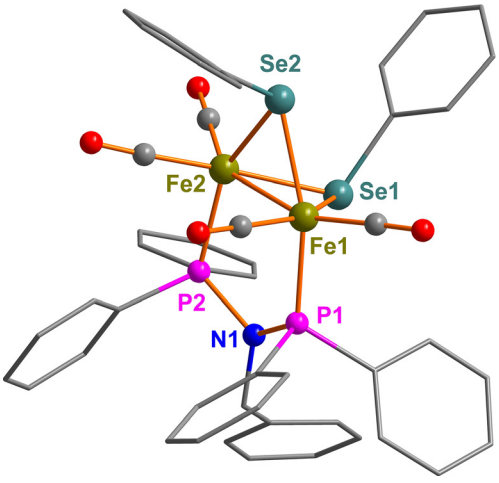
Crystal structure of bis(μ-benzeneselenolato)-(μ-[*N*-benzyl-*N*-(diphenylphosphanyl)-*P*,*P*-diphenylphosphinous amide])-tetracarbonyl diiron (Fe–Fe), $C_{47}H_{37}Fe_2NO_4P_2Se_2$



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Abstract

$C_{47}H_{37}Fe_2NO_4P_2Se_2$, monoclinic, $P2_1/n$ (no. 14), a = 12.8144(11) Å, b = 17.9714(15) Å, c = 19.1077(17) Å, β = 104.329(4)°, V = 4263.5(6) Å^3, Z = 4, $R_{gt}(F)$ = 0.0420, w$R_{ref}(F^2)$ = 0.0968, T = 298(2) K.

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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.

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Table 1: Data collection and handling.

Crystal:	Red block
Size:	0.40 × 0.30 × 0.20 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	2.51 mm^{-1}
Diffractometer, scan mode:	φ and ω
θ_{max}, completeness:	25.0°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	20,752, 7497, 0.063
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4783
$N(param)_{refined}$:	523
Programs:	Bruker [1], SHELX [2, 3], Olex2 [4]

1 Source of material

A mixture of $[Fe_2(CO)_6(\mu\text{–}SeC_6H_5)_2]$ (59 mg, 0.1 mmol) and $(Ph_2P)_2NCH_2C_6H_5$ (48 mg, 0.1 mmol) was dissolved in 10 ml of xylene. The reaction mixture was stirred at reflux for 2 h. After the solvent was removed under vacuum, the residue was subjected to preparative TLC separation using dichloromethane/pentane (1:2, v/v) as the eluent. From the main band, the title complex was obtained as a deep-red solid (yield 42 %). The single crystals were obtained from diffusion of dichloromethane solution into a hexane solution at room temperature.

2 Experimental details

The structure was solved by Direct Methods 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.

3 Comment

As an important branch of Fe/E (E = S, Se) cluster complexes, diiron diselenolato complexes have received a growing amount of attention, mainly due to their unique structures

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Se1	0.34560 (4)	0.39990 (2)	0.12828 (2)	0.03566 (13)
Se2	0.17327 (4)	0.39943 (3)	0.21405 (3)	0.04247 (14)
Fe1	0.31532 (5)	0.48452 (3)	0.21620 (3)	0.03467 (17)
Fe2	0.35025 (5)	0.34935 (3)	0.24377 (3)	0.03460 (17)
N1	0.5685 (3)	0.44975 (17)	0.23994 (17)	0.0312 (8)
O1	0.2162 (3)	0.6175 (2)	0.1442 (3)	0.1006 (15)
O2	0.3225 (3)	0.5187 (2)	0.36395 (19)	0.0723 (11)
O3	0.3354 (3)	0.1951 (2)	0.1987 (2)	0.0847 (13)
O4	0.3460 (3)	0.3088 (2)	0.3879 (2)	0.0796 (12)
P1	0.47984 (9)	0.52223 (6)	0.23050 (6)	0.0324 (3)
P2	0.52543 (9)	0.36803 (6)	0.27027 (6)	0.0316 (3)
C1	0.2545 (4)	0.5640 (3)	0.1720 (3)	0.0570 (14)
C2	0.3195 (4)	0.5058 (3)	0.3051 (3)	0.0465 (13)
C3	0.3400 (4)	0.2558 (3)	0.2163 (3)	0.0504 (13)
C4	0.3483 (4)	0.3272 (3)	0.3317 (3)	0.0467 (12)
C5	0.5138 (4)	0.5785 (2)	0.1601 (2)	0.0392 (11)
C6	0.4659 (5)	0.5652 (3)	0.0895 (3)	0.0640 (16)
H6	0.411974	0.529400	0.077266	0.077*
C7	0.4967 (5)	0.6045 (3)	0.0354 (3)	0.0799 (19)
H7	0.464258	0.594000	−0.012720	0.096*
C8	0.5726 (5)	0.6573 (3)	0.0517 (3)	0.0719 (17)
H8	0.593520	0.682988	0.015111	0.086*
C9	0.6180 (5)	0.6728 (3)	0.1208 (3)	0.0770 (18)
H9	0.669804	0.710037	0.132193	0.092*
C10	0.5889 (4)	0.6343 (3)	0.1755 (3)	0.0585 (14)
H10	0.620709	0.646344	0.223370	0.070*
C11	0.5239 (4)	0.5833 (2)	0.3076 (2)	0.0366 (11)
C12	0.4668 (4)	0.6485 (3)	0.3076 (3)	0.0507 (13)
H12	0.412230	0.660874	0.267279	0.061*
C13	0.4894 (5)	0.6950 (3)	0.3658 (3)	0.0600 (15)
H13	0.449727	0.738430	0.365293	0.072*
C14	0.5703 (5)	0.6778 (3)	0.4249 (3)	0.0639 (16)
H14	0.585778	0.709722	0.464447	0.077*
C15	0.6275 (4)	0.6151 (3)	0.4262 (3)	0.0595 (15)
H15	0.682844	0.603759	0.466455	0.071*
C16	0.6041 (4)	0.5674 (3)	0.3677 (2)	0.0436 (12)
H16	0.643565	0.523712	0.369232	0.052*
C17	0.5849 (3)	0.2931 (2)	0.2300 (2)	0.0358 (11)
C18	0.5935 (4)	0.2967 (3)	0.1598 (3)	0.0515 (13)
H18	0.578647	0.341162	0.134266	0.062*
C19	0.6239 (5)	0.2352 (4)	0.1270 (3)	0.0734 (17)
H19	0.631483	0.238500	0.079885	0.088*
C20	0.6430 (5)	0.1697 (4)	0.1630 (4)	0.080 (2)
H20	0.663029	0.128170	0.140318	0.097*
C21	0.6331 (4)	0.1643 (3)	0.2314 (4)	0.0701 (17)
H21	0.645831	0.119223	0.255878	0.084*
C22	0.6039 (4)	0.2262 (3)	0.2648 (3)	0.0498 (13)
H22	0.596944	0.222348	0.311930	0.060*
C23	0.6018 (3)	0.3680 (2)	0.3639 (2)	0.0337 (10)
C24	0.7070 (4)	0.3441 (2)	0.3854 (2)	0.0441 (12)
H24	0.738486	0.320677	0.352375	0.053*
C25	0.7660 (4)	0.3544 (3)	0.4551 (3)	0.0533 (13)
H25	0.837064	0.338178	0.468760	0.064*
C26	0.7217 (4)	0.3882 (3)	0.5044 (3)	0.0591 (14)
H26	0.761918	0.395070	0.551597	0.071*
C27	0.6176 (4)	0.4118 (3)	0.4838 (3)	0.0524 (13)
H27	0.586768	0.434986	0.517318	0.063*
C28	0.5580 (4)	0.4019 (2)	0.4148 (2)	0.0400 (11)
H28	0.486951	0.418157	0.401850	0.048*
C29	0.7416 (4)	0.4357 (3)	0.1994 (3)	0.0471 (12)
C47	0.6856 (3)	0.4673 (2)	0.2525 (2)	0.0409 (11)
H47A	0.693721	0.520932	0.252806	0.049*
H47B	0.722053	0.449372	0.300201	0.049*
C30	0.7166 (5)	0.4580 (4)	0.1293 (3)	0.086 (2)
H30	0.663353	0.493561	0.113209	0.104*
C31	0.7707 (7)	0.4277 (4)	0.0820 (4)	0.124 (3)
H31	0.751924	0.441906	0.033689	0.149*
C32	0.8509 (6)	0.3773 (5)	0.1048 (4)	0.112 (3)
H32	0.886782	0.357085	0.072480	0.135*
C33	0.8779 (5)	0.3572 (4)	0.1746 (4)	0.098 (2)
H33	0.933579	0.323433	0.191022	0.118*
C34	0.8237 (4)	0.3861 (3)	0.2217 (3)	0.0646 (15)
H34	0.843204	0.371645	0.269969	0.077*
C35	0.2133 (3)	0.3777 (2)	0.0600 (2)	0.0380 (11)
C36	0.1846 (3)	0.3063 (2)	0.0402 (2)	0.0511 (13)
H36	0.225931	0.267134	0.064048	0.061*
C37	0.0952 (4)	0.2916 (3)	−0.0148 (2)	0.0602 (15)
H37	0.077305	0.242546	−0.027787	0.072*
C38	0.0326 (4)	0.3473 (3)	−0.0504 (3)	0.0670 (16)
H38	−0.028288	0.336970	−0.087098	0.080*
C39	0.0614 (5)	0.4190 (3)	−0.0310 (4)	0.112 (3)
H39	0.021560	0.458153	−0.056161	0.134*
C40	0.1488 (4)	0.4339 (3)	0.0255 (3)	0.092 (2)
H40	0.164164	0.482800	0.040424	0.110*
C41	0.1158 (4)	0.4118 (3)	0.2972 (3)	0.0544 (14)
C42	0.1027 (4)	0.3510 (4)	0.3371 (3)	0.0767 (17)
H42	0.125055	0.304232	0.325927	0.092*
C43	0.0547 (5)	0.3604 (5)	0.3954 (4)	0.098 (2)
H43	0.044689	0.319732	0.423142	0.117*
C44	0.0237 (7)	0.4285 (6)	0.4106 (5)	0.117 (3)
H44	−0.005788	0.434530	0.450115	0.141*
C45	0.0340 (6)	0.4892 (5)	0.3699 (5)	0.106 (3)
H45	0.009584	0.535541	0.380624	0.127*
C46	0.0808 (5)	0.4811 (3)	0.3128 (3)	0.0751 (17)
H46	0.088883	0.522111	0.284893	0.090*

and particularly the close resemblance to [FeFe]-hydrogenases [5–7]. A series of phosphine mono- and disubstituted diiron diselenolato complexes were reported [8–12]. Herein, we carried out the CO substitution reaction of $[Fe_2(CO)_6(\mu\text{–}SeC_6H_5)_2]$ with a disphosphine ligand $(Ph_2P)_2NCH_2C_6H_5$, and obtained the title complex. The title complex contains a Fe_2Se_2 cluster bearing four carbonyls and one diphosphine ligand (see the figure). The two phenyl substituents are attach to the Se1 and Se2 by axial Se1–C35 and Se2–C41 equatorial bonds. The two P atoms of diphosphine ligand occupy the cisoid dibasal site and are symmetrically bridged between the two Fe atoms,

which is similar to the reported analogues [13, 14]. The bond length of Fe1–Fe2 [2.5025(9) Å] is slightly longer than that of the sulphur analogues [15–18].

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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. Lubitz W., Ogata H., Rüdiger O., Reijerse E. Hydrogenases. *Chem. Rev.* 2014, *3*, 4081–4148.
6. Li Y., Rauchfuss T. B. Synthesis of diiron(I) dithiolato carbonyl complexes. *Chem. Rev.* 2016, *116*, 7043–7077.
7. 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.
8. Abul–Futouh H., Abaalkhail S. J., Harb M. K., Görls H., Weigand W. Structural studies and electrochemical catalysis investigation of [FeFe]-hydrogenase H-cluster mimics mediated by monophosphane ligands. *Polyhedron* 2021, *207*, 115382.
9. El-khateeb M., Abul–Futouh H., Alshurafa H., Görls H., Weigand W. Influence of bidentate phosphine ligands on the chemistry of [FeFe]-hydrogenase model: insight into molecular structures and electrochemical characteristics. *Appl. Organomet. Chem.* 2020, *34*, e5940.
10. Lü S., Gong S., Qin C.–R., Li Q.–L. Synthesis, characterization and electrochemical properties of phosphine-disubstituted diiron bis(monoselenolate) carbonyls. *Polyhedron* 2021, *207*, 115359.
11. Bai S.–F., Du X.–M., Tian W.–J., Xu H., Zhang R.–F., Ma C.–L., Wang Y.–L., Lü S., Li Q.–L., Li Y.–L. Di-, tri- and tetraphosphine-substituted Fe/Se carbonyls: synthesis, characterization and electrochemical properties. *Dalton Trans.* 2023, *51*, 11125–11134.
12. Bai S.–F., Ma J.–W., Guo Y.–N., Du X.–M., Wang Y.–L., Li Q.–L., Lü S. Aminophosphine-substituted Fe/E (E = S, Se) carbonyls related to [FeFe]-hydrogenases: synthesis, protonation, and electrocatalytic proton reduction. *J. Mol. Struct.* 2023, *1283*, 135287.
13. Li Q.–L., Lü S., Zhang R.–F., Zhao D., Ma C.–L. Substitution reactions of diiron diselenolato complex with bisphosphine ligands. *Polyhedron* 2019, *160*, 255–260.
14. 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.
15. 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.
16. 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.
17. 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.
18. 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 $Fe_2(\mu\text{-pdt})(CO)_4\{(Ph_2P)_2NR\}$ together with related monophosphine complexes for the 2Fe(H) subsite of FeFe-hydrogenases: preparation, structure, and electrocatalysis. *Organometallics* 2018, *37*, 1280–1290.