A Molecular Low-Coordinate [Fe-S-Fe] Unit in Three Oxidation States

Christian Schneider,[a] Serhiy Demeshko,[b] Franc Meyer,[b] and C. Gunnar Werncke*[a]

This manuscript is dedicated to Prof. Dr. Wolfgang Kaim on the occasion of his 70th birthday.

Abstract: A [Fe-S-Fe] subunit with a single sulfide bridging two low-coordinate iron ions is the supposed active site of the iron-molybdenum co-factor (FeMoco) of nitrogenase. Here we report a dinuclear monosulfido bridged diiron(II) complex with a similar complex geometry that can be oxidized stepwise to diiron(II/III) and diiron(III/III) complexes while retaining the [Fe-S-Fe] core. The series of complexes has been characterized crystallographically, and electronic structures have been studied using, inter alia, $^{57}$Fe Mössbauer spectroscopy and SQUID magnetometry. Further, cleavage of the [Fe-S-Fe] unit by CS$_2$ is presented.

Introduction

Nitrogenase (N$_2$ase) is an important enzyme that catalyzes primarily the reduction of dinitrogen to ammonia. The reaction takes place at the iron-molybdenum co-factor (FeMoco), which constitutes a ligated [MoFe$_7$S$_9$C] unit.[1] Despite tremendous advances in the structural elucidation of the co-factor and some intermediate clusters under substrate conversion, as well as detailed studies of the co-factor’s electronic structures, the exact iron site for substrate binding and involved reaction mechanisms are still not fully understood.[2,3] Increasing evidence points to the importance of the Fe-S-Fe belt unit (Figure 1, top).[4,5] This unit is assumed to open up during substrate turnover, as experimentally shown by displacement of the sulfide unit by CO or selenide.[2,6] As such there is inherent interest in molecular models that feature an unsupported [Fe-S-Fe] unit with iron ions in a low-coordinate environment. However, the only known examples bearing three-coordinate metal ions are a β-diketiminato (nacnac) based iron(II) complex as well as its two-fold reduced iron(I) derivative (Figure 1, bottom).[7,8] The iron(II) complex is susceptible to coordination by ammonia and hydrazines, and is even able to cleave the N–N bond of the latter.[7,9] We now report on the synthesis of a dinuclear [2Fe-1S]$^{2+}$ complex with an unsupported monosulfide bridge via the reaction of a two-coordinate iron(I) silylamide with elemental sulfur. Subsequent oxidation leads to the first example of a mixed valent [2Fe-1S]$^{1+}$ and an “all ferric” [2Fe-1S]$^{3+}$ form. The series of complexes was examined with respect to their spectroscopic and physical properties. The initial [2Fe-1S]$^{2+}$ complex was further subjected to a variety of small molecule substrates that are transformed by the N$_2$-ase, however showing only a limited reactivity or stability. Most notably, its reaction with CS$_2$ led to rupture of the Fe-S-Fe motif and formation of a mononuclear iron(II) thiocarbonate complex, revealing the structural ability of the [Fe-S-Fe] unit.

Results and Discussion

The reaction of a suspension of K[18c6][FeL] ($L = N$(Dipp)SiMe$_3$, Dipp = 2,6-diisopropylphenyl), 1,[10] in Et$_2$O with 1/16...
S₄ for 16 h led to the formation of a colorless solid. X-Ray diffraction analysis of suitable single crystals showed the formation of the dinuclear complex \((K[18c6])_2[(FeL)_2(\mu-S)]\), 2 (Scheme 1, Figure 2).

2 features two three-coordinate iron(II) ions bridged by a single sulfide in a nearly linear fashion \((Fe-S-Fe \approx 167.78(2)^\circ)\) with slightly different \(Fe-S\) distances of 2.2404(5) Å and 2.2375(5) Å (Table 1). The linear arrangement is unusual as in dinuclear metal complexes with an unsupported bridging S⁻⁻⁻ ligand \(Fe-S-Fe\) bond angles of 90° to 140° are commonly found\(^{[7,8]}\). A linear Fe-S-Fe axis was only observed in related \([2Fe-1S]\)²⁺ complexes (Figure 1)\(^{[7,11]}\) and in a higher coordinate salen based compound\(^{[12]}\) and was attributed to steric constraints. 2 represents only the second example of a dinuclear, low-coordinate iron(II) complex bearing an unsupported sulfide bridge\(^{[13]}\).

As the iron ions in the FeMo co-factor are supposed to switch between oxidation states +2 and +3 during substrate conversion\(^{[3]}\), we were interested if the oxidation state of 2 can be adjusted accordingly. The cyclic voltammogram of 2 in THF showed two quasi-reversible one-electron oxidation processes at \(E_{1/2} = -1.55\) V and \(-0.55\) V (versus \(Fc/\text{Fc}^+\), Figure 3), which were tentatively assigned to the \([2Fe-1S]\)²⁺/¹⁺ and the \([2Fe-1S]\)¹⁺/⁰⁺ redox couple.\(^{[14]}\) The related bis(sulfido) diferric complex \([LFe(\mu-S)]_2\) (monoanionic ligand \(L^- = \text{nacnac}\)) reported by Drieds and co-workers features redox events in THF at \(E_{1/2} = -1.25\) V for the \([2Fe-2S]\)²⁺/¹⁺ and \(E_{1/2} = -2.55\) V (\(\Delta E_{1/2} = 1.10\) V) for the \([2Fe-2S]\)¹⁺/⁰⁺ redox couple.\(^{[15]}\) For the similar diatomic complex \([LFe(\mu-S)]_2\) (dianionic ligand \(L^2^- = \text{bis(benzimidazolato})\)), reported by some of us, the reduction of the dimeric \([2Fe-2S]\)²⁺ core in MeCN occurred at \(E_{1/2} = -1.14\) V (\(2Fe-2S\)²⁺/¹⁺) and \(E_{1/2} = -2.10\) V (\(2Fe-2S\)¹⁺/⁰⁺, \(\Delta E_{1/2} = 0.96\) V).\(^{[15]}\) The difference between their respective redox events is consistent with the one found for 2 (\(\Delta E_{1/2} = 0.98\) V). In contrast, the positions of the redox events of these bis(μ-sulfido) complexes are shifted by around 0.9 V or 0.6 V to lower potentials, respectively, reflecting the additional sulfide ligation and higher coordination number of the iron ions in the two previously reported \([2Fe-2S]\) systems.\(^{[14,15]}\)

Given the electrochemical data we attempted the chemical oxidation of 2. Treatment of 2 with one equivalent of AgOTf in Et₂O yielded reddish K[18c6][L(Fe)₂(μ-S)], 3 (Scheme 2, Figure 4). Treatment of 2 with two equivalents of AgOTf in Et₂O (or 3 with one equivalent of AgOTf) led to a colour change to dark green, and the neutral complex \([L(Fe)₂(μ-S)]\), 4, was obtained from a saturated pentane solution.

---

**Table 1.** Selected bond lengths (Å) and angles (°) of complexes 2–4.

| Compound  | 2         | 3         | 4         |
|-----------|-----------|-----------|-----------|
| Fe₁–S₁    | 2.2400(5) | 2.1911(11)| 2.1746(7) |
| Fe₂–S₁    | 2.3375(5) | 2.1943(11)| 2.1739(7) |
| Fe₁–N₁    | 1.9961(13)| 1.928(3)  | 1.8871(19) |
| Fe₁–N₂    | 1.9778(14)| 1.927(3)  | 1.8902(19) |
| Fe₂–N₃    | 2.0123(13)| 1.925(3)  | 1.8862(2)  |
| Fe₂–N₄    | 1.9871(13)| 1.921(3)  | 1.8859(19) |
| Fe₁–S₁–Fe₂| 161.78(2) | 175.2(7)  | 172.31(4)  |

---

**Figure 2.** Molecular structure of 2 in the solid state. K⁺[18c6] counter ions and H atoms are omitted. See Table 1 for important bond lengths and angles.

**Figure 3.** Cyclic voltammogram of Fe(II) in THF, 0.1 M NBu₄PF₆ vs. Fc/Fc⁺.

**Scheme 1.** Synthesis of the monosulfide bridged complex 2.

**Scheme 2.** Synthesis of complexes 3 and 4 by stepwise oxidation of 2.
Important structural parameters of 3 and 4 are shown in Table 1. Compared to 2, complexes 3 and 4 retain both a more or less linear Fe-S-Fe core. A gradual decrease of the Fe–S and Fe–N bond lengths was observed upon oxidation due to the contraction of the ionic radii of the metal ions. The structural features found for both iron ions are largely identical in 3 and 4, which prohibited an assignment of localized oxidation states for mixed-valent 3 on a structural level.

With this unprecedented series of low-coordinate [2Fe-1S] complexes in three different oxidation states in hand, their spectroscopic and electronic features were studied in detail.

UV/Vis spectroscopic examination of 2 showed no absorption beyond 400 nm (Figure 5A), which is common for low-coordinate iron(II) compounds, but unusual for μ-sulfido diiron(II) complexes. In contrast, the mixed valent species 3 exhibited three rather intense maxima at 380 nm ($\lambda = 11800$ L mol$^{-1}$ cm$^{-1}$), 470 nm ($\lambda = 5940$ L mol$^{-1}$ cm$^{-1}$) and 700 nm ($\lambda = 2270$ L mol$^{-1}$ cm$^{-1}$), and it is tempting to assign the low-energy absorption to an intervalence charge transfer (IVCT) transition. For 4 just one pronounced band at 430 nm ($\lambda = 5710$ L mol$^{-1}$ cm$^{-1}$) was observed. Zero field $^{57}$Fe Mössbauer spectroscopy (Figure 5B) revealed for the iron(II/II) complex 2 a doublet with $\delta = 0.59$ mm s$^{-1}$ and $|\Delta E_Q| = 0.22$ mm s$^{-1}$, in agreement with data for a related three-coordinate iron(II) complex. These values are slightly smaller than those of the only other known monosulfido-bridged iron(II/II) complex shown in Figure 1 (bottom left; $\delta = 0.86$ mm s$^{-1}$ and $|\Delta E_Q| = 0.58$ mm s$^{-1}$), which can be explained by the weaker donor strength of the silylamide ligands as well as a less distorted trigonal planar ligand arrangement.

The all ferric complex 4 is represented by a doublet with $\delta = 0.29$ mm s$^{-1}$ and $|\Delta E_Q| = 3.70$ mm s$^{-1}$ indicating the presence of high-spin iron(III) ions. The spectrum of the mixed valent complex 3, recorded at 7 K, showed two doublets with $\delta = 0.36$ mm s$^{-1}$ ($|\Delta E_Q| = 3.70$ mm s$^{-1}$) and $\delta = 0.57$ mm s$^{-1}$ ($|\Delta E_Q| = 0.71$ mm s$^{-1}$). This evidences distinguishable iron(II/III) positions in solid 3 on the $^{57}$Fe Mössbauer timescale at 7 K, whereas the smaller separa-
tion in the isomer shifts (\(\Delta\delta(3) = 0.21 \text{ mm s}^{-1}\) vs. \(\Delta\delta(2/4) = 0.30 \text{ mm s}^{-1}\)) is indicative of some degree of valence delocalization. Given the lack of literature precedent of the three-coor-
dinate \(\mu\)-sulfido complexes 3 and 4 their Mössbauer spectroscopic features are compared best to low coordinate iron com-
plexes bearing a [2Fe-2S] motif in the same oxidation states.\[^{[14,15,18–20]}\] Most importantly, such mixed valent [2Fe-2S] compounds are shown to exhibit moderate\[^{[15,19,20]}\] or strong\[^{[14]}\] antiferromagnetic coupling, and give Mössbauer spectra (at < 10 K) that correspond to either valence localized or delocal-
ized states, respectively.

Additional insights into the electronic situation of 2–4 in solid state were obtained by SQUID measurements (Figure
5D–F). 2 exhibited at 300 K a \(\gamma T\) value of 1.8 cm\(^3\) mol\(^{-1}\) K which linearly dropped to ca. 0.1 cm\(^3\) mol\(^{-1}\) K at 30 K. This indicated a moderate antiferromagnetic interaction between the two iron(II) \((S = 2)\) ions with a \(S = 0\) ground state. The coupling constant was determined to be \(J = -53 \text{ cm}^{-1}\) using \(\hat{H} = -2J \sum S_i S_j\) with \(g_1 = g_2 = 2.01\).

The mixed valent compound 3 showed at 295 K a significantly lower \(\gamma T\) value of 0.96 cm\(^3\) mol\(^{-1}\) K which decreased to 0.44 cm\(^3\) mol\(^{-1}\) K at 80 K with a further drop to 0.38 cm\(^3\) mol\(^{-1}\) K below 20 K, which implies a ground state of \(S = 1/2\). The anti-
ferromagnetic coupling is stronger with \(J = -115 \text{ cm}^{-1}\) (\(g_1 =
2.08, g_2 = 2.02\)). For the all-ferric compound 4 a similar value \(J = -104 \text{ cm}^{-1}\) (\(g_1 = 2.10, S_1 = S_2 = 5/2\)) was observed with \(\gamma T = 1.3 \text{ cm}^{-1}\) K at 300 K that decreased linearly to ca. 0.2 cm\(^3\) mol\(^{-1}\) K below 50 K due to a \(S = 0\) ground state. The dif-
f erences in exchange coupling can be explained using a simplified orbital scheme under assumption of an idealized \(C_{4v}\) symmetric ligand environment for each iron atom (Figure 5C, \(z\) axis along the Fe-S-Fe unit). Upon oxidation, electrons are re-
moved from the lowest-lying, \(d_{xy}/d_{xz/yz}\) orbitals, which have no impact onto the exchange mechanism. As such the
variation in \(J\) values for 2–4 can be mainly attributed to differences in Fe–Fe distances, with different superexchange contributions due to changes in Fe-(\(\mu\)-S) covalency likely play-
ing a further role. A significant stabilization of the antiferro-
magnetically coupled ground state upon oxidation from the di-
rion(II) to the mixed-valent iron(II)/iron(III) and diiron(III)
states was observed for the series of complexes \([\{\text{LFe}\}^2(\mu-S)]_2\) \((\text{L}^2 = \text{bis(benzimidazolato)})\).\[^{[15,19]}\]

Having evaluated the redox and electronic properties of 2 we continued with investigations concerning its reactivity to-
wards nitrogenase related small molecules.\[^{[21]}\] No reaction with \(\text{NH}_2, \text{H}_2, \text{or CO was observed whereas treatment of 2 with hydra-
line derivatives and proton or methyl group sources only led}
to decomposition. Exposure of 2 to \(\text{CO}_2\) caused a visible colour
change but did not yield any identifiable product, probably due to parallel insertion of \(\text{CO}_2\) into the iron silylamide bonds.\[^{[22]}\] As such we examined the behavior of 2 towards the heavier congener \(\text{CS}_2\), which is an inhibitor of nitrogenase-
mediated proton or acetylene reduction but can also serve as a
substrate that is mainly converted to \(\text{H}_2\).\[^{[23–25]}\] This led to the iso-
lization of the monomeric iron thiocarbonate complex \([\{\text{L}(18c6i)\}_2(\text{Fe}(\text{n}^2-\text{CS}_2)\text{[L]}_2)]\), 5 (Scheme 3, Figure 6).

In 5 the iron ion is coordinated by two silylamides and one bidentate thiocarbonate ligand in a distorted tetrahedral fash-
ion. The two \(\text{K}^+\) (18c6i) cations are connected further to the thi-
ocarbonate ligand, each via two sulfur atoms. We explain the formation of 5 by initial insertion of \(\text{CS}_2\) into one of the iron-
sulfur bonds of 2, giving a thiocarbonate bridged dimer. The insertion of \(\text{CS}_2\) into an unsupported M-S-M unit was so far only
reported for diuranium complexes.\[^{[26]}\] One neutral iron(II)
bisamide is then replaced by the potassium crown-ether moi-
eties, which themselves act as a Lewis acid. The mixed valent
complex 3 reacted with \(\text{CS}_2\) also under rupture of the \([\text{Fe-S-Fe]}\) motif. This yielded the iron(III) thiocarbonate complex 7, which
could alternatively be obtained via the oxidation of 6 by silver
triflate. For the neutral complex 4 the reaction with \(\text{CS}_2\) re-
mained inconclusive. The observation of facile Fe–S bond clea-
vages suggests a rather weak \(\text{Fe}^{2+}\)–\(\text{S}\) interaction. The displace-
ment of an iron(II) ion by other Lewis acids has possible impli-
cations for the situation found in the FeMo cofactor where
cleavage of the belt Fe-S-Fe unit is discussed during substrate
turnover using the local Lewis acid/base properties of the sur-
roundings of the enzyme pocket.\[^{[5]}\] The facile insertion of \(\text{CS}_2\)
into a \([\text{Fe-S-Fe]}\) function also reveals how \(\text{CS}_2\) might act as an
inhibitor of nitrogenase FeMo (and other iron-sulfur clusters)
which is thought to proceed by blocking of coordination
sites\[^{[24,25,27]}\] or by insertion into other metal–ligand bonds.\[^{[28]}\]
Conclusions

We have synthesized a unique series of low-coordinate [Fe-S-Fe] complexes in three oxidation states which resembles a Fe-S-Fe belt unit in the iron/sulfur/molybdenum co-factor of the nitrogenase enzyme. These complexes were characterized for their magnetic and spectroscopic properties. Mössbauer spectroscopy showed for the mixed valent [2Fe-1S]− complex localized valence states in solid at low temperatures. Magnetic measurements revealed for the diron [2Fe-1S]2+ a moderate antiferromagnetic coupling which becomes significantly enhanced for the [2Fe-1S]3+ and [2Fe-1S]4+ compounds. Reactivity studies on these complexes towards different nitrogenase relevant substrates revealed for CS2 the facile cleavage of the Fe-S-Fe unit. This led to the formation of an iron thiocarbonate which may suggest a possible inhibitory mechanism of CS2 with respect to the reactivity of FeMoco and related Fe/S clusters.

Experimental Section

General considerations: All manipulations were carried out in a glovebox, or using Schlenk-type techniques under a dry argon atmosphere. Used solvents were dried by continuous distillation over sodium metal for several days, degassed via three freeze-pump cycles and stored over molecular sieves 4Å. K[18c6][FeL] was synthesized according to the literature procedure. For details concerning data acquisition of solution and solid-state analyses ([H-NMR spectra, X-ray diffraction analysis, cyclovoltametry, magnetic measurements and Mössbauer spectra), see the Supporting Information.

Syntheses

[K18c6][[FeL]2(μ-S)] (2): [K18c6][FeL], 1 (267 mg, 0.31 mmol, 2 equiv) was suspended in 5 mL of Et2O. The slow addition of elemental sulfur (5.0 mg, 0.16 mmol, 1 equiv) led to an immediate colour change of the solution from red to brown and the precipitation of a pale yellow solid. Decanting off the supernatant, washing the residue with 2×5 mL of pentane and drying under reduced pressure afforded the crude product as a pale yellow crystalline solid. Recrystallization in THF/pentane at −35 °C led to colourless crystals of 2 (141 mg, 0.08 mmol, 52%), suitable for X-ray diffraction. [H-NMR (500.1 MHz, [D8]THF, 300 K): δ = 14.23, 9.30, 3.50, −0.94, −1.70 ppm. Evans: (500.1 MHz, [D8]THF + 1% SiMe4, 300 K): μ5eff = 3.98 μBS IF-IR (ATR); (cm−1): ν = 2896 (w), 1418 (w), 1352 (w), 1314 (w), 1235 (m), 1192 (w), 1103 (vs.), 962 (w), 907 (s), 835 (vs.), 775 (s), 664 (w), 529 (w), 423 (m). CHNS: calc. (C15H12Fe2K4N2O14S6)1744.44 g mol−1: C 57.84 H 8.78 N 3.21 S 1.84 found: C 57.93 H 8.69 N 3.58 S 1.36.

[K18c6][[FeL]3(μ-S)] (3): [K18c6][[FeL]2(μ-S)], 2 (150 mg, 0.086 mmol, 1 equiv) was suspended in 5 mL of Et2O. Upon the addition of AgOTf (22 mg, 0.086 mmol, 1 equiv) the pale yellow suspension turned into a red solution with beginning precipitation of a dark solid (elemental silver). After stirring for 2 hours, the mixture was filtered, the residue washed with 2×3 mL Et2O and the combined filtrates were layered with 5 mL of pentane. Storing the solution at −35 °C for several days yielded to a dark red crystalline solid, suitable for X-ray diffraction analysis. Decanting off the supernatant, washing the residue with 2×5 mL of pentane and drying under reduced pressure afforded [K18c6][[FeL]3(μ-S)], 3 as a dark red crystalline solid (40 mg, 0.023 mmol, 33%). The aforementioned procedure to synthesize 3 leads to a pure product according to elemental analysis (vide infra). To obtain a magnetic pure sample several recrystallization steps in Et2O/pentane were required, which led to a decrease of the yield to less than 10%. [H-NMR: (500.1 MHz, [D8]THF, 300 K): δ = 14.58, 14.10, 3.26, 3.07, −0.92, −2.01 ppm. Evans: (300.3 MHz, [D8]THF + 1% SiMe4, 300 K): μ5eff = 3.70 μBS IF-IR (ATR); (cm−1): ν = 2954 (w), 1456 (w), 1421 (m), 1353 (w), 1309 (w), 1232 (s), 1179 (s), 1101 (vs.), 961 (m), 896 (m), 832 (vs.), 783 (s), 673 (s), 637 (w), 541 (s). UV/VIS (THF): λ/nm (I / L mol−1 cm−1) = 310 (8800), 470 (9540), 700 (2270). CHNS: calc. (C15H12Fe3K4N2O14S6)1441.03 g mol−1: C 60.01 H 8.95 N 3.89 S 2.22 found: C 59.66 H 8.64 N 4.07 S 1.51.

Conclusions

We have synthesized a unique series of low-coordinate [Fe-S-Fe] complexes in three oxidation states which resembles a Fe-S-Fe belt unit in the iron/sulfur/molybdenum co-factor of the nitrogenase enzyme. These complexes were characterized for their magnetic and spectroscopic properties. Mössbauer spectroscopy showed for the mixed valent [2Fe-1S]− complex localized valence states in solid at low temperatures. Magnetic measurements revealed for the diron [2Fe-1S]2+ a moderate antiferromagnetic coupling which becomes significantly enhanced for the [2Fe-1S]3+ and [2Fe-1S]4+ compounds. Reactivity studies on these complexes towards different nitrogenase relevant substrates revealed for CS2 the facile cleavage of the Fe-S-Fe unit. This led to the formation of an iron thiocarbonate which may suggest a possible inhibitory mechanism of CS2 with respect to the reactivity of FeMoco and related Fe/S clusters. The Supporting Information contains details concerning data acquisition of solution and solid-state analyses ([H-NMR spectra, X-ray diffraction analysis, cyclovoltametry, magnetic measurements and Mössbauer spectra).
X-ray diffraction. It exhibits no identifiable $^1$H NMR spectroscopic signature.

Deposition Numbers 2048096 (2), 2048164 (3), 2048165 (4), 2048166 (5) and 2048167 (6) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Acknowledgements

Funding by the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged: grants WE 5627/4-1 (to G. W.) and Me 1313/13-2 (to F.M. in the framework of the Priority Program SPP1927 “Iron Sulfur for Life”), Open access funding enabled and organized by Projekt DEAL.

Conflict of interest

The authors declare no conflict of interest.

Keywords: $^{57}$Fe Mössbauer spectroscopy · electrochemistry · iron sulfide complex · magnetism · nitrogenase

1. a) K. M. Lancaster, M. Roemelt, P. Ettenhuber, Y. Hu, M. W. Ribbe, F. Neese, U. Bergmann, S. DeBeer, Science 2011, 334, 974; b) T. Spatzal, M. Aksoyoglu, L. Zhang, S. L. A. Andrade, E. Schleicher, S. Weber, D. C. Rees, O. Einsle, Science 2011, 334, 940; c) O. Einsle, F. A. Tezcan, S. L. A. Andrade, B. Schmid, M. Yoshida, J. B. Howard, D. C. Rees, Science 2002, 297, 1666; d) D. C. Rees, F. Alif Tezcan, C. A. Haynes, M. Y. Walton, S. Andrade, O. Einsle, J. B. Howard, Philos. Trans. R. Soc. A 2005, 363, 971.

2. T. Spatzal, K. A. Perez, O. Einsle, J. B. Howard, D. C. Rees, Science 2014, 345, 1620.

3. a) T. Spatzal, J. Schlesier, E.-M. Burger, D. Sippel, L. Zhang, S. L. A. Andrade, D. C. Rees, O. Einsle, Nat. Commun. 2016, 7, 10902; b) B. M. Hoffman, D. Lukoyanov, Z.-Y. Yang, D. R. Dean, L. C. Seefeldt, Chem. Rev. 2014, 114, 4041; c) B. K. Burgess, D. J. Lowe, Chem. Rev. 1996, 96, 2983.

4. W. Kang, C. C. Lee, A. J. Jasieniowski, M. W. Ribbe, Y. Hu, Science 2020, 368, 1381.

5. D. Sippel, M. Rohde, J. Netzer, C. Tnicket, C. Gies, K. Grunau, I. Djurdjevic, L. Decamps, S. L. A. Andrade, O. Einsle, Science 2018, 359, 1484.

6. T. Spatzal, K. A. Perez, J. B. Howard, D. C. Rees, eLife 2015, 4, e11620.

7. J. Vela, S. Stoian, C. L. Flaschenhui, E. Münch, P. L. Holland, J. Am. Chem. Soc. 2004, 126, 4522.

8. M. M. Rodriguez, B. D. Stubbert, C. C. Scarborough, W. W. Brennessel, E. Bill, P. L. Holland, Angew. Chem. Int. Ed. 2012, 51, 8247; Angew. Chem. 2012, 124, 8372.

9. B. D. Stubbert, J. Vela, W. W. Brennessel, P. L. Holland, Z. anorg. allg. Chem. 2013, 639, 1531.

10. C.-Y. Lin, J. C. Fettinger, F. Grandjean, G. J. Long, P. P. Power, Inorg. Chem. 2014, 53, 9400.