Model studies for a possible new role of iron sulfur enzymes: the reaction of [2Fe2S] clusters with C-centered radicals

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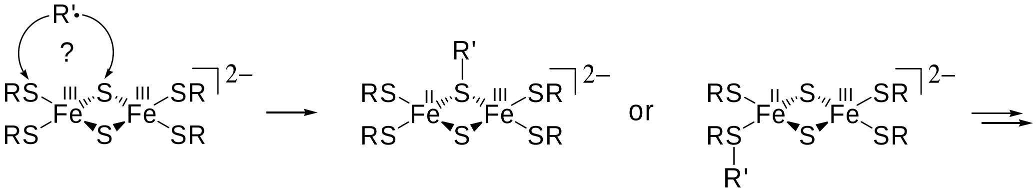
Iron-sulfur cofactors are ubiquitous in biological systems and have been of prime importance in nature since the beginning of terrestrial life. A prominent member of this class is biotin synthase, which catalyzes sulfur insertion in dethiobiotin, i.e. the final step in the biotin biosynthesis. Spectroscopic and crystallographic evidence points to the presence of distinct [4Fe4S] and [2Fe2S] clusters in the biotin synthase enzyme and suggests that the latter supplies the sulfur atom for the biotin tetrahydrothiophene ring.[1]

The investigation of synthetic model complexes provides valuable insight into the properties and function of biological iron-sulfur sites.[2] The present work now concerns the proposed role of the [2Fe2S] cluster in biotin synthase. First results on the model reaction of C-centered radicals with synthetic $[Fe_2S_2(SR)_4]^{2-}$ complexes are reported, and are complemented by DFT calculations.[3] Some new (and particularly stable) [2Fe2S] complexes have been developed during the course of these studies.



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