Synthesis of [2Fe–2S] and [4Fe–4S] Clusters Having Terminal Amide Ligands from an Iron(II) Amide Complex

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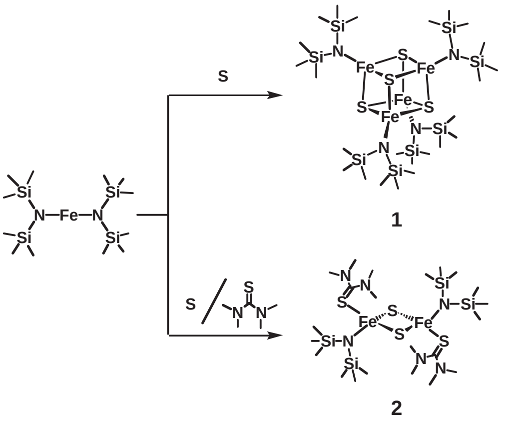
The reaction of iron(II) bis-amide Fe{N(SiMe$_3$)$_2$}$_2$ with elemental sulfur afforded a direct entry to new [Fe$_2$S$_2$] and [Fe$_4$S$_4$] clusters with terminal amide groups, Fe$_4$S$_4${N(SiMe$_3$)$_2$}$_4$ (**1**) and Fe$_2$S$_2${N(SiMe$_3$)$_2$}$_2$(tmtu)$_2$ (**2**), whose structures have been determined by X-ray crystallography. Tetrameric cubane cluster **1** exhibits one reversible and one quasireversible processes in the cyclic voltammetry, whereas dimeric rhombus complex **2** reveals one irreversible reduction process.

The extensive development of the chemistry of iron–sulfido cluster complexes has resulted in the isolation and detailed characterization of several structural types of complexes such as Fe$_2$S$_2$, Fe$_3$S$_4$, and Fe$_4$S$_4$, which are analogous to the redox sites in iron–sulfur proteins.[1] Despite the development of the chemistry of Fe$_2$S$_2$ and Fe$_4$S$_4$ clusters since these types were first synthesized in 1970's,[2] there has been only one Fe$_4$S$_4$ cluster having terminal amide groups on iron (unpublished),[3] and no Fe$_2$S$_2$–amide cluster. Recently we have demonstrated that the iron(II) bis-amide complex Fe{N(SiMe$_3$)$_2$}$_2$[4] serves as a suitable precursor for a Fe$_8$S$_7$ cluster in which core structure represents the P-cluster core of nitrogenases. It was synthesized from a self-assembly reaction using Fe{N(SiMe$_3$)$_2$}$_2$, thiols, elemental sulfur, and tetramethylthiourea (tmtu).[5] The successful isolation of metastable Fe$_8$S$_7$ cluster presumably relies on the property of amide group. The amide group promotes the solubility in nonpolar solvents and is readily replaced with thiolate by a proton-transfer reaction with thiols. In our attempts to develop synthetic routes to new iron–sulfido clusters, we have examined the reactions of Fe{N(SiMe$_3$)$_2$}$_2$ with elemental sulfur, and this reaction system has afforded direct entry to the ferric Fe$_2$S$_2$ and Fe$_4$S$_4$ clusters having terminal amide moiety. Herein we report the synthesis, structures, and redox properties of Fe$_2$S$_2$ and Fe$_4$S$_4$ amide clusters.

Treatment of iron(II) bis-amide Fe{N(SiMe$_3$)$_2$}$_2$ with one equiv. of elemental sulfur in toluene afforded a dark brown solution, from which an all-ferric Fe$_4$S$_4$ cluster Fe$_4$S$_4${N(SiMe$_3$)$_2$}$_4$ (**1**) was isolated in 31% yield as black crystals (Scheme 1). Cluster **1** is alternatively synthesized from the reaction of ferric amide complex (THF)FeCl{N(SiMe$_3$)$_2$}$_2$[6] with NaSH (in 86% yield as crystals in our case).[3] In contrast to the typical synthetic Fe$_4$S$_4$ clusters, cluster **1** is well soluble in nonpolar solvents such as hexane and toluene, and is very sensitive toward moisture. The stoichiometry of the reaction between Fe{N(SiMe$_3$)$_2$}$_2$ and elemental sulfur can be explained by concomitant formation of iron(III) tris-amide Fe{N(SiMe$_3$)$_2$}$_3$ which was evaporated as dark green liquid from the residue under vacuum at 130 °C.

The structure of **1** was determined by an X-ray diffraction study using single crystals obtained from hexane (Figure 1).[7]



Scheme 1.

Cluster **1** consists of a Fe$_4$S$_4$ core and four terminal amide ligands bound to iron. The Fe–Fe distances varying in the range of 2.8667(7)–3.0014(5) Å are significantly longer than those in the representative [Fe$_4$S$_4$(SR)$_4$]$^{2-}$ clusters (2.71–2.82 Å)[1] probably owing to the steric repulsion among the amide ligands. The geometry around amide nitrogen is planar, with variation of 356.2–360.0° for the angle around the nitrogen atom. This results in the strong π-donation to iron which electronically stabilizes the ferric centers in the Fe$_4$S$_4$ core. Indeed, the Fe–N dis-

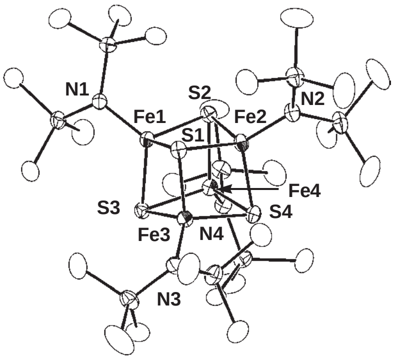


Figure 1. Molecular structure of Fe$_4$S$_4${N(SiMe$_3$)$_2$}$_4$ (**1**) with thermal ellipsoids at 50% probability level. Selected bond distances (Å): Fe1–Fe2 2.8724(7), Fe1–Fe3 2.9425(5), Fe1–Fe4 2.8831(5), Fe2–Fe3 2.8823(5), Fe2–Fe4 3.0014(5), Fe3–Fe4 2.8667(5), Fe1–S1 2.3124(8), Fe1–S2 2.2799(8), Fe1–S3 2.2967(7), Fe2–S1 2.2800(8), Fe2–S2 2.3096(8), Fe2–S4 2.3045(7), Fe3–S1 2.3032(7), Fe3–S3 2.2985(8), Fe3–S4 2.2728(7), Fe4–S2 2.3092(7), Fe4–S3 2.2543(8), Fe4–S4 2.3247(8), Fe1–N1 1.866(2), Fe2–N2 1.865(2), Fe3–N3 1.863(2), Fe4–N4 1.866(2).

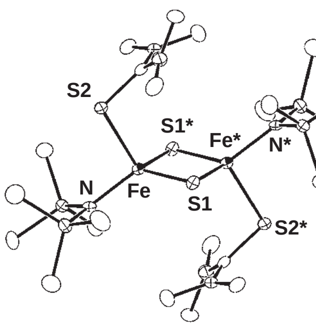


Figure 2. Molecular structure of $Fe_2S_2\{N(SiMe_3)_2\}_2(tmtu)_2$ (**2**) with thermal ellipsoids at 50% probability level. Selected bond distances (Å) and angles (°): Fe–Fe* 2.783(2), Fe–S1 2.212(2), Fe–S2 2.421(2), Fe–N 1.930(5), Fe–S1–Fe* 78.11(6), S1–Fe–S1* 101.89(6).

tances (1.863(2)–1.866(2) Å) are shorter than the other known terminal Fe^{II}–$N(SiMe_3)_2$ distances (1.88–1.98 Å).[8]

Whereas treatment of $Fe\{N(SiMe_3)_2\}_2$ with elemental sulfur led to the formation of a tetrameric cubane cluster **1**, similar reaction under the presence of tetramethylthiourea gave a ferric dimer $Fe_2S_2\{N(SiMe_3)_2\}_2(tmtu)_2$ (**2**), which can be crystallized from toluene and hexane in 33% yield. Thus in the reaction of $Fe\{N(SiMe_3)_2\}_2$ with elemental sulfur, redistribution of amide ligand occurs to give tris-amide $Fe\{N(SiMe_3)_2\}_3$ and transient "$Fe^{III}S\{N(SiMe_3)_2\}$" species in solution, the latter of which makes available the iron–sulfide–amide clusters of tetrameric $[Fe_4S_4]$ cubane **1** and $[Fe_2S_2]$ rhombus **2** as a result of association. Tetramethylthiourea coordinates to the dimeric $Fe_2S_2\{N(SiMe_3)_2\}_2$ intermediate, giving rise to **2**.

The dimeric nature of **2** was proven by a crystal structure determination (Figure 2).[7] The entire structure has centrosymmetry with a planar Fe_2S_2 core. The terminal amide and tmtu ligands on each iron atom are located anti with respect to the Fe_2S_2 plane to minimize the steric repulsion. Within the Fe_2S_2 core, the Fe–S–Fe angle is 78.11(6)°, which results in a shorter Fe–Fe distance of 2.783(2) Å than those in **1**. The Fe–tmtu distance of 2.421(2) Å is longer than that in the Fe_8S_7 cluster (2.3488(7) Å),[5] indicating that the coordination of tmtu is labile.

The redox properties of **1** and **2** have been examined by cyclic voltammetry (CV) in THF at room temperature. Cluster **1** exhibits one reversible and one quasireversible reduction processes at $E_{1/2} = -0.088$ and -1.22 V vs Cp_2Fe^+/Cp_2Fe, respectively, which are ascribed to one-electron reduction processes to the corresponding $[Fe_4S_4\{N(SiMe_3)_2\}_4]^-$ and $[Fe_4S_4\{N(SiMe_3)_2\}_4]^{2-}$ species. The CV spectrum of **1** suggests that the unusually high oxidation state in the $Fe^{III}{}_4S_4$ cluster is stabilized by the strong π donation from amide ligands, whereas the typical redox process for $[Fe_4S_4(SR)_4]^{n-}$ ($n = 2, 3$) clusters are between $Fe^{II}{}_2Fe^{III}{}_2$ and $Fe^{II}{}_3Fe^{III}$, and they can not be oxidized to the all-ferric form. Even in the $Fe^{III}{}_3Fe^{II}$ state, there has been only one isolated example to date.[9] Dinuclear complex **2** reveals one irreversible reduction process at $E_p = -1.13$ V vs Cp_2Fe^+/Cp_2Fe. Since the reduction potential is comparable to those for known $[Fe_2S_2(SR)_4]^{2-}$ complexes which generally afford a reversible reduction process with $E_{1/2}$ between -0.8 to -1.1 V vs SCE,[10] liberation of tmtu ligand following the reduction is a possible reason for irreversibility. It is notable that the dinuclear complexes with halides $[Fe_2S_2(X)_4]^{2-}$ (X = Cl, Br) also exhibit irreversible reduction peak in the CV spectrum due to the lability of halide ion.[11]

The ready availability of iron–sulfide–amide clusters from the reaction of iron–amide precursor with elemental sulfur may provide useful reaction system for the synthesis of yet larger iron–sulfur clusters.

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