Nitrogen reduction by the Fe sites of synthetic [Mo₃S₄Fe] cubes

Nitrogen (N₂) fixation by nature, which is a crucial process for the supply of bio-available forms of nitrogen, is performed by nitrogenase. This enzyme uses a unique transition-metal–sulfur–carbon cluster as its active-site co-factor ([R-homocitrate]MoFe₇S₉C], FeMoco)¹,² and the sulfur-surrounded iron (Fe) atoms have been postulated to capture and reduce N₂ (refs. ³–⁶). Although there are a few examples of synthetic counterparts of the FeMoco, metal–sulfur cluster, which have shown binding of N₂ (refs. ⁷–⁹), the reduction of N₂ by any synthetic metal–sulfur cluster or by the extracted form of FeMoco¹⁰ has remained elusive, despite nearly 50 years of research. Here we show that the Fe atoms in our synthetic [Mo₃S₄Fe] cubes¹¹,¹² can capture a N₂ molecule and catalyse N₂ silylation to form N(SiMe₃)₃ under treatment with excess sodium and trimethylsilyl chloride. These results exemplify the catalytic silylation of N₂ by a synthetic metal–sulfur cluster and demonstrate the N₂-reduction capability of Fe atoms in a sulfur-rich environment, which is reminiscent of the ability of FeMoco to bind and activate N₂.

Nitrogen (N₂) is an essential element to maintain every known form of life on Earth. Although the element is inexhaustible in the atmosphere as N₂, only diazotrophs or lightning in thunderstorms can transform this stable molecule into bio-available forms (for example, ammonia (NH₃) and nitrogen oxides) in the natural world. Other organisms consequently rely on the products of the fixation processes and limited pre-existing sources to afford the necessary nitrogen. In this sense, N₂ fixation is one of the most crucial bottlenecks in Earth's ecosystem. Key players of N₂ fixation are nitrogenase enzymes that reduce N₂ to NH₃. The most studied of these, molybdenum (Mo)-nitrogenase, has a unique metal–sulfur–carbon co-factor described as [(R-homocitrate)MoFe₇S₉C] (FeMoco; Fig. 1)¹¹,¹² and performs the catalytic reduction at ambient temperature and pressure. As FeMoco is found only in nitrogenase, its chemical and physical properties have attracted significant interest regarding its desirable N₂-reduction activity. How FeMoco reduces N₂ has long been studied by biochemical analyses of the enzyme¹,¹,¹³ and by structural and functional modelling of FeMoco with small-molecule complexes¹⁴,¹⁵ and metal–sulfur (M–S) clusters¹⁶,¹⁷.

Although the detailed N₂-reduction mechanism of FeMoco remains elusive, a growing number of studies suggest that FeMoco eliminates one of the μ₃-bridging sulfur (S) atoms and captures substrates at the produced vacant coordination sites on the iron (Fe) atoms¹¹,¹⁶. Analogously, a common approach to generating small-molecule N₂ complexes has been removal of a metal-bound ligand under reducing conditions. However, applying this method to the available synthetic counterparts of FeMoco, namely, M–S clusters, has been challenging. As these clusters contain coordinative S atoms in their inorganic cores, a vacant metal site often attracts core S atoms of M–S clusters rather than N₂, which leads to aggregation¹⁷. Limiting the number of vacant metal atoms in the core is thus a plausible approach and led to the isolation of N₂-bound clusters in several previous and recent examples, including ours¹⁷. Nevertheless, catalytic reduction of N₂ by these clusters remains unknown despite its relevance to the natural system.

Our framework to overcome these hurdles implements a triangular [Mo₃S₄] fragment bearing robust Mo–CpR bonds (CpR = C₅Me₅ (Cp*), C₅Me₅SiMe₃ (Cp*) and C₅Me₅SiEt₃ (Cp*₃), where Si is silicon, Me is methyl and Et is ethyl)¹¹,¹² as a platform to structurally encumber and protect a fourth metal incorporated into the vertex (Fig. 1). A titanium (Ti) derivative [Cp°₃Mo₃S₄Ti] captures and activates N₂ in the presence of potassium graphite (KC₈), indicating that the [Mo₃S₄Ti] cube is robust under reducing conditions and avoids undesirable aggregation¹⁸. In contrast, catalytic reduction of the bound N₂ was not observed, probably owing to the strong Ti–N bond that inhibits product release. We then hypothesized that a softer Fe atom as found in the biological systems might function more successfully to carry out N₂ reduction instead of the harder Ti atom. The results below demonstrate the capture and catalytic silylation of N₂ by the vertex Fe atoms of [Mo₃S₄Fe] cubes. Although it is likely that there are mechanistic differences between the silylation of N₂ and NH₃ production by nitrogenase, our results demonstrate that an Fe centre built into a M–S core and in a S-rich coordination environment can activate inert N₂ sufficiently for chemical conversion.

The treatment of our reported [Mo₃S₄Fe] clusters, [Cp°₃Mo₃S₄FeCl] (Cp° = Cp* (1a), Cp° = Cp* (1b) and Cp° = Cp*–(1c))¹¹,¹² with strong reductants (KC₈ for 1a and sodium naphthalenide Na(C₈H₇)₄ for 1b and 1c) under N₂ in tetrahydrofuran (THF) led to the formation of the corresponding N₂ clusters (Fig. 2a). The N₂ coordination mode varies...
depending on the bulkiness of the Cp\(^h\) ligands, so that a [Mo\(_3\)S\(_4\)Fe] dimer bridged by N\(_2\), [(Cp\(^*\)Mo\(_3\)S\(_4\)Fe)\(\mu\)-N\(_2\)]\(^2\) (2a), and monomers each bearing a terminal N\(_2\) ligand, [Cp\(^*\)Mo\(_3\)S\(_4\)Fe(N\(_2\))]\(^–\) (Cp\(^*\) = Cp\(^*\) (2b) and Cp\(^*\) = Cp\(^{3\text{SiMe}_3}\) (2c)), were obtained. The N\(_2\) binding modes of 2a–2c were assigned primarily from the \(^1\)H NMR spectra of \(^{15}\)N-labelled clusters (Supplementary Figs. 1–3). Cluster 2a exhibited a single signal at a chemical shift \(\delta = -40.9\) ppm as expected from the equivalent N atoms of the bridging \(^{15}\)N\(_2\). Conversely, 2b and 2c gave two signals at \(\delta = 22.0\) ppm and \(\delta = -5.3\) ppm for 2b and \(\delta = 22.6\) ppm and \(\delta = -5.7\) ppm for 2c, corresponding to the inequivalent proximal and distal N atoms in these molecules. Terminal N\(_2\) binding in 2b and 2c was further confirmed by infrared-active N–N stretches observed at 1,896 cm\(^{-1}\) and 1,902 cm\(^{-1}\), respectively, both of which exhibited a bathochromic shift compared to those reported for N\(_2\) complexes of Fe\(^{II}\) or Fe\(^{I}\) (ref. 18), and the activation N–N stretching frequencies of 2b and 2c are close to the lower end of the range observed for N\(_2\) (1.252 Å), suggesting a weakened N–N bond. Likewise, the \(\delta\) values for 2a were detectable via resonance-Raman spectroscopic analyses revealing the molecular structures of 2a and 2c, and Supplementary Figs. 6, perhaps owing to slightly broken symmetry of the N\(_2\) binding mode. X-ray crystallographic analyses revealed the molecular structures of 2a and 2c (Fig. 2b,c, Supplementary Figs. 11 and 12, and Supplementary Table S5). The structure of 2a is an N\(_2\)-bridged [Mo\(_3\)S\(_4\)Fe] dimer with an inversion centre at the middle of the two N atoms, whereas 2c is a monomeric cluster bearing a terminal bound N\(_2\). The N–N distances (1.151(4) Å for 2a and 1.136(5) Å for 2c) are in between those of free N\(_2\) (1.098(1) Å) and N\(_2\)H\(_2\) (1.252 Å), suggesting a weakened N–N bond. Likewise, the N–N stretching frequencies of 2b and 2c are close to the lower end of those reported for N\(_2\) complexes of Fe\(^0\) or Fe\(^1\) (ref. 19), and the activation levels are even comparable to an Fe\(^0\)–N\(_2\) complex supported by S- and carbon (C)-based ligands\(^{9\text{a}}\).

Successful activation of N\(_2\) at the Fe atoms of 2a–2c prompted us to pursue the catalytic reduction of N\(_2\) using the [Mo\(_3\)S\(_4\)Fe] cubes. Reduction to NH\(_3\) was observed but was not catalytic, giving at most 1.6 ± 0.1 equiv. NH\(_3\) (per 2c) under typical conditions\(^{11\text{a},12\text{a},20\text{a}}\) (Supplementary Table 4). Protonation of S atoms possibly occurs in this reaction, which weakens the Fe–S bonds and releases a vertex Fe atom from [Mo\(_3\)S\(_4\)Fe\(^{3\text{SiMe}_3}\)], in a relevant manner to degradation of the cubes under electrochemical oxidation\(^{11\text{a},11\text{b}},20\text{a} \). Nonetheless, more importantly, we found that the chloride (Cl) clusters 1a–1c and N\(_2\) clusters 2b and 2c all catalytically reduce N\(_2\) to N(Si\(_3\)Me\(_3\))\(_3\), in the presence of excess sodium (Na) and trimesitylsilylethyl chloride (CISMe\(_3\)). A minimum of 122.9 ± 3.0 equiv. (per 1c) and up to 248.0 ± 15.6 equiv. (per 1b) of N(Si\(_3\)Me\(_3\))\(_3\) were generated after 100 h under a N\(_2\) (1 atm) atmosphere at room temperature (Table 1 and Supplementary Tables 1 and 2). Although the cause of the differences in the activity of these complexes has not been conclusively identified at this point, we assume that the steric, not electronic, effects of the Cp\(^h\) ligands play a major role (vide infra) because the Cp\(^h\) substituents did not notably affect the redox behaviours of 1a–1c (half-wave potentials \(E_{1/2}([\text{Mo}_3\text{S}_4\text{Fe}]^{3+/2+}) = –0.17\) V (1a), –0.19 V (1b) and –0.24 V (1c) versus Ag/Ag\(^+\)) or the redox features of 2b and 2c observed in cyclic voltammetry (Supplementary Fig. 14).

The N(Si\(_3\)Me\(_3\))\(_3\) yields, on a per-active-metal basis produced by 1b and 2c, are about three-times higher than those of other Fe catalysts reported so far (Supplementary Table 3)\(^{11\text{b},12\text{b},14\text{b}}\), and are comparable to the highest yields by Mo (ref. 29) and Co (refs. 22,23) catalysts. Similar to known systems, the catalytic reactions in THF concurrently formed Me\(_3\)SiMe\(_3\), Me\(_3\)SiOC\(_4\)H\(_4\), and Me\(_3\)SiOC\(_4\)H\(_3\)Me, as by-products (Supplementary Figs. 15–17). These by-products should originate from reactions of the trimethylsilyl radical-SiMe\(_3\), with itself or the THF solvent\(^{29\text{b}}\), as treatment of ClSi\(_3\)Me\(_3\) with alkaline metals has been accepted to generate SiMe\(_3\), (ref. 26). Although the THF solvent is much more abundant than the N\(_2\), reactant, the selectivity for N(SiMe\(_3\))\(_3\) was high in the case of 1b and reached 37.2% (Table 1, entry 2). It is striking that any of the corresponding [Mo\(_3\)S\(_4\)] platforms, [Cp\(^*\)Mo\(_3\)S\(_4\)]\(^–\) (Cp\(^*\) = Cp\(^*\) (4a), Cp\(^*\) = Cp\(^{4\text{SiMe}_3}\) (4b) and Cp\(^*\) = Cp\(^{3\text{SiMe}_3}\) (4c)), several relevant Fe\(_2\) clusters or FeCl\(_2\) (ref. 29) did not provide N(SiMe\(_3\))\(_3\), at significant levels under the same conditions (Table 1 and Supplementary Table 3). After a catalytic run using 1a, a mass spectrum of the reaction mixture revealed [Mo\(_3\)S\(_4\)Fe] cubes binding ring-opening products of THF (Supplementary Fig. 19), indicating sufficient stability of the cubic core during catalysis. Moreover, a carbon monoxide (CO)-trapping experiment revealed the formation of a low yield (11%) of [Cp\(^{3\text{SiMe}_3}\)Mo\(_3\)S\(_4\)Fe(4CO)] (5) from a catalytic reaction mixture with 1c, Na and CISMe\(_3\) (200 equiv. each) under N\(_2\) (Supplementary Figs. 24–27), implying the generation of [Mo\(_3\)S\(_4\)Fe] species with labile ligands (for example, THF or N\(_2\)) on Fe. These results suggest that the Fe centre of each [Mo\(_3\)S\(_4\)Fe] cube is the actual N\(_2\)-reduction site.

Considering previous proposals for analogous reactions\(^{26,28}\), we propose a mechanism for N\(_2\) silylation by our [Mo\(_3\)S\(_4\)Fe] cubes (Supplementary Fig. 18). In this pathway, we suppose that the Cl atom

| Entry | Precatalyst | N(SiMe\(_3\))\(_3\) yield (equiv. per catalyst)\(^*\) |
|-------|-------------|--------------------------------------------------|
| 1     | 1a          | 127.0 ± 34.6                                    |
| 2     | 1b          | 248.0 ± 15.6                                    |
| 3     | 1c          | 122.9 ± 3.0                                     |
| 4     | 2a          | 142.5 ± 16.0                                    |
| 5     | 2b          | 227.1 ± 40.8                                    |
| 6     | 2c          | 258.3 ± 63.1                                    |
| 7     | Cp\(^*\)Mo\(_3\)S\(_4\) (4a) | 6.5 ± 1.5                                      |
| 8     | Cp\(^*\)Mo\(_3\)S\(_4\) (4b) | 9.6 ± 2.7                                      |
| 9     | Cp\(^*\)Mo\(_3\)S\(_4\) (4c) | 12.9 ± 8.7                                      |

\(^*\)Yields were obtained from three independent experiments (n=3) and are shown as means ± s.d.
and subsequent silylation of the bound N2 to give clusters.

ν(N–N) in accordance with a weakened N–N bond (stretching frequency distance (1.193(7) Å) from that found in the N2-bound 3 cluster 20% yield (Fig. 2a,d and Supplementary Figs. 4, 9 and 13). The same to furnish a monosilylated N2 species ([CpXL2.3 equiv. KC8) was treated with 1.1 equiv. ClSiPh3 (where Ph is phenyl) in N2 reduction. To validate it, the in situ-generated that indicate the feasibility of the initial silylation of N2.

The irreversible chemical modification of the bound N2 molecule highlights a reactivity difference between our system and a N2-bridged [MoFe3S4] dimer reported recently. Treatment of [[Cp*MoFe3S4(IPr)]2(µ-N2)(CpL)] (IPr = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene) with [Cp3Ti] has been reported to give an equilibrium mixture of the [MoFe3S4]2(µ-N2) dimer and a heterometallic N2-bridged complex [[Cp*MoFe3S4(IPr)2(µ-N2)](Cp3Ti)] , but no further chemical conversions or catalytic reduction of the bound N2 was reported. The difference in reactivity between this N2-bridging system and the terminal bound N2 system reported herein points to the importance of a terminal Fe–N2 moiety for the successful reduction of N2. In addition, the isolation of a stable intermediate analogue by our [Mo3S4Fe] platform indicates its potential utility as a synthetic toolkit to investigate catalytic as well as stoichiometric activation of other small molecules.

reported for Fe complexes bearing [N2SiR3] ligands (Supplementary Table 6)22,29,30. Although the phenyl substituents on the Si atom of 3 differ from the methyl groups employed in the catalytic process, the isolation of 3 supports the possible generation of an Fe–NNSiMe3 analogue of 2c in the catalytic cycle. This assumption was further reinforced when 3 was used as the precursor for the successful catalytic silylation of N2, yielding 258.3 ± 6.1 equiv. of N(SiMe3)3 (Table 1, entry 6).

2a (1/2 equiv.) is omitted for readability. Carbon and oxygen atoms are drawn as capped sticks for clarity.

The initial silylation of the N2 ligand is arguably the most vital step in N2 reduction. To validate it, the in situ-generated 2c from 1c and 2.3 equiv. KC8 was treated with 1.1 equiv. C2SiPh3 (where Ph is phenyl) to furnish a monosilylated N2 species ([(CpXL2.3Mo3S4Fe(N2SiMe3)], 3) in 20% yield (Fig. 2a,d and Supplementary Figs. 4, 9 and 13). The same cluster 3 was alternatively generated from 2c and C2SiPh3 in C6D6 (Supplementary Fig. 5). The X-ray structure of 3 shows an elongated N–N distance (1.193(7) Å) from that found in the N2-bound 2c (1.136(5) Å), in accordance with a weakened N–N bond (stretching frequency $\nu_{N-N} = 1,706$ cm$^{-1}$). These values are close to those previously

on Fe is removed by SiMe3 to generate a vacant Fe site that binds N2. In the resultant Fe–N2 species, the more exposed distal N atom probably undergoes the first silylation to generate the Fe–NNSiMe3 species. Further silylation and reduction would dissociate a hydrazido anion [Me3SiN–N(SiMe3)2], as theoretically proposed for Mo- and Co-catalysed reactions26,28. Dissociation of the hydrazido anion can ably undergoes the first silylation to generate the Fe–NNSiMe3 species.

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Structural models of the N₂-bound clusters reveal that the Cp³ ligands surround the N₂ ligand and the [Mo₃S₄Fe] cores (Fig. 3). The –SiMe₃ and –SiEt₂ groups of the Cp³ ligands are forced into the space around the Fe sites of the [Mo₃S₄Fe] cubes (Fig. 3b,c) to minimize steric repulsion between the Cp³ ligands. Thus, the –SiR₃ groups efficiently offer steric protection of the [Fe–N₄] moiety and prevent dimerization of cubes through either an Fe–N₂–Fe bridge or an inter-cube Fe–S interaction. In contrast, the less bulky Cp³ ligands lead to a more exposed Fe site (Fig. 3a) and allow the approach of the Fe site of another [Mo₃S₄Fe] cube to give an Fe–N₂–Fe dimer. The bulkiness of the Cp³ ligands should affect the catalytic activities as well, as we suggest that the first N–Si bridging of the N₂ molecule. These results imply that suppression of intermolecular aggregation of M–S cores is a key to stabilizing a terminal N₂-bound species and maintaining the reactivity at the distal N atom of the bound N₂ molecule. In this sense, the steric protection given by the Cp³ ligands loosely mirrors the role of a protein matrix isolating metal centres to control reactivity and avoid undesirable decomposition. Although N₂ reduction to NH₃ or to N(SiMe₃)₃ should have substantial mechanistic differences, our results provide compelling clues that the N₂ molecule can become susceptible to reduction by Fe centres in S-rich environments, as is the case with FeMoco.

**Online content**

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Data availability

X-ray data are available free of charge from the Cambridge Crystallographic Data Centre under reference numbers CCDC 2079174–2079176 and 2141451. All other experimental, spectroscopic, crystallographic and computational data are included in the Supplementary Information.

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Author contributions

Y.O. designed the study. K.M., Y.M., R.H., M.K., K.U. and K.T. conducted the experiments. M.T. participated in the discussion. Y.O. and K.T. interpreted the data. R.E.C. analysed the single-crystal XRD data. W.M.C.S. collected and analysed the computational data. T.T. and Y.S. collected and analysed the Mössbauer spectra. S.K. and Y.N. conducted experiments for ammonia synthesis. Y.O. and K.T. wrote the manuscript with input from all authors.

Competing interests

The authors declare no competing interests.

Additional information

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