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A DFT Investigation on Structural and Redox Properties of a synthetic Fe_6S_6 assembly closely related to [FeFe]-hydrogenases active site

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Abstract:

In the present contribution, a Density Functional Theory (DFT) investigation is described regarding a recently synthesized Fe_6S_6 complex [Pickett et al., Nature 433 (2005) 610] that is structurally and functionally related to the [FeFe]-hydrogenases active site (the so called H-cluster, which include a binuclear subsite directly involved in catalysis, and a Fe_4S_4 cubane). The analysis of relative stabilities and atomic charges of different isomers evidenced that the structural and redox properties of the synthetic assembly are significantly different from those of the enzyme active site. This observation is possibly correlated with the reduced catalytic efficiency of the biomimetic assembly. A comparison between the hexanuclear cluster and simpler synthetic diiron models is also described; the results indicates that the cubane moiety can favour the stabilization of the cluster in a structure closely resembling the H-cluster geometry when the synthetic Fe_6S_6 complex is in its dianionic state. However, the opposite effect is observed when the synthetic cluster is in its monoanionic form.

1. Introduction

[FeFe]-hydrogenases are enzymes that are able to catalyze the reversible oxidation of molecular hydrogen: $H_2 \leftrightarrows 2H^+ + 2e^-$. Such a very simple reaction could have fundamental importance for the possible future development of a hydrogen-based economy [1]. However, the current approaches for molecular hydrogen oxidation imply the use of expensive platinum-containing catalysts, while H_2 production at industrial level still depends on hydrocarbons. In this framework, [FeFe]-hydrogenases represent a promising model for the development of new-generation catalysts; in fact, these iron-containing enzymes are generally very efficient in H_2 production, and they are able to evolve molecular hydrogen directly from acidic aqueous solutions supplied with a convenient source of electrons [2].

The [FeFe]-hydrogenase active site is generally referred to as the "H-cluster" (see Figure 1); this is a peculiar Fe_6S_6 cluster which can be subdivided in two distinct portions: a classical Fe_4S_4 moiety, and a Fe_2S_2 subcluster (commonly termed "$[2Fe]_H$") bearing CO and CN^- ligands [3]; these subclusters are linked to each other through the sulphur atom of a cysteine residue. The two iron atoms of the binuclear sub-site are termed "proximal" (Fe_p) or "distal" (Fe_d), depending on their positions with respect to the Fe_4S_4 moiety. Notably, one of the carbonyl groups included in the $[2Fe]_H$ subsite bridges the Fe_p and Fe_d centers, and it moves to a semibridging position when the enzyme is in its completely reduced form. The coordination environment of the iron ions in the binuclear cluster is completed by a bidentate ligand that has been proposed to correspond either to a di(thiomethyl)amine (DTMA) or to a propanedithiolate (PDT) residue [3b,4].

Different redox states of the $[2Fe]_H$ cluster have been characterized spectroscopically [5]. The fully oxidized and fully reduced forms of the enzyme are EPR silent and have been proposed to correspond, on the basis of similarities between the FT-IR spectra of the enzyme and of model compounds, to Fe(II)Fe(II) and Fe(I)Fe(I) species, respectively. The partially oxidized form is paramagnetic and should correspond to the Fe(I)Fe(II) redox state [6]. Moreover, spectroscopic

studies of [FeFe]-hydrogenases are consistent with a [2Fe(II)2Fe(III)] oxidation state for Fe_4S_4

moiety of the H-cluster, both in the oxidized and reduced forms of the enzyme [xxx].
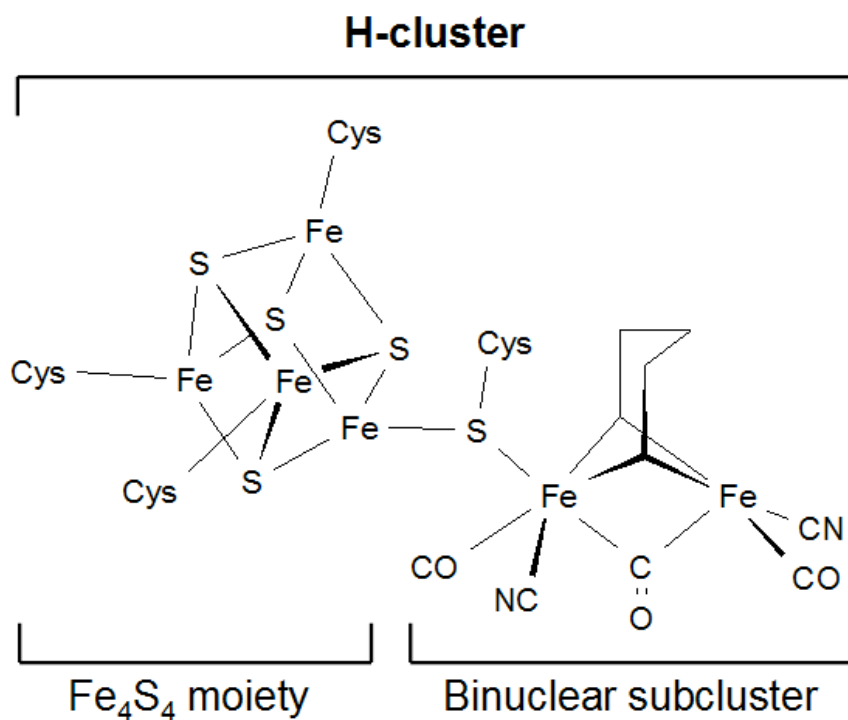
Figure 1: Schematic structure of the H-cluster

As for the catalytic mechanism of [FeFe]-hydrogenases, the most plausible picture [4b-d,7] involves

binding of a proton to the Fe(I)Fe(I) $[2Fe]_H$ subsite, which would lead to the formation of a Fe_d-

bound terminal hydride ligand; a second protonation reaction and two mono-electron reduction

steps would then precede H_2 evolution, thus closing the catalytic cycle (Figure 2). Alternative

mechanisms have been proposed, involving the formation of a μ-H ligand [8]; however, recent

works [7,9] reported evidences that a terminal hydride group – which can be formed also by

protonation of biomimetic assemblies [10]– is more reactive then a hydride ligand in bridging

position between Fe_p and Fe_d.
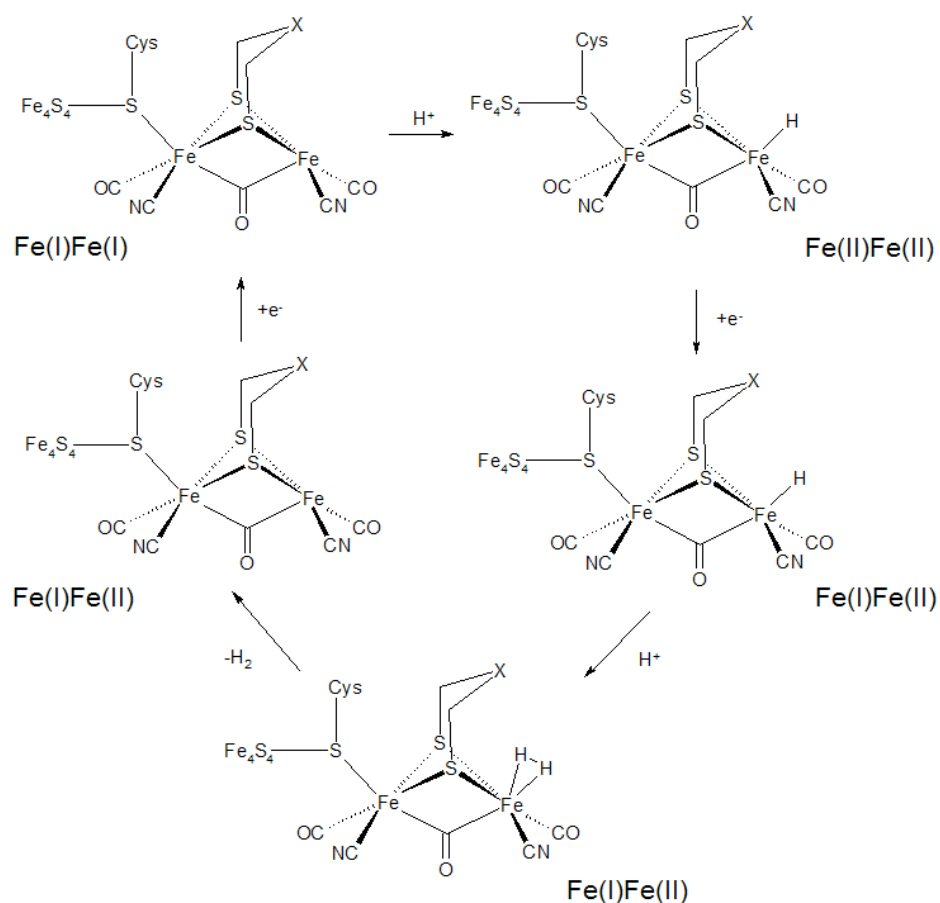
Figure 2. A plausible catalytic mechanism for molecular hydrogen evolution in [FeFe]-hydrogenases

The apparent structural simplicity of the Fe_2S_2 site has stimulated several research groups towards the synthesis of biomimetic diiron clusters that could reproduce the geometric and functional features of the $[2Fe]_H$ moiety [11]; however, the reproduction of the μ-CO structure (the so called "rotated" conformation, see Figure 3) typical of the $[2Fe]_H$ subsite has not been achieved until recently [12]; in fact, most synthetic biomimetic assemblies are characterized by an all-terminal disposition of ligands (i.e. they show an "eclipsed" conformation, see Figure 3).

Figure 3. Structure of the [FeFe]-hydrogenase binuclear subsite, and geometry of the synthetic complex $(\mu\text{-pdt})[Fe(CN)(CO)_2]_2^{2-}$ [13]

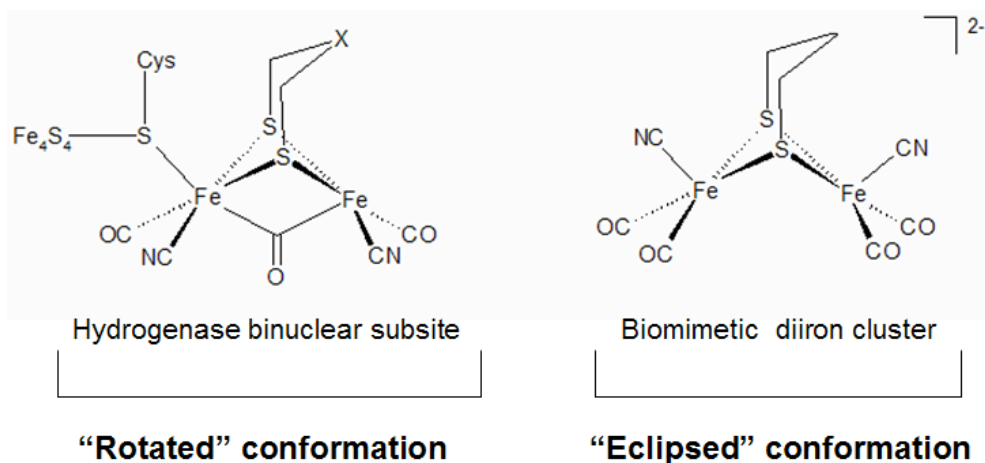Another challenge in this research area is the reconstitution of the whole Fe_6S_6 framework in a synthetic complex; such a goal has been recently achieved by Pickett and coworkers [14], who obtained and characterized the complex $[Fe_4S_4(L)_3\{Fe_2(CH_3C(CH_2S)_3)(CO)_5\}]^{2-}$ (L= 1,3,5-tris (4,6-dimethyl-3-mercaptophenylthio)-2,4,6-tris-(p-tolyl-thio)benzene; see Figure 4). In variance to the H-cluster in [FeFe]-hydrogenases, the binuclear portion of this organometallic complex does not include cyanide ligands. In fact, the only diatomic ligands included are CO groups, which are disposed in an eclipsed conformation around the iron centers of the binuclear subsite. As far as the interaction between the biomimetic complex and protons is concerned, the eclipsed disposition of CO ligands is expected to favour the formation of slowly reacting μ-H adducts; in fact, the biomimetic Fe_6S_6 complex is able to electrocatalyze H^+ reduction, but it is significantly less efficient then the enzyme in favouring H_2 evolution from protons and electrons. A conformational rearrangement of the Fe_6S_6 cluster towards the rotated geometry is expected to facilitate the formation of highly reactive terminal hydride groups, but there are no experimental evidences of the formation of rotated adducts during the electrocatalytic process.
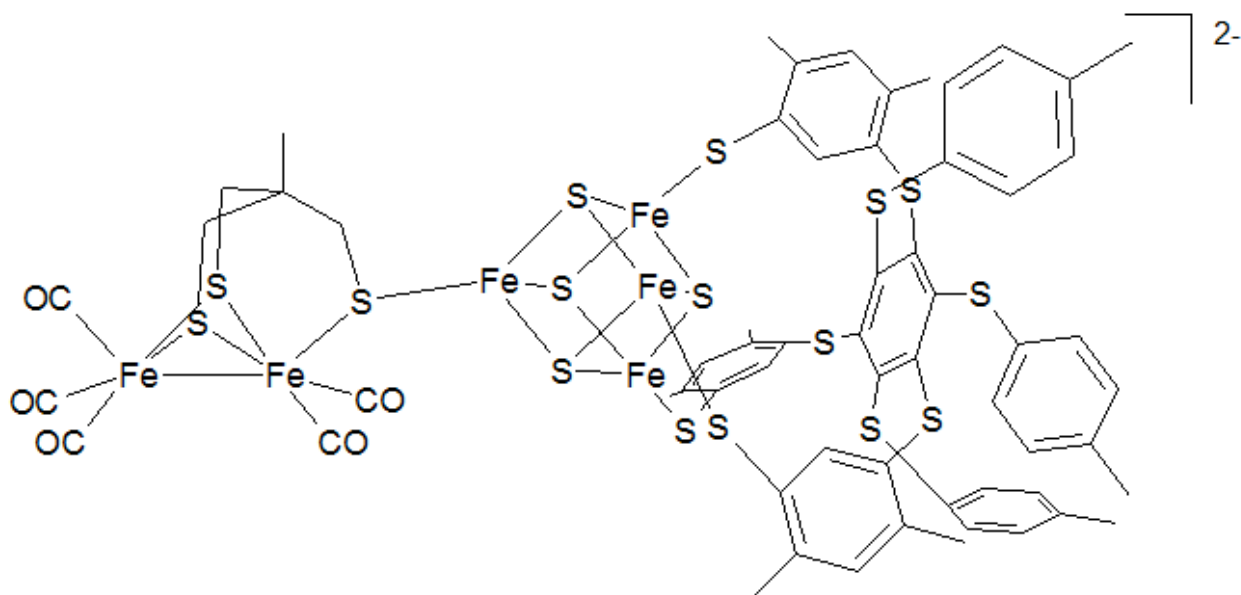
Figure 4. Schematic structure of the biomimetic Fe_6S_6 complex recently synthesized by Pickett and coworkers [14]

Prompted by these observations, we have performed a Density Functional Theory (DFT) investigation of the structural properties of the biomimetic Fe_6S_6 assembly in two different redox states: the dianionic state, in which the pentacarbonyl binuclear subcluster should attain the Fe(I)Fe(I) state, and the monoanionic form, which should represent a model of the partially oxidized H-cluster. For these two states, both the rotated and the eclipsed conformations were optimized, in order to evaluate the relative stabilities of the isomers, and the effects that mono-electron oxidation can have in terms of ligands redisposition around the metal centers of the binuclear subsite. Comparisons between the binuclear subcluster in the biomimetic Fe_6S_6 assembly and simpler synthetic diiron models like $Fe_2CO_6(\mu\text{-PDT})$ and $Fe_2(CO)_6(S_2C_6H_4)$ are also discussed, in order to give further insights into the effects of the introduction of a cubane moiety in a biomimetic assembly.

2. Methods.

DFT calculations were carried out using the pure functional BP86 [15] and a valence triple-ζ basis set with polarization on all atoms (TZVP) [16]. Calculations were run with the TURBOMOLE 5.7 suite [17] applying the resolution-of-the-identity technique [18].

Stationary points of the energy hypersurface were located by means of energy gradient techniques. The effect of the solvent (acetonitrile, $\varepsilon = 36.64$, which was the solvent used in the experimental investigation []14) was evaluated according to the COSMO approach [19]. For all models, geometry optimizations were also carried out in a vacuum, but if not otherwise stated the discussion is based on the COSMO results. Theoretical investigations of the models of the H-cluster are a non-trivial task because the Fe_4S_4 subunit is composed by two Fe_2S_2 layers with high-spin (HS) Fe atoms coupled antiferromagnetically to give an overall low-spin ground state. The ground-state wavefunction of such spin-coupled systems corresponds to a linear combination of determinants that would require a multi-configurational treatment, not possible within the DFT scheme. However, in the single determinant approximation, the antiferromagnetic interactions can be modeled according to the broken symmetry (BS) approach, introduced by Noodleman [20,21]. The BS approach consists in the localisation of opposite spins of the mono-determinant wave function in different parts of the molecule.

As noted by Brunold [22], the Fe atoms of Fe_4S_4 are not equivalent in the H-cluster, and therefore six different BS configurations can be generated for each species. However, we only considered one of the six possible BS wave function variants. In fact, previous theoretical studies have indicated that the structural differences among H-cluster models characterized by different BS configurations are very small [4d]; moreover, the computed relative stabilities never differ by more than 10 kJ/mol, when rotated and eclipsed models of the partially oxidized and reduced forms of the enzyme with different BS configurations are concerned [4d].

Geometry optimization were performed on models of the synthetic Fe_6S_6 assembly in which the bulky L ligands coordinated to the cubane irons (see the Introduction section) were replaced by CH_3S^- groups. Thus, the Fe_6S_6 models here discussed are complexes of general formula $[Fe_4S_4(SCH_3)_3\{Fe_2(CH_3C(CH_2S)_3)(CO)_5\}]^{n-}$, where n = 1 or 2.

The overall charges of the cubane moiety was calculated from the Mulliken atomic charges of the $Fe_4S_4(SCH_3)_3$ portion of the model. The rest of the charge was assigned to the Fe_2S_2 subsite.

3. Results and Discussion

Before discussing the results of our work, we define the nomenclature that will be used in this paper. All the models of the synthetic Fe_6S_6 cluster have the "$\mathbf{Fe_6S_6}$" tag in their names, in square brackets. The presence of a bridging carbonyl ligand in the eclipsed conformers is evidenced by a subscript "$\mathbf{b}$", whereas eclipsed models with only terminal ligands are marked with a subscript "$\mathbf{t}$"

subscript is present in their names. The charge of the Fe_6S_6 complex is also always included as a superscript.

3.1. DFT characterization of dianionic model compounds

In a previous study [14], the structure of the eclipsed, dianionic form of the synthetic Fe_6S_6 assembly $\mathbf{[Fe_6S_6]_t^{2-}}$ was obtained. The distance between iron atoms in the binuclear subcluster (2.6 Å) is indicates the presence of a Fe-Fe bond. Moreover, the authors concluded that the redox state of the binuclear subcluster is Fe(I)Fe(I), thus implying that the cubane moiety attains the [2Fe(II)2Fe(III)] state.

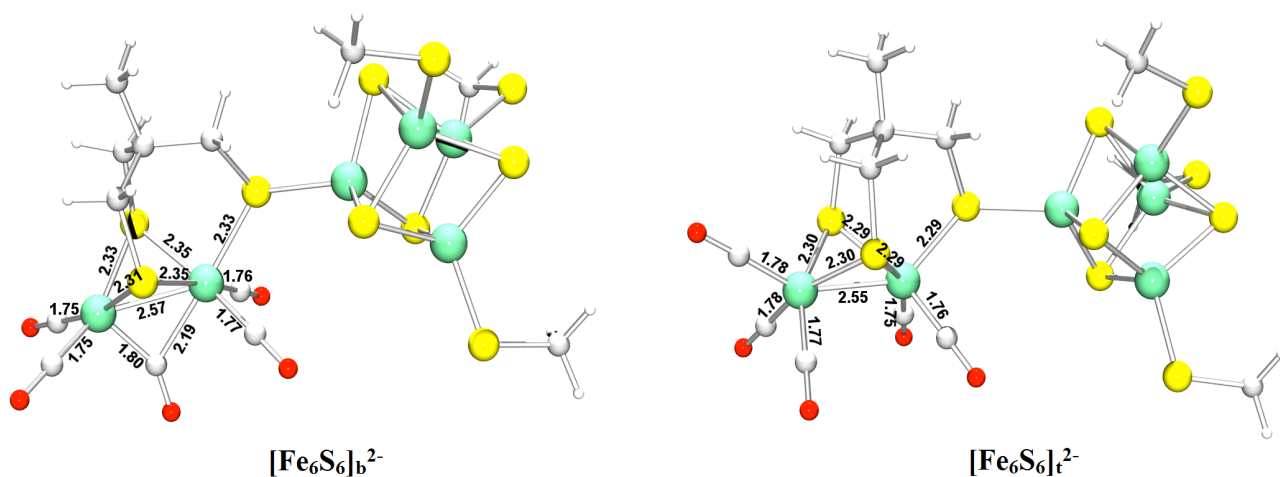**Figure 5.** Optimized geometries of model complexes $\mathbf{[Fe_6S_6]_b^{2-}}$ and $\mathbf{[Fe_6S_6]_t^{2-}}$. Selected distances are given in Å

In the present contribution, we carried out the geometry optimization of both the eclipsed and the rotated conformation of the dianionic hexanuclear cluster; a comparison between the two isomers is presented, in terms of their structural properties, spin density values and relative stabilities.

Model $\mathbf{[Fe_6S_6]_t^{2-}}$, when optimized in a polarizable continuum medium at $\varepsilon = 36.64$, shows a Fe_p-Fe_d distance of 2.55 Å. The spin density on the Fe_p and Fe_d atomsis negligible (-0.03 and -0.01, respectively), and the overall charges of the Fe_2S_2 and Fe_4S_4 subsites are -0.56 and -1.44, respectively; these observations are compatible with a Fe(I)Fe(I) redox state for the diiron

subcluster.

The bridging CO ligand binds asymmetric, with the Fe_p-C and Fe_d-C distances of 2.19 Å and 1.80 Å, respectively. In the crystal structure of the reduced enzyme, the binding is even more asymmetric, with Fe-C distances of 2.56 Å and 1.69 Å [4a]. However, previous DFT results showed that the energy landscape associated with the movement of the semibridging CO is very flat [4d].

Further insight regarding the chemistry of the synthetic hexanuclear cluster is obtained by the study of rotated conformer $[Fe_6S_6]_b^{2-}$ (see Figure 5). In $[Fe_6S_6]_b^{2-}$, the Fe_p-Fe_d bond distance (2.57 Å) is only slightly larger than that in $[Fe_6S_6]_t^{2-}$. Such a Fe-Fe distance reproduce the Fe_p-Fe_d bond length in the reduced enzyme (2.55-2.61 Å) [4a] well. The Fe_p and Fe_d spin densities are still close to zero (-0.02 and -0.01, respectively). The total energies indicate that the μ-CO adduct ($[Fe_6S_6]_b^{2-}$) is 11 kJ mol^{-1} less stable than the eclipsed conformer ($[Fe_6S_6]_t^{2-}$) by (7 kJ/mol in a vacuum). Interestingly, this energy difference is significantly smaller than for the Fe(I)Fe(I) form of the hexacarbonyl diiron complex $Fe_2(CO)_6$(μ-PDT), for which the energy difference is 34 kJ/mol (in vacuum) [23].If one considers that the difference between the first coordination spheres of $Fe_2(CO)_6$(μ-PDT) and of the binuclear subcluster in the synthetic Fe_6S_6 adduct is limited to the substitution of a CO group with a cubane moiety, one can argue that a Fe_4S_4 assembly in its [2Fe(II)2Fe(III)] is better than a carbonyl ligand to stabilize the rotated form of the binuclear cluster.

3.2. DFT characterization of monoanionic model compounds.

In a recent paper, Lichtenberger and coworkers noted that the one-electron oxidation of the hexacarbonyl Fe(I)Fe(I) diiron complex $Fe_2(CO)_6(S_2C_6H_4)$ facilitates the rotation of CO groups bound around one of the iron centers, thus leading to the stabilization of the rotated conformer with respect to the corresponding eclipsed isomer [24]. Such a structural reorganization is expected to be correlated with the desymmetrization of the cluster in terms of redox states of the iron centers, one of which formally becomes divalent after the mono-electron oxidation of the Fe(I)Fe(I) adduct. This

observation prompted us to investigate the structural and redox properties of the monoanionic hexanuclear compounds $[Fe_6S_6]_b^{1-}$ and $[Fe_6S_6]_t^{1-}$ (see Figure 6).

First of all, let us discuss the main features of the rotated adduct $[Fe_6S_6]_b^{1-}$. The Fe_p and Fe_d spin densities (-0.01 and -0.02, respectively) clearly show that the unpaired electron of this open-shell species does not reside in the binuclear subcluster. This suggests that the oxidation exclusively involves the Fe_4S_4 subcluster. This conclusion is also supported by the computed charge of the Fe_4S_4 moiety, which is -1.44, i.e. 0.80 e lower than for $[Fe_6S_6]_b^{2-}$.

This indicates that the redox state of the iron centers in $[Fe_6S_6]_b^{1-}$ is Fe(I)Fe(I)-[3Fe(III)Fe(II)]. Notably, the [3Fe(III)Fe(II)] state has never been observed **xxx experimentally or theoretically** in the cubane moiety of the enzyme active site, which normally maintains the [2Fe(III)2Fe(II)] state [xxx]. The fact that the binuclear subcluster in $[Fe_6S_6]_b^{1-}$ remains in the Fe(I)Fe(I) redox state has relevant bearings on the structural features of the diiron subsite, the geometry of which preserves most of the features that characterize the diiron subsite in $[Fe_6S_6]_b^{2-}$. In particular, the Fe_p-Fe_d distance is still as large as 2.57 Å, and the μ-CO group asymmetrically bridges Fe_p and Fe_d (the Fe_p-C(μ-CO) and Fe_d-C(μ-CO) distances are 1.80 Å and 2.23 Å, respectively).
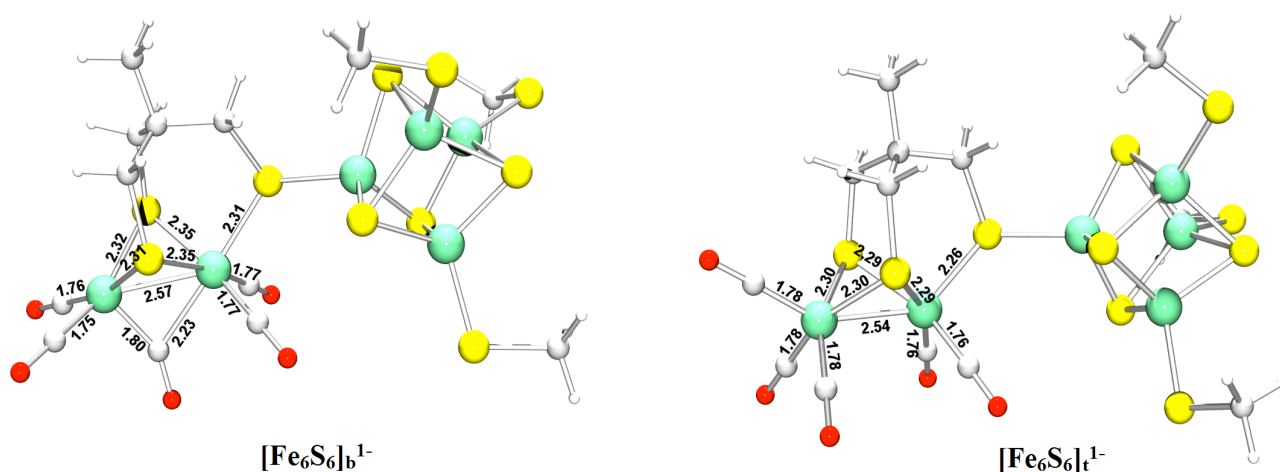

$[Fe_6S_6]_b^{1-}$ $[Fe_6S_6]_t^{1-}$

Figure 6. Optimized geometries of model complexes $[Fe_6S_6]_b^{1-}$ and $[Fe_6S_6]_t^{1-}$. Selected distances are given in Å

Next, we evaluated the possibility that the oxidation of the hexanuclear dianionic cluster could lead to a stabilization of its rotated conformation, analogously to what has recently been proposed for the diiron synthetic assembly $Fe_2(CO)_6(S_2C_6H_4)$ [24]. To this end, the $[Fe_6S_6]_t^{1-}$ structure was optimized (see Figure 6). It turned out that $[Fe_6S_6]_b^{1-}$ is 17 kJ/mol less stable than $[Fe_6S_6]_t^{1-}$, an energy difference which surprisingly is larger then the corresponding stability difference for the dianionic compounds (11 kJ/mol, see Section 3.1). In other words, the inclusion of the cubane moiety in the synthetic cluster disfavours the rotation of the ligands around Fe_d upon one-electron oxidation of the H-cluster.

Finally, the unpaired electron in $[Fe_6S_6]_t^{1-}$ still resides in the cubane moiety, as witnessed by Fe_p and Fe_d spin densities, which still are small (-0.02 and -0.01, respectively). This observation, together with the computation of the overall charge of the cubane subcluster in $[Fe_6S_6]_t^{2-}$ and $[Fe_6S_6]_t^{1-}$ (-1.47 and -0.74, respectively), clearly show that the one-electron oxidation leading to the monoanionic eclipsed derivative does not involve the binuclear subcluster, similarly to the case of the rotated conformer.

4. Conclusions

In the present contribution, an investigation was presented regarding computational models of a recently synthesized Fe_6S_6 complex structurally related to [FeFe]-hydrogenases active site. All the DFT models share the same atomic composition, but differ in terms of charge and ligands disposition around the metal centers of their binuclear subsite (their general formula is $[Fe_4S_4(SCH_3)_3\{Fe_2(CH_3C(CH_2S)_3)(CO)_5\}]^{n-}$, where n = 1 or 2).

Two main issues were investigated for each redox state of the complex: (i) the relative stabilities of the rotated and eclipsed conformations, and (ii) the redox state of the iron centers in the Fe_2S_2 and Fe_4S_4 subsites.

The results can be summarized as follows: the dianionic complex shows a Fe(I)Fe(I)-[2Fe(II)2Fe(III)] redox state, both in its rotated and eclipsed conformation. However, the rotated

conformation turned out to be slightly less stable then the eclipsed adduct (ΔE=11 kJ mol^{-1} and 7 kJ mol^{-1} at ε=36.64 and 1, respectively). The energy difference for the corresponding rearrangement in the Fe(I)Fe(I) binuclear complex Fe$_2$(CO)$_6$(μ-PDT) is much larger (34 kJ mol^{-1}, considering models optimized in a vacuum), indicating that a cubane moiety in trans position with respect to the CO bridging Fe$_p$ and Fe$_d$ can favor the rotation of ligands on the distal iron atom.

As far as one-electron oxidation of the dianionic complex is concerned, computation of spin density values and atomic charges clearly indicates that the Fe$_4$S$_4$ moiety is directly involved in the redox step, while the binuclear subcluster maintains a Fe(I)Fe(I) redox state.

It is known that a one-electron oxidation of simple Fe(I)Fe(I) models of [FeFe]-hydrogenases binuclear subsite can lead the rotated geometry to be more stable than the corresponding eclipsed adduct [24]. However, such a stabilization of the rotated isomer was not observed in the monoanionic Fe$_6$S$_6$ synthetic model, probably because the binuclear subsite remains in its Fe(I)Fe(I) redox state after a one-electron oxidation of the dianionic, Fe(I)Fe(I)-[2Fe(II)2Fe(III)] assembly. This point represents a major difference between the synthetic assembly and the enzyme active site; in fact, the completely reduced H-cluster attains the Fe(I)Fe(I)-[2Fe(II)2Fe(III)] state, but its binuclear subsite switches to the Fe(I)Fe(II) state upon partial oxidation of the enzyme. Future studies will be devoted to the elucidation of the structural and electronic determinants underlying the difference in redox properties between the H-cluster and the biomimetic Fe$_6$S$_6$ model.

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