Synthesis and Electronic Properties of Iron-Sulfur Clusters Relevant to Metalloenzymes

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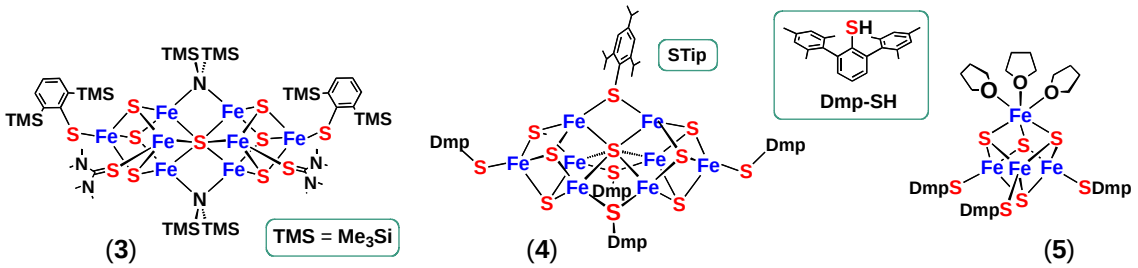
The iron-sulfur proteins in nature are represented by those consisting of [4Fe-4S], [3Fe-4S], and [2Fe-2S] clusters. In most of the cases, these clusters are thermodynamically stable, and the core geometries are constructed by spontaneous self-assembly reactions in polar aprotic solvents. We have recently found a new method to synthesize Fe/S clusters, which utilizes the bis-amide complex of iron, $Fe\{N(SiMe_3)_2\}_2$, as the precursor. This new route has allowed us to build Fe/S clusters in non-polar solvents, and resulted in a series of unprecedented cluster structures, some of which resemble closely the active sites of nitrogenase and hydrogenase.

For instance, the unusual [8Fe-7S] inorganic core structure of the reduced form of P-cluster (P^N) of nitrogenase was self-assembled by the reaction of $Fe\{N(SiMe_3)_2\}_2$, tetramethylthiourea (*tmtu*), 2, 4, 6-triiso-propylbenzenethiol(HS-tip), and S_8 in the ratio of 8(Fe):3(*tmtu*):12(HS-tip):7(S), which gave rise to $[\{N(TMS)_2\}\{SC(NMe_2)_2\}Fe_4S_3]_2(\mu_6\text{-}S)\{\mu\text{-}N(TMS)_2\}_2$ (TMS = $SiMe_3$)(**1**). Interestingly, the cluster **1** consists of irons with a 6Fe(II)+2Fe(III) oxidation state as manifested by the Mössbauer study, while P^N has been thought to carry 8 Fe(II) ions. Although cluster **1** degrades to a Fe_4S_4 cubane cluster under the presence of thiols, as the P-cluster does so, it was possible to isolate $(NEt_4)_2[\{N(TMS)_2\}(SAr)Fe_4S_3]_2(\mu_6\text{-}S)\{\mu\text{-}N(TMS)_2\}_2$ (**2**) (Ar = 4-^{t}Bu-C_6H_4, 2-$SiMe_3$-C_6H_4 etc.) and $[(SAr)\{SC(NMe_2)_2\}Fe_4S_3]_2(\mu_6\text{-}S)\{\mu\text{-}N(TMS)\}_2$ (Ar={2,6-$(SiMe_3)_2$-C_6H_4}) (**3**) from the reactions of **1** with corresponding thiolates and thiol. We have isolated yet another type of [8Fe-7S] cluster, $[(SDmp)Fe_4S_3]_2(\mu_6\text{-}S)(\mu\text{-}SDmp)_2(\mu\text{-}STip)\}$ (**4**), from the reaction of the preformed di-iron complex $[Fe(Stip)]_2(\mu\text{-}SDmp)_2$ with S_8, which is topologically analogous to FeMo-co of nitrogenase and has an intriguing 5Fe(II)+3Fe(III) oxidation state with a doublet ground state.

We have also synthesized an unusual [4Fe-4S] cluster, $Fe_4S_4(SDmp)_3(THF)_3$ (**5**) from $Fe_4S_4\{N(TMS)_2\}_4$ in toluene. Cluster **5** was further converted to $Fe_4S_4(SDmp)_3$-(Imd) (**6**) (Imd = tetramethyl imidazole), which serves as the first model of the histidine-bound unique [4Fe-4S] cluster found in hydrogenase.



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