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A [2Fe-1S] Complex that Affords Access to Bimetallic and Higher Nuclearity Iron-Sulfur Clusters

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Abstract

Small, coordinatively unsaturated iron-sulfur clusters are conceived as building blocks for the diverse set of shapes for iron-sulfur clusters in biological and synthetic chemistry. Here, we describe a synthetic method for preparing [2Fe-1S] clusters containing two iron(II) ions, which are supported by a relatively unhindered β -diketiminato supporting ligand. The [2Fe-1S] cluster can be isolated in the presence of trimethylphosphine, and the compound with one PMe_3 on each iron(II) ion is crystallographically characterized. The PMe_3 ligands may be removed with $\text{B}(\text{C}_6\text{F}_5)_3$ to give a spectroscopically characterized species with solvent ligands. This species is a versatile synthon for [2Fe-2S], [4Fe-3S], and [10Fe-8S] clusters. Crystallographic characterization of the 10Fe cluster shows that it has all iron(II) ions, and the core has two [4Fe-4S] cubes that share a face in a novel arrangement. This cluster also has two iron sites that are coordinated to solvent donors, suggesting the potential for using this type of cluster for reactivity in the future.

Graphical Abstract

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Supporting Information. Synthetic, spectroscopic, and crystallographic details (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

Introduction

Iron-sulfur clusters are required by all forms of life, and their reactivity and interconversion is an area of active research.¹ In nature, the lability of iron-sulfur clusters is leveraged to modulate reactivity. In nitrogenase, for example, Fe–S bond cleavage has been proposed to expose unsaturated Fe sites in the iron-molybdenum cofactor (FeMoco) and thereby activate the cluster for substrate binding.² Cluster lability has also been observed in response to redox transformations of FeS clusters, as revealed in the O₂-tolerant hydrogenase, where the [4Fe-4S] active site is protected from oxidative degradation by a [4Fe-3S] cluster that is oxidized with Fe–S bond cleavage.³ Additionally, iron-sulfur cluster interconversions are essential in the biosynthesis of enzymatic cofactors. One interesting example is the biosynthesis of the FeMoco of nitrogenase, which proceeds through [2Fe-2S] clusters that combine to form a pair of [4Fe-4S] cubanes known as the K-cluster. The cubanes of the K-cluster are subsequently coupled to generate a [8Fe-9S-C] core that eventually matures into the FeMoco.⁴

Lability in synthetic iron-sulfur clusters is also well established. For example, [2Fe-2S] clusters can combine to form [4Fe-4S] cubanes with loss of thiolate,⁵ and [3Fe-4S] clusters react with iron(II) and thiolate to form [4Fe-4S] clusters.⁶ More elaborate transformations can give rise to higher nuclearity iron-sulfur clusters, including ones with structural similarities to the P-cluster and the FeMoco of nitrogenase.⁷ These synthetic clusters are important because they enable detailed investigations of cluster reactivity that may not be feasible in a complex protein environment, and they can also reveal fundamentally new chemical transformations.^{1b}

The simplest multimetallic iron sulfide is the [2Fe-1S] structure. This type of cluster has not yet been observed in natural systems, although it has been implicated as a product in the radical SAM enzyme biotin synthase, which installs the S atom of biotin using sulfur transfer from a [2Fe-2S] cluster near the substrate-binding [4Fe-4S] cubane.⁸ This S donation would give a [2Fe-1S] cluster (though it has not been observed in the enzyme). The synthesis and reactivity of [2Fe-1S] complexes may therefore be relevant to biological iron-sulfur clusters, in addition to uncovering new chemical reactivity. Synthetic [2Fe-1S] complexes have been reported at oxidation levels ranging from diiron(I) to diiron(III).⁹ Our group has prepared a three-coordinate diiron(II) sulfide complex that is supported by diketiminate ligands and reacts with N-donor ligands at the unsaturated iron centers.^{9a, 9d} This system can be reduced to the diiron(I) oxidation level^{9b} that is rare in iron sulfide complexes and is more reduced than known biological clusters. The Peters group has reported a diiron sulfide system with phosphine supporting ligands, which is isolable at the diiron(I), iron(I)/iron(II), and diiron(II) redox levels.^{9c} These precedents reveal some initial aspects of the electronic and geometric structures of [2Fe-1S] clusters, but the reactivity and cluster interconversions accessible at [2Fe-1S] species remain largely unexplored.

We reasoned that the use of a less bulky diketiminate supporting ligand might lead to a [2Fe-1S] complex in which the more accessible metal sites lead to enhanced reactivity, including the possibility for rearrangement to form higher nuclearity iron-sulfur clusters. Here, we report the synthesis of a four-coordinate [2Fe-1S] complex and its characterization by crystallography and spectroscopy. Abstraction of one donor ligand from each iron center is proposed to give highly reactive three-coordinate sites that undergo transformation into various iron-sulfur clusters, including a partially characterized [10Fe-8S] cluster. This investigation reveals some of the fundamental cluster transformations possible from a [2Fe-1S] complex, and suggests that unsaturated diiron sulfide species may be precursors to more complex iron-sulfur clusters in natural systems as well.

Results and Discussion

Reduction of the previously reported iron(II) dimer [L^{Me}FeCl]₂¹⁰ with 2 equiv of sodium naphthalenide in thawing THF, followed by the addition of 1 equiv of trimethylphosphine sulfide and 1 equiv of trimethylphosphine, forms one major species (**1**) as judged by ¹H NMR spectroscopy (Scheme 1). X-ray diffraction on a single crystal revealed **1** to have a [2Fe-1S] core in which two quasitetrahedral Fe sites ($\tau_4 = 0.77$)¹¹ are linked by a single bridging sulfide (Figure 1). The fourth coordination site at each metal is occupied by one PMe₃ ligand. In the solid state, **1** is *C*₂ symmetric, with a *C*₂ axis relating the Fe-diketiminate units but no planes of symmetry (angle between planes defined by P1-Fe1-S1/P2-Fe2-S1 = 45.4(5)°). In solution there are eight resonances in the proton NMR spectrum (see Figure S2), which indicates rapid rotation around the Fe-S bonds on the NMR time scale. The *ortho*-CH₃ substituents within the same arene fragment are chemically inequivalent, indicating that rotation about the diketiminate *N*-C_{aryl} bonds is slow on the NMR timescale (or absent), because the coordination sphere at each metal site is somewhat congested.

Previously reported [2Fe-1S] clusters range in oxidation level from diiron(III), including salen supported^{9e, 12} and imide-sulfide complexes,^{9f} to the more unusual diiron(I) oxidation level of which there are only two examples.^{9b, 9c} The Fe–S bond lengths in **1** (avg. 2.2176(7) Å) are similar to those in other four-coordinate ferrous [2Fe-1S] complexes in the literature (avg. 2.23(7) Å).^{9a, 9c, 9d, 13} The Fe–S bonds in **1** are ~0.01 Å shorter than those in a previously reported diketimate [2Fe-1S] complex (complex **2**),^{9a} and also shorter than those in a related complex in which the NH₃ ligands in **2** are replaced by a bridging hydrazine ligand (Fe–S = 2.256(1) Å).^{9d} We ascribe the shorter Fe–S bonds in **1** to the less bulky diketimate ligand used in the present study compared to those in **2** (see Figure 1 and Table 1). Compared to the Fe–S bonds in a related diiron(II) [2Fe-1S] complex reported by the Peters group (Figure 1, complex **3**),^{9c} the Fe–S bond lengths in **1** are longer by 0.1 Å. Additionally, the Fe-S-Fe bond angle in **1** is 138° while that in Peters' diiron sulfide is linear. The zero-field Mössbauer spectrum of solid **1** at 80 K (Figure 2) exhibits a single quadrupole doublet with an isomer shift of 0.70 mm/s that is characteristic of four-coordinate high-spin Fe²⁺ supported by nitrogen and sulfide ligands (typically 0.7-0.8 mm/s).^{9a, 14} The high-spin electronic structure of **1** is corroborated by the paramagnetically shifted proton NMR resonances and a solution magnetic moment of 3.8(2) B.M. at room temperature. This value is lower than the spin-only value of 6.9 B.M. expected for two uncoupled *S* = 2 ions, indicating antiferromagnetic coupling between the two high-spin iron(II) sites. The solution magnetic moment of **1** is similar to that of the four-coordinate high-spin iron(II) complex **2** (4.1(3) B.M.).^{9a}

We hypothesized that abstraction of PMe₃ ligands could afford a reactive low-coordinate iron sulfide for additional transformations. Accordingly, we found that addition of 2 equiv of the strong Lewis acid tris(pentafluorophenyl)borane in a THF/diethyl ether mixed solvent system gives a single major species (**4**) as judged by proton NMR spectroscopy. The new species **4** is very likely to have the same core structure, as it can be converted back to **1** quantitatively (>95% spectroscopic yield using ¹H NMR spectroscopy) upon the addition of 2.5 equiv of PMe₃ (Figure 3). In THF-*d*₈, the NMR spectrum of this new species has five resonances in an integration ratio indicative of a C_{2v}-symmetric diketimate ligand environment. The Mössbauer spectrum of a frozen solution of **4** in THF at 80 K reveals a single quadrupole doublet with parameters similar to those of **1**, but with a higher isomer shift (Figure 2). Harder ligands typically lead to higher isomer shifts,¹⁵ so the ~0.1 mm/s higher isomer shift in **4** is consistent with replacement of phosphine ligands with O donors in coordinated THF from the solvent. In conjunction with the high symmetry from NMR spectroscopy, these data suggest the coordination of two THF ligands to **4** to give equivalent Fe sites; however, our data do not rule out the possibility that **4** contains only one coordinated THF which is in rapid exchange between the two Fe centers in solution. Attempts to isolate solid samples of **4**, or solutions in solvents other than THF, led to decomposition to multiple unidentified species as judged by ¹H NMR spectroscopy (see SI Figures S6 and S7). The solution and solid-state instability of **4** prevents us from isolating it for X-ray diffraction and microanalysis.

Despite our inability to isolate solid samples, solutions of complex **4** can be generated *in situ* and used as a building block for additional iron sulfide products (Figure 4). Addition of 1/8

equiv of S₈ or 1 equiv of propylene sulfide yields the previously reported diiron(III) [2Fe-2S] complex¹⁶ in 71% or 75% spectroscopic yield, respectively. Compared to the literature synthesis, which proceeds from [L^{Me}FeCl]₂ in 85% spectroscopic yield, **4** is a useful building block for alternative syntheses of the diamond core [2Fe-2S]. Adding 1 equiv of sodium triethylborohydride to solutions of **4** at -78 °C forms a known diiron(II) hydride-sulfide complex (Figure 4)^{13a} in 71% yield as judged by ¹H NMR spectroscopy (Figure S8). Thus, **4** is a useful building block for other diiron clusters.

Interestingly, reduction of **4** leads to more complicated products. Addition of 2 equiv of the strong reductant KC₈ to a THF solution of **4** forms an unusual [4Fe-3S] cluster in 22% spectroscopic yield (Figure S9); the characterization of this [4Fe-3S] cluster was recently described elsewhere.¹⁷ Multiple other uncharacterized products are formed in this reaction, but despite the low yield this result demonstrates that the [2Fe-1S] cluster **4** can be converted to other iron-sulfur clusters, in reactions that apparently result from disproportionation of the core.

Another example of the ability of [2Fe-1S] cluster **4** to assemble into higher nuclearity clusters arises from its thermolysis in THF solution. Nearly one week is required to completely consume **4** at 80 °C, and this treatment results in a mixture of products (Figure S14). Crystallization from the resultant mixture at -40 °C reveals one product to be an unusual [10Fe-8S] cluster (**5**). Though the crystals were isolated in only 10% isolated yield, ¹H NMR spectroscopy of small-scale reactions indicates that **5** is present in ~90% spectroscopic yield in the crude reaction solution (Figures S14 and S15). Due to significant purification challenges (see SI for details), **5** has not been obtained in adequate purity for complete characterization. Sufficient quantities of **5** can, however, be obtained for assignment of its ¹H NMR spectrum (Figure S11) and verification of its identity by crystallography.

Figure 5 shows a view of the core of **5**, which has C_{2h} symmetry. The chemically equivalent diketimate ligands are related by a mirror plane bisecting the two THF oxygen atoms and the two central sulfide ligands. In addition, an axis of rotation orthogonal to this mirror plane passes through the two central Fe sites (Fe3 and Fe3* in Figure 5). The NMR spectrum of **5** shows 13 resonances with integrations that are consistent with equivalent diketimate environments and restricted C-N_{aryl} bond rotation (Figure S11).

The shape of the [10Fe-8S] cluster can be viewed as two [4Fe-4S] cubanes that share a 2Fe-2S face, and each cubane also shares another face with a [4Fe-4S] partial cubane. The iron atoms at the extremities of the [10Fe-8S] cluster (Fe1 and Fe5) are surrounded by two sulfides and one diketimate supporting ligand. Although several bridging modes between [4Fe-4S] cubanes are known, including edge-sharing, corner-sharing, and those linked by a bridging heteroatom,^{7a} we are aware of no literature Fe-S clusters with the cofacial arrangement of cubanes observed in the molecular structure of **5**. Holm has reported several high-nuclearity iron(II) clusters, including [8Fe-8S] clusters¹⁸ that contain two cubanes that share an edge, in addition to a [16Fe-16S] cluster comprised of four edge-sharing cubanes (Table 2).^{18a} Formally, all the iron centers in **5** have the iron(II) oxidation state, and consistent with this description the mean Fe-S bond distance in **5** (2.34(7) Å) is within error

of that in other large iron(II) clusters.¹⁸ The metrical parameters of **5** also agree well with the three other structurally characterized [4Fe²⁺-4S] cubanes (Table 2).^{18b, 19} Ohki and Tatsumi have reported a corner-sharing [8Fe-7S] cluster comprised of two cubanes linked by a sulfide ligand.^{7b} Although this cluster is more oxidized, formally containing Fe²⁺₅Fe³⁺₃, the Fe–S distances of this cluster are within error of those of the clusters in Table 2.

Several interesting structural features differentiate **5** from previous cubane-type iron-sulfur clusters. One is the highly distorted shape of each face-sharing cubane. The two most central Fe atoms (Fe3 and Fe3* in Figure 5) have coordination spheres that deviate significantly from tetrahedral toward seesaw geometries ($\tau_4 = 0.69^{11}$). These two central iron ions pucker inward toward one another, leading to a very short Fe-Fe distance of 2.446(1) Å. The remaining two Fe centers that constitute each cubane (Fe2 and Fe4) are likewise pulled toward one another, with a separation of 2.520(1) Å. These Fe-Fe distances are shorter than twice the covalent radius for high-spin iron,²⁰ and are within error of the average Fe–Fe single bond in the Cambridge Structural Database (2.6(1) Å; see SI Figure S21 and Table S1),²¹ which may be indicative of an Fe–Fe bond. Computations are needed to evaluate this hypothesis, but given the well-precedented challenges that iron-sulfur clusters pose in computational analyses,²² such an investigation will be the subject of an independent inquiry. Another unusual feature of **5** is that two of the ten Fe sites are supported by three sulfides and capped with a THF ligand. Four-coordinate iron(II) ions in highly reduced clusters are typically supported by more strongly donating ligands, such as NHCs, phosphines, and halides.²³ Ligand exchange is often observed in iron-sulfur clusters that do feature coordinated solvent molecules,²⁴ and we therefore evaluated the lability of the THF ligands in **5**. Accordingly, we grew single crystals of **5** from diethyl ether, which gave an X-ray crystal structure that indicates the same cluster shape, but with two Et₂O ligands in place of the two THF ligands (see SI Figures S19 and S20). The apparent exchange of solvent donors at these sites suggests that these sites could engage in small-molecule reactions, but such studies will await a synthetic route that yields pure material on a larger scale.

Conclusions

A new [2Fe-1S] complex, which has a smaller supporting ligand than in previous diiron sulfides, can be isolated through stabilization by trimethylphosphine supporting ligands. Removal of the phosphine gives a highly reactive building block that leads to a variety of iron-sulfur clusters. Particularly interesting is an unusual [10Fe-8S] cluster, which is all-iron(II) and features two iron centers that have bonds only to three sulfides and one solvent molecule. These results indicate that [2Fe-1S] complexes are useful synthons for elaboration into diverse iron-sulfur clusters.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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SYNOPSIS

A new [2Fe-1S] cluster leads to various cluster types, showing its ability to model intermediates in the assembly of biological and synthetic iron-sulfur clusters.

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Figure 1.

Crystal structures of **1** and two previously reported ferrous [2Fe-1S] clusters, complexes **2** and **3**.^{9a, 9c} Thermal ellipsoids are shown at 50% probability. Iron is shown in orange, sulfur in yellow, phosphorus in teal and boron in purple. Hydrogen atoms omitted for clarity except on the ammonia ligands of **2**, and aryl groups shown in wireframe. For selected metrical parameters, see Table 1.

Figure 2.

Zero-field Mössbauer spectra collected at 80 K of solid **1** and a frozen solution of **4**.

Parameters of **1**: $\delta = 0.70$ mm/s, $|E_Q| = 1.51$ mm/s. Parameters of **4**: $\delta = 0.83$ mm/s, $|E_Q| = 1.78$ mm/s.

Figure 3.

Phosphine abstraction from **1** forms **4** in >95% spectroscopic yield as determined by proton NMR spectroscopy. **1** is regenerated in >95% spectroscopic yield after addition of 2.5 equiv of trimethylphosphine.

Figure 4.

Preparation of iron sulfide complexes from [2Fe-1S] complex **4**. Spectroscopic yields are shown in parentheses.

Figure 5.

Thermal ellipsoid plots (50% probability) showing two views of the X-ray crystal structure of [10Fe-8S] (**5**). *N*-Aryl groups and protons are omitted for clarity. An analogous cluster with two diethyl ethers in place of the THF molecules is presented in the Supporting Information.

Scheme 1.
Synthesis of [2Fe-1S] (**1**).

Table 1.Metrical parameters of **1** and previously reported [2Fe-1S] complexes.

	[2Fe-1S] (1)	2^{9a}	3^{9c}
mean Fe–S (Å)	2.2176(7)	2.227(3)	2.079(3)
Fe–S–Fe (°)	138.37(3)	126.6(1)	180.0(3)
τ_4^{11}	0.77	0.78	0.77

Table 2.Comparison of select structural parameters of **5** with other iron(II)-sulfur clusters.

	mean Fe–S (Å)	mean Fe–Fe (Å)	Fe–O (Å)
[10Fe-8S] (5)	2.34(7)	2.6(1)	2.33
[8Fe-8S](NHC) ₆ ^{18b}	2.32(1)	2.69(1)	--
[8Fe-8S(PCy ₃) ₆] ^{18a}	2.33(2)	2.64(6)	--
[16Fe-16S(P ^t Bu ₃) ₈] ^{18a}	2.32(5)	2.7(1)	--
[8Fe-7S] ^{7b}	2.28(1)	2.82(1)	--
[4Fe-4S](NHC) ₄ ^{18b}	2.33(2)	2.68(1)	--
[4Fe-4S](CN) ₄ ^{19b}	2.33(2)	2.67(2)	--
<i>Av</i> ^a Fe protein ^{19a}	2.33	2.65(9)	--

^a *Azotobacter vinelandii*