Synthesis of Iron/Sulfur Clusters in Non-Polar Solvents
- Toward Better Clusters Modeling the Nitrogenase Active Sites -

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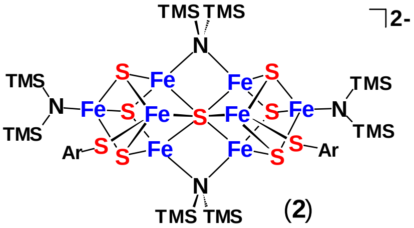
The iron sulfide proteins in nature are represented by those consisting of [4Fe-4S], [3Fe-4S], and [2Fe-2S] clusters. In most of the cases, these clusters are stable, and the core geometries are readily synthesized by spontaneous self-assembly reactions in polar aprotic solvents. We have recently found a new methodology to construct Fe sulfide 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 iron/sulfide clusters in non-polar solvents, and resulted in a series of unprecedented cluster structures, some of which resemble closely the active sites of nitrogenases.

The unusual [8Fe-7S] inorganic core structure of the reduced form of P-cluster (P^N) was self-assembled by the reaction of $Fe\{N(SiMe_3)_2\}_2$, tetramethylthiourea (*tmtu*), 2, 4, 6-triisopropylbenzenethiol(HS-tip), and elemental sulfur in the ratio of 8(Fe):3(*tmtu*):12(HS-tip):7(S). Interestingly the complex $[\{N(SiMe_3)_2\}\{SC(NMe_2)_2\}Fe_4S_3]_2(\mu_6\text{-}S)\{\mu\text{-}N(SiMe_3)\}_2$ (**1**), obtained therefrom, 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 synthesize $(NEt_4)_2[\{N(SiMe_3)_2\}(SAr)Fe_4S_3]_2(\mu_6\text{-}S)\{\mu\text{-}N(SiMe_3)\}_2$ (**2**) (Ar = 4-^{t}Bu-C_6H_4, 2-$SiMe_3$-C_6H_4 etc.) from the reactions of **1** with corresponding ammonium salts of thiolates. We have also isolated $[(S\text{-}dmp)Fe_4S_3]_2(\mu_6\text{-}S)(\mu\text{-}S\text{-}dmp)_2\{\mu\text{-}N(SiMe_3)\}$ (**3**) from the reaction of $Fe\{N(SiMe_3)_2\}_2$, HS-dmp, HS-tip, and elemental sulfur (8:6:10:7), which is topologically analogous to FeMo-co and has an intriguing 5Fe(II)+3Fe(III) oxidation state.



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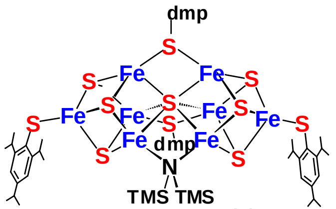

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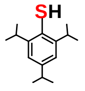
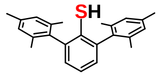


tip-SH



dmp-SH

TMS = Me_3Si