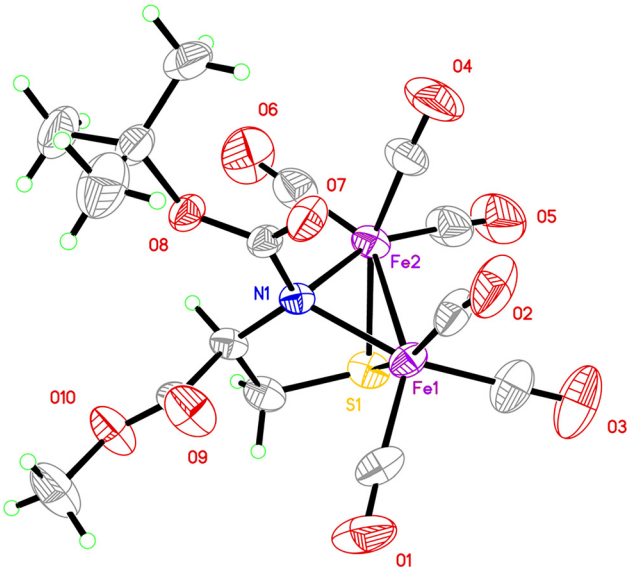
Yu-Pei Xia*

Crystal structure of bis(tricarbonyl)-{(*S*)-(*tert*-butoxycarbonyl)(1-methoxy-1-oxo-3-sulfido-k^2*S*:*S*′-propan-2-yl)amido-k2N:N′}diiron(I) *(Fe—Fe)*, $C_{15}H_{15}Fe_2NO_{10}S$



https://doi.org/10.1515/ncrs-2022-0435
Received August 30, 2022; accepted October 10, 2022; published online October 20, 2022

Abstract

$C_{15}H_{15}Fe_2NO_{10}S$, orthorhombic, $P2_12_12_1$ (no. 19), a = 10.801(2) Å, b = 13.240(3) Å, c = 15.545(3) Å, β = 90°, V = 2223.1(8) Å^3, Z = 4, $R_{gt}(F)$ = 0.0321, w$R_{ref}(F^2)$ = 0.0814, T = 298(2) K.

CCDC no.: 2189310

The crystal 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.

Source of materials

The reagents were purchased from J&K Chemica and used as received. $Fe_3(CO)_{12}$ (1 g, 1.93 mmol), tetrahydrofuran (THF, 30 mL), methyl (t-butoxycarbonyl)–L-cysteinate (H_2L, 2 mmol) and triethylamine (0.4 mL) were mixed in a 100 mL Schlenk tube under the protection of nitrogen flow. The mixture was stirred for 12 h and filtered through vacuum filtration. The residue was extracted and concentrated by using CH_2Cl_2/petroleum ether (v/v, 1:4) and a rotary evaporator, respectively. The obtained solid substance was purified through column chromatography by using CH_2Cl_2/ethyl acetate/petroleum ether (v/v/v, 1:1:20) as the eluent. Red block crystals of the title complex were obtained, yielding 23.4%.

Table 1: Data collection and handling.

Crystal:	Block, clear light red
Size:	0.29 × 0.25 × 0.18 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	1.45 mm^{-1}
Diffractometer, scan mode:	Bruker D8, φ and ω-scans
θ_{max}, completeness:	25°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	11547, 3924, 0.025
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 $\sigma(I_{obs})$, 3502
$N(param)_{refined}$:	266
Programs:	Bruker programs [1], OLEX-II [2], SHELXT [3], SHELXL [4]

Experimental details

Using Olex2 software, the structure was solved with the SHELXT program and refined with the SHELXL program. The hydrogen atoms were placed in their idealized positions with isotropic thermal parameters.

Comment

The metal complexes containing the active site of Fe-only hydrogenase ([FeFe] hydrogenase) have attracted intensive attention for their excellent catalytic hydrogen production [5–7]. Due to the flexibility and bridging nature of methyl (t-butoxycarbonyl)–L-cysteinate (H_2L), it has been used to build such a complex contains an Fe_2S_2 core with $[Fe_2(\mu\text{–}SCH_2)_2N(tBu)(CO)_6]$ [8]. To further enrich the family

***Corresponding author: Yu-Pei Xia**, College of Chemistry and Chemical Engineering, Weifang University, Weifang, Shandong 261061, P. R. China, E-mail: yopoxia@126.com. https://orcid.org/0000-0002-9084-6653

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Fe1	0.38800 (5)	0.55016 (4)	0.38330 (3)	0.05360 (17)
Fe2	0.41249 (6)	0.36781 (5)	0.37641 (4)	0.0599 (2)
N1	0.2544 (3)	0.4473 (2)	0.37257 (18)	0.0440 (6)
O1	0.2580 (5)	0.7298 (3)	0.4480 (3)	0.1208 (17)
O2	0.4066 (4)	0.6221 (4)	0.2062 (2)	0.1096 (15)
O3	0.6375 (5)	0.6290 (5)	0.4040 (4)	0.154 (2)
O4	0.4527 (5)	0.3451 (4)	0.1917 (3)	0.1318 (19)
O5	0.6723 (5)	0.3207 (5)	0.4064 (4)	0.149 (2)
O6	0.3019 (5)	0.1685 (4)	0.4045 (4)	0.149 (2)
O7	0.2093 (3)	0.4732 (3)	0.22840 (17)	0.0702 (9)
O8	0.0989 (3)	0.3628 (2)	0.30691 (17)	0.0593 (7)
O9	0.0505 (3)	0.5666 (3)	0.3993 (2)	0.0855 (10)
O10	−0.0066 (3)	0.4808 (3)	0.5145 (2)	0.0894 (12)
S1	0.41553 (11)	0.45420 (10)	0.50061 (7)	0.0657 (3)
C1	0.3060 (5)	0.6602 (4)	0.4242 (3)	0.0774 (14)
C2	0.3928 (5)	0.5900 (4)	0.2723 (3)	0.0710 (13)
C3	0.5397 (5)	0.5985 (5)	0.3963 (4)	0.0919 (17)
C4	0.4330 (5)	0.3546 (4)	0.2627 (4)	0.0840 (15)
C5	0.5707 (6)	0.3373 (5)	0.3941 (4)	0.0992 (19)
C6	0.3480 (6)	0.2443 (4)	0.3964 (4)	0.0892 (17)
C7	0.2555 (4)	0.4425 (4)	0.5317 (3)	0.0651 (11)
H7A	0.244900	0.384342	0.568936	0.078*
H7B	0.229558	0.502290	0.562984	0.078*
C8	0.1776 (4)	0.4301 (3)	0.4506 (2)	0.0503 (9)
H8	0.146221	0.360704	0.448911	0.060*
C9	0.0673 (4)	0.5019 (3)	0.4497 (3)	0.0558 (10)
C10	−0.1134 (5)	0.5461 (5)	0.5232 (5)	0.114 (2)
H10A	−0.161683	0.543693	0.471399	0.171*
H10B	−0.086392	0.614169	0.533287	0.171*
H10C	−0.163064	0.523803	0.570808	0.171*
C11	0.1856 (3)	0.4319 (3)	0.2946 (2)	0.0488 (9)
C12	0.0168 (5)	0.3278 (4)	0.2360 (3)	0.0784 (15)
C13	−0.0570 (6)	0.2445 (5)	0.2813 (5)	0.111 (2)
H13A	−0.108832	0.273966	0.324706	0.166*
H13B	−0.000933	0.197405	0.307475	0.166*
H13C	−0.107646	0.209818	0.239945	0.166*
C14	−0.0648 (6)	0.4151 (6)	0.2098 (5)	0.121 (3)
H14A	−0.121824	0.393168	0.166259	0.181*
H14B	−0.014487	0.468826	0.187592	0.181*
H14C	−0.110159	0.438767	0.258974	0.181*
C15	0.0906 (7)	0.2878 (6)	0.1632 (4)	0.132 (3)
H15A	0.143068	0.234243	0.183265	0.198*
H15B	0.140549	0.340909	0.139523	0.198*
H15C	0.035837	0.262312	0.119648	0.198*

of cysteinate-based complexes contain the [FeFe] hydrogenases centre, the title complex with a novel Fe_2SN core was synthesized at room temperature.

The composition of the asymmetric unit can be represented as $[Fe_2L(CO)_6]$. The unit contains one L^{2-} ligand (the –SH and –NH- are deprotonated), two Fe and six carbonyl groups. Both Fe-centers show almost the same coordination environment, take Fe1 as an example. Fe1(I) ion is six-coordinated with N1, S1, Fe2 and three carbonyl groups. The Fe1–S1 and Fe1–N1 bond distances are 2.2423(12) and 1.991(3) Å, respectively. Notably, a Fe–Fe bond can be found in the $[Fe_2L(CO)_6]$ unit, the Fe1–Fe2 bond distance is 2.4311(9) Å, agreeing well with the published Fe-complexes including similar coordination environment [9, 10].

Author contributions: The author has accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: This work was supported by the Research Fund for the Doctoral Program of Weifang University (No. 2021BS09).

Conflict of interest statement: The author declares no conflicts of interest regarding this article.

References

1. Bruker. SAINT and SADABS; Bruker AXS Inc.: Madison, Wisconsin, USA, 2000.
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. SHELXT – integrated space-group and crystal-structure determination. *Acta Crystallogr.* 2015, *A71*, 3–8.
5. Shi Y.-C., Shi Y., Li J.-P., Tan Q., Yang W., Xie S. Syntheses, crystal structures, and electrochemistry of novel Fe_2SN and FeSN carbonyl complexes with pendant bases. *J. Coord. Chem.* 2015, *68*, 2620–2632.
6. Apfel U. P., Kowol C. R., Halpin Y., Kloss F., Kubel J., Gorls H., Vos J. G., Keppler B. K., Morera E., Lucente G., Weigand W. Investigation of amino acid containing [FeFe] hydrogenase models concerning pendant base effects. *J. Inorg. Biochem.* 2009, *103*, 1236–1244.
7. He C., Wang M., Zhang X., Wang Z., Chen C., Liu J., Akermark B., Sun L. An unusual cyclization in a bis(cysteinyl–S) diiron complex related to the active site of Fe-only hydrogenases. *Angew. Chem. Int. Ed.* 2004, *43*, 3571–3574.
8. Song L. C., Ge J. H., Yan J., Wang H. T., Luo X., Hu Q. M. Iron-only hydrogenase active site models containing a cysteinyl group coordinated through its sulfur atom to one iron atom of the diiron subsite. *Eur. J. Inorg. Chem.* 2007, *2008*, 164–171.
9. Mayr A. J., Pannell K. H., Carrasco-Flores B., Cervantes-Lee F. Transition-metal heterocyclic chemistry. 10. A dimeric selenoketoketene complex and doubly reduced thioketohydrazonato complexes from reactions of 1,2,3-selena- and 1,2,3-thiadiazoles with diiron enneacarbonyl in the presence of alcohol. *Organometallics* 2002, *8*, 2961–2964.
10. Wu C.-Y., Chen L.-H., Hwang W.-S., Chen H.-S., Hung C.-H. Syntheses and structures of iron carbonyl complexes derived from N-(5-methyl-2-thienylmethylidene)-2-thiolethylamine and N-(6-methyl-2-pyridylmethylidene)-2-thiolethylamine. *J. Organomet. Chem.* 2004, *689*, 2192–2200.