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N_2 activation by iron–sulfur complexes

A theoretical contribution

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Abstract. Inspired by the determination of the structure of the nitrogenase enzyme cofactor by Rees et al., the binding of an N_2 molecule to some model iron–sulfur compounds was investigated using *ab initio* calculations. Side-on and end-on coordination to one two and four iron centers were investigated. In most cases, the N_2 is loosely bound and retains its internal triple bond, but a few examples are found where the N_2 is "activated" and has a longer N–N bond length.

Key words: N_2 activation – Nitrogenase

1 Introduction

The reduction of molecular nitrogen to ammonia occurs under ambient temperature and atmospheric pressure catalyzed by an enzyme known as nitrogenase. This enzyme consists of two proteins, the molybdenum–iron protein and the iron protein. However, some nitrogenases were isolated containing exclusively iron or substituting vanadium for molybdenum. For a historical review, see Refs. [1–10] and references therein.

The molybdenum–iron protein contains the molybdenum iron cofactor (MoFeco), a complex consisting of iron, molybdenum, and sulfur, that is recognized as the active site where bonding, activation and reduction of the N_2 molecule occur [5, 11]. Due to the importance of the active center, the search for synthetic compounds containing the essential components of the cofactor was stimulated, and based on this research, several models of the cofactor have been proposed [3, 12, 13].

Recently, the X-ray crystal structure analysis of the molybdenum–iron protein allowed for a new perspective to be taken on the structure of the MoFeco. This was

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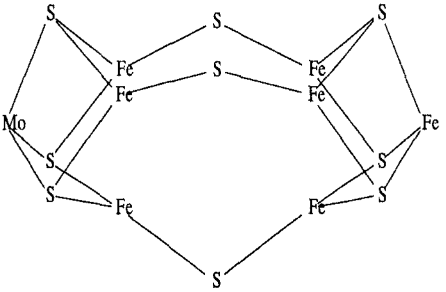

Fig. 1. Core of molybdenum iron cofactor

determined by Rees et al. (with 2.7, 2.2 and 3.0 Å resolution) [14–17], and from these a new model was proposed for the cofactor structure. It consists of two cubane clusters consisting of 4Fe : 3S and 1Mo : 3Fe : 3S which are linked by two S^{2-} and a third ligand "Y". This Y ligand has a lower electronic density than the two S^{2-} and was considered to be a nitrogen, oxygen or a less ordered sulfur. However, more recently it was referred to as another sulfur atom [18]. See Fig. 1. It should be emphasized that this is the "resting" state of the enzyme and the activated form may differ somewhat from this.

Based on this structure of the cofactor, some models have been proposed concerning the binding of the N_2 molecule. Side-on and end-on coordination to the two iron atoms, which are linked to one another by the S^{2-} bridge, have been speculated [19, 20]. Also, it has been suggested that the nitrogen atoms are sp^3 hybridized, forming a single bond with each other, and to the six iron atoms [16, 20, 21]. Some other models were proposed, including the possibility of the N_2 molecule binding to the Mo atom [20, 22].

The aim of this study is to contribute to the understanding of the features required for a synthetic compound that could serve as a catalyst for reduction of N_2. Our assumption is that such a compound should borrow some structural features from nitrogenase and that N_2 bound to it should show significant perturbation compared to the electron distribution and bond length of a free N_2 molecule. Recently, Deng and Hoffmann [22] studied the binding of the N_2 molecule to nitrogenase using the extended Hückel method. Based on the old assumption of N_2 coordination to the molybdenum atom, another contribution to the literature using the extended Hückel method also exists [23]. Also, Bauschlicher et al. [24] and Siegbahn [25] studied the coordination mode of the N_2 molecule in the Fe_2N_2 system using post-Hartree–Fock methodologies.

2 Methodology

Inspired by the cofactor structure of Rees et al. (Fig. 1) [14–17], we studied N_2 coordination utilizing the following two types of models. The first assumes that the N_2 binds with two iron atoms in a cubane cluster, replacing the one sulfur atom between them. The models having two monomer (FeS_2Ln) units, with $L = H$, Li, Mg and $n = 1, 2$ were investigated (Fig. 2). L and n were chosen to constrain the formal oxidation state of the Fe atom. The oxidation states + 2 and + 3 were investigated. A complete geometry optimization was carried out for the monomers and for the complexes having N_2 binding end-on or side-on. MP2 and

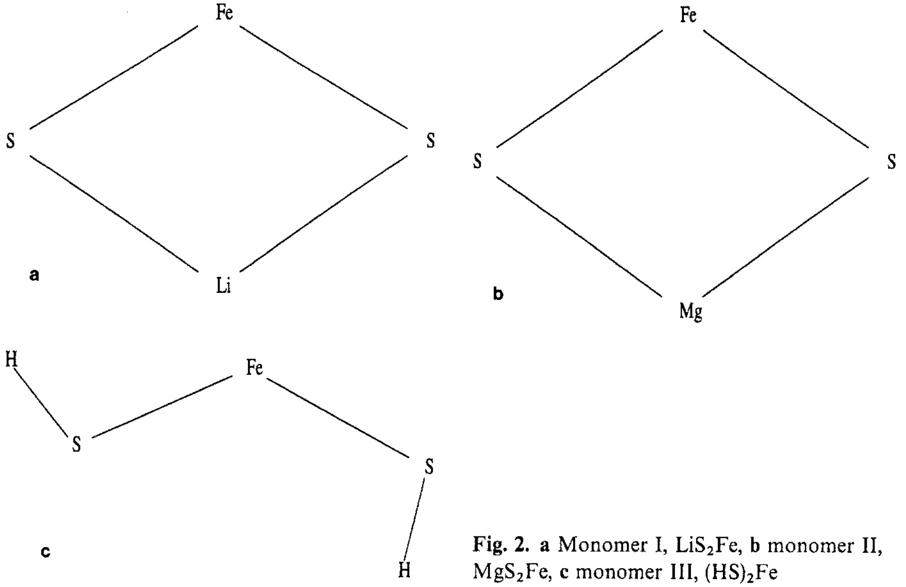

Fig. 2. **a** Monomer I, LiS_2Fe, **b** monomer II, MgS_2Fe, **c** monomer III, $(HS)_2Fe$

CI calculations were also carried out for some chosen structures. For comparison, the interaction of N_2 with only one monomer unit was also considered.

Second, we investigated the possibility of N_2 being inserted in the surface site formed by four iron atoms in Fig. 1. For that, we assumed that the cage is formed by an Fe_4S_4 model. In all of the calculations with this model, the four iron atoms had oxidation form +2. The geometry of Fe_4S_4 was fixed, having C_{2v} point symmetry. All Fe–Fe and Fe–S bond lengths were equal to 2.662 and 2.294 Å, respectively, as in the nitrogenase crystal structure. Many different possibilities to insert the dinitrogen were calculated at fixed geometry using *ab initio* and semi-empirical methods. Some partially optimized structures (N–N and N–Fe bond lengths and Fe–S–Fe bond angles) were also found at the Hartree–Fock level. These calculations are not reported here because all attempts failed to find a geometry in which the N_2 was actually bound to the Fe_4S_4 cage.

In all *ab initio* calculations, split valence basis functions were used. The Dunning and Hay basis [26] was used for hydrogen and for the first row elements. For iron and for the second row elements, we used the Hay and Wadt basis [27, 28] where the core electrons are represented by relativistic effective core potentials.

The free monomers are expected to contain high-spin iron centers. The dimers are expected to anti-ferromagnetically couple these iron centers to form a complex with low spin but many localized singly occupied orbitals. If N_2 were covalently bound to two such iron centers, it would have to break one of its bonding pairs of electrons and recouple the spins to the free iron spins, thereby reducing the number of singly occupied orbitals in the system by 2. The actual total spin of the anti-ferromagnetic iron system would remain at zero.

None of the *ab initio* programs are written to handle this multiple-open-shell low-spin case easily. Calculating two such iron centers is difficult and calculating four such centers is nearly impossible, so we have resorted in this paper to treating only ferromagnetically coupled iron centers. In this case, the eigenvalue of S_z would directly reflect the number of singly occupied orbitals in the system if S^2 were $M(M+1)$. The UHF and MP2 calculations were carried out with the Gaussian 92 program [29]. The CI calculations were performed using the MELD suite of electronic structure codes developed in this laboratory [30]. Semi-empirical calculations were carried out using the ZINDO program [31] in order to get a preliminary feel for some of the complexes (not reported here). None of the results were corrected for basis set superposition error since the goal was to gain chemical insight rather than precise results for these model compounds. A serious problem in all calculations was the tendency of UHF to converge to non-optimal orbitals. This often required repeating calculations from different guesses to the orbitals and coordinates.

3 Results and Discussion

3.1 N_2 binding to monomer I ($LiFeS_2$)

The monomer I ($LiFeS_2$) model was generated as a model where the iron atom could have oxidation form +3. Table 1 contains the optimized geometries of the $LiFeS_2$ monomer and its anion in which the iron has formal oxidation number +2. These were calculated with the expectation that the iron atom could have oxidation forms +2 or +3 in the complex of interest. Also, the table presents the Mulliken atomic charge and spin populations calculated at the UHF level. In all the tables, it should be remembered that in the UHF formalism, "$2S+1$" actually specifies M_S rather than S.

Analysis of the molecular orbitals and spin densities shows the iron atom in both systems having the oxidation form $+2(d^6)$. In the sextet C_{2v} structure (neutral), one open shell electron is delocalized over the two sulfur atoms, which are each in an average oxidation state of $-3/2$. This also explains the differences in the Li–S bond lengths and in the Li–Fe–S angles between the two systems. In SCF calculations, delocalized holes are generally less stable than localized holes. For

Table 1. $LiFeS_2$ optimized UHF C_{2v} and C_s structure results[a]

State	$^6B_2$ (C_{2v})	$^6A'$ (C_{2v})	Anion $^5A_1$ (C_{2v})
Energy	−48.840	−48.846	−48.930
Geometry			
Fe–S	2.3721	2.482, 2.299	2.3592
Li–S	2.4316	2.484, 2.450	2.6249
S–Fe–S	96.918	102.875	116.822
Mulliken atomic charge and spin densities (in brackets)			
Fe	0.615 (3.810)	0.566 (4.004)	0.268 (4.185)
Li	0.477 (−0.115)	0.512 (−0.030)	0.281 (−0.053)
S_1	−0.546 (0.652)	−0.448 (0.987)	−0.774 (−0.066)
S_2		−0.630 (0.040)	
Total	0.000 (5.000)	0.000 5.000	−1.000 (4.000)

[a] Energies in Hartrees, distances in Å, and angles in degrees

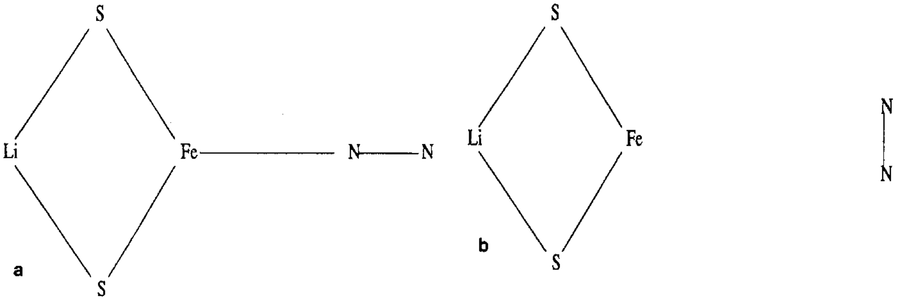

Fig. 3. **a** "End-on" arrangement of N_2 and monomer I, **b** "side-on" arrangement of N_2 and monomer I

$LiFeS_2$, this is also true and we obtained a lower energy broken symmetry solution, also included in Table 1, with one open shell electron localized on one of the sulfur centers.

For the two C_{2v} systems (neutral and anion), we also carried out full CI calculations in the valence space. The high spin ROHF molecular orbitals were used to expand the full CI wave functions. For the anion, the ground state still has high spin coupling (^{5}[Fe d^6]). For the neutral structure, the more stable state is the $^4B_2$ state, which presents diamagnetic coupling $^4(^5[\mathrm{Fe}\ d^6]^2[\mathrm{S}\ p^1])$. Like the high spin, $^6B_2$ state with coupling $^6(^5[\mathrm{Fe}\ d^6]^2\ [\mathrm{S}\ p^1])$ found by the UHF calculation, this is still a high spin Fe(II) center coupled to an S^{-1} open shell sulfur center.

We investigated the possibility of the N_2 molecule binding to this monomer in either end-on or side-on coordination (see Fig. 3). The optimized geometries for the cation and for the anion structures were obtained at the UHF level applying C_{2v} symmetry constraints. The results are shown in Table 2.

Table 2. $LiFeS_2N_2$ optimized UHF structure results with C_{2v} symmetry constraints[a]

	Neutral ($^6B_2$)		Anion ($^5A_1$)
	end-on	side-on	end-on
Binding energy (K cal/mol	11	1	5
Geometry			
Fe–S	2.3743	2.3715	2.3613
Li–S	2.4117	2.4323	2.4359
Fe–N	2.4687	3.9946	2.5704
N–N	1.1096	1.1002	1.0964
S–Fe–S	95.678	97.016	116.260
Mulliken atomic charge and spin densities (in brackets)			
Fe	0.595 (3.777)	0.586 (3.810)	0.254 (4.069)
Li	0.464 (− 0.105)	0.475 (− 0.115)	0.269 (− 0.447)
$S_1=S_2$	− 0.571 (0.665)	− 0.545 (0.653)	− 0.797 (− 0.107)
N_1	0.032 (− 0.048)	0.014 (0.000)	0.117 (0.030)
N_2	0.052 (0.048)	0.014 (0.000)	− 0.046 (− 0.032)
Total	0.000 (5.000)	0.000 (5.000)	− 1.000 (4.000)

[a] Distances in Å and angles in degrees. In end-on structures, N_1 is closest to Fe

In all structures, as observed in the calculations for the monomers, the iron atom has oxidation form +2. The end-on conformations are the most stable ones. All C_{2v} structures have lower energy than the sum of the energies of the monomers plus the energy of the N_2 molecule in its ground state. The N_2 free molecule optimized geometry (N–N = 1.0999 A) has its energy equal to − 108.87816 Hartrees. The experimental bond length for N_2 is 1.0975 A [32].

In the neutral structures, the side-on optimized conformation has a very large Fe–N bond length and a very small bond energy. For this coordination mode, we hoped to find a structure where N–N would have a double bond. However, UHF converges to a structure with an N–N bond length practically equal to the free molecule. In the end-on coordination, the optimized structure corresponds to a somewhat stronger Fe–N bond but N_2 still has the triple bond length. The interaction between the iron atom and the N_2 molecule can be understood as a weak donation from the nitrogen lone pair to *spd*-hybrids on the iron atom.

When symmetry is lowered to C_s and all coordinates including the Fe–N–N angle are optimized, a bent structure with the Fe–N–N angle equal to 173.2° is found to be more stable by 2 milliHartrees. The other angles and distances are practically unchanged. In this conformation, the open shell electron that was delocalized over the two sulfur atoms is now localized on one of them. Of course, the $LiFeS_2$ monomer itself gained 6 milliHartrees by breaking the symmetry and localizing the hole, so in some sense, this broken symmetry N_2 calculation shows less binding by 4 milliHartrees than the C_{2v} constrained calculation. We also considered side-on structures with the N_2 rotated by 90° to give an alternative C_{2v} structure. The calculation gave the lowest energy for this structure at infinite separation. An alternative local minimum was found to be 90 kcal/mol higher in energy, corresponding to fully dissociated N_2 molecules with the two N atoms independently bound to the Fe.

In the anion structures, the side-on conformation optimization converges to the separated fragments. In the end-on conformation, the binding energy of the iron atom to the N_2 molecule is weaker than for the neutral system. Here, all the open shell electrons are centered at the iron atom and therefore the bent structure is not favorable.

3.2 N_2 binding to two monomer I units

Of more interest to us was the coordination mode in which the N_2 molecule bridges between two iron atoms located in different monomers. We have investigated different complexes whose structures have end-on or side-on coordination modes. In Fig. 4, the different models of bonding are presented. Structures 4a and 4b are planar while 4c–e have the LiS_2Fe rings perpendicular to the Fe_2N_2 plane.

When two $LiFeS_2$ units were used as the monomers, the neutral systems were assumed to have spin multiplicity equal to 11. The optimized geometries, energies and Mulliken atomic charge and spin densities calculated using the UHF method are presented in Table 3.

The total energy of all structures is lower than the sum of the energies of the two monomers and a free N_2. In fact, the binding energies are all more than double the bond strength obtained for N_2 attached to only one monomer. The energy of the end-on structures is much lower than the energy of the side-on structure. However, the μ-1, 1-N_2 structure with a strongly perturbed N_2 unit has similar energy to the end-on structures. The end-on trans structure with the sulfur open shell electrons

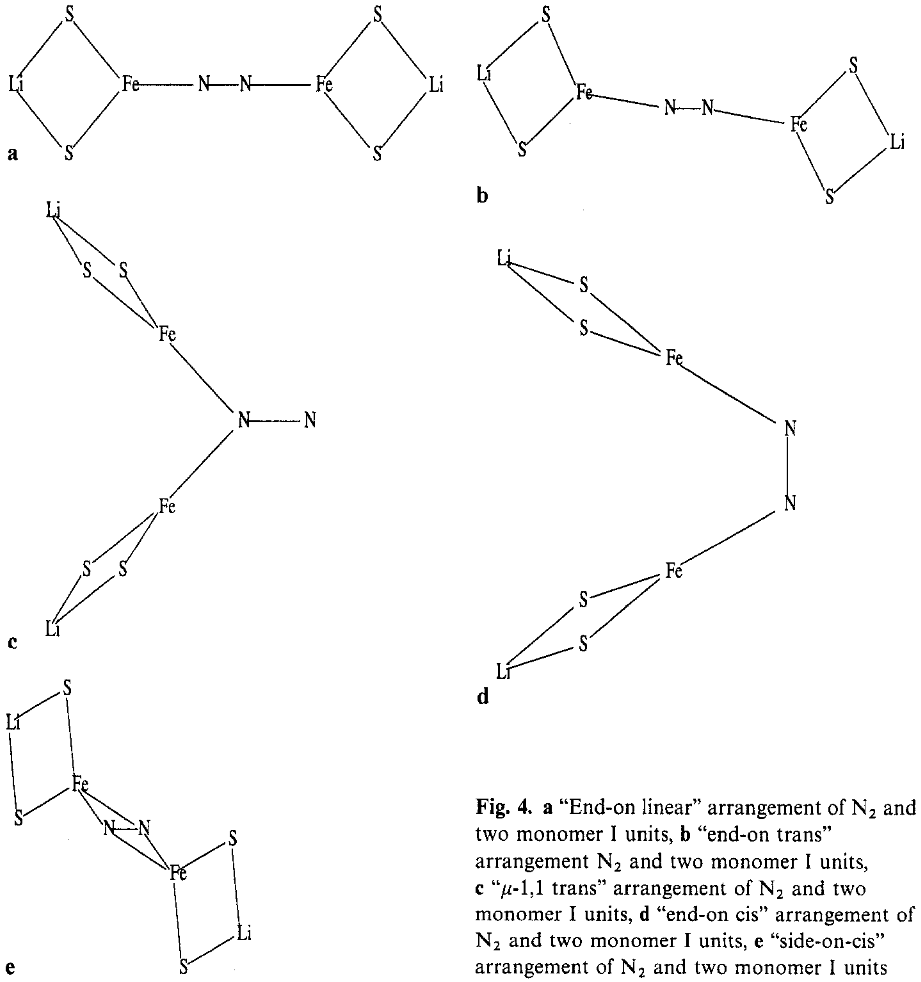

Fig. 4. **a** "End-on linear" arrangement of N_2 and two monomer I units, **b** "end-on trans" arrangement N_2 and two monomer I units, **c** "μ-1,1 trans" arrangement of N_2 and two monomer I units, **d** "end-on cis" arrangement of N_2 and two monomer I units, **e** "side-on-cis" arrangement of N_2 and two monomer I units

localized as discussed before, has the lowest calculated energy but a slightly smaller binding energy (relative to the corresponding monomers) than the end-on linear structure.

The strongly perturbed μ-1,1-N_2 structure has an N–N bond length equal to 1.217 A, which is close to the double bond distance in the PhN =NPh compound (1.255 A) [33]. The μ-1, 1-N_2 structure presents a negative charge on the nitrogen atom closest to Fe and, on the other, a much larger spin density. Therefore, we can see that this structure shows a covalent interaction between one of the nitrogen atoms and the two iron atoms and that the nitrogen molecule has a double bond.

3.3 N_2 binding to two monomer II ($MgFeS_2$) units

The $MgFeS_2$ monomer was generated to model an iron atom with oxidation form +2. The UHF optimized geometry for the high spin state (multiplicity equal to 5)

Table 3. Complexes formed by N_2 molecule and two monomer $LiFeS_2$ units. UHF optimized structures results

	End-on linear D_{2h}	End-on trans C_{2h}	End-on cis C_{2v}	Side-on D_{2h}	μ-1,1-N_2 C_{2v}
Binding energy	27	25[b]	26	10	27
Geometry					
Fe–S	2.4742	2.3814	2.5041	2.4658	2.5087
Li–S	2.4453	2.4807	2.4521	2.4513	2.4540
Fe–N	2.0872	2.6242	2.1641	2.3344	2.1666
N–N	1.1658	1.0935	1.1856	1.1934	1.2171
S–Fe–N	129.448	125.114	129.432		129.522
Fe–N–N	180.000	170.115	120.182		133.063
Mulliken atomic charge and spin densities (in brackets)					
$Fe_1=Fe_2$	0.757 (3.736)	0.478 (4.010)	0.586 (3.570)	0.679 (3.737)	0.627 (3.549)
$S_1=S_2$	−0.438 (0.926)	−0.346 (−0.008)	−0.389 (0.997)	−0.426 (0.931)	−0.393 (0.998)
$S_3=S_4$	−0.438 (0.926)	−0.638 (1.073)	−0.389 (0.997)	−0.426 (0.931)	−0.393 (0.998)
$Li_1=Li_2$	0.435 (−0.134)	0.451 (−0.073)	0.469 (−0.102)	0.464 (−0.131)	0.485 (−0.094)
N_1	−0.316 (−0.454)	0.055 (−0.002)	−0.277 (−0.462)	−0.290 (−0.468)	−0.675 (0.465)
N_2	−0.316 (−0.454)	0.055 (−0.002)	−0.277 (−0.462)	−0.290 (−0.468)	0.023 (−1.368)
Total	0.000 (10.000)	0.000 (10.000)	0.000 (10.000)	0.000 (10.000)	0.000 (10.000)

[a] Distances in Å and angles in degrees. In the μ-1,1 structure, N_1 is closest to Fe

[b] Relative to broken symmetry monomers

Table 4. Complexes formed by N_2 molecule and two monomer $MgFeS_2$ units. UHF optimized structures results for the high spin states (multiplicity equal to 9)[a]

	End-on liner D_{2h}	Side-on D_{2h}	μ-1,1-N_2 C_{2v}
Binding energy (kcal/mol)	11	− 63	− 47
Geometry			
Fe–S	2.4101	2.5083	2.4952
Mg–S	2.3646	2.3626	2.3606
Fe–N	2.7002	2.3407	2.1719
N–N	1.0936	1.1946	1.2232
S—Fe–N	127.045		129.548
Fe–N–N	180.000		120.548
Mulliken atomic charge and spin densities (in brackets)			
$Fe_1 = Fe_2$	0.375 (3.988)	0.623 (3.922)	0.627 (3.913)
$S_1 = S_2 = S_3 = S_4$	− 0.690 (0.020)	− 0.640 (0.293)	− 0.632 (0.285)
$Mg_1 = Mg_2$	0.947 (− 0.025)	0.949 (− 0.032)	0.962 (− 0.028)
N_1	0.057 (− 0.003)	− 0.292 (− 0.477)	− 0.666 (0.487)
N_2	0.057 (− 0.003)	− 0.292 (− 0.477)	0.016 (− 1.398)
Total	0.000 (8.000)	0.000 (8.000)	0.000 (8.000)

[a] Distances in Å and angles in degrees. In μ-1,1 structure, N_1 is closest to Fe

yields a structure with S–Fe and Mg–S bond lengths equal to 2.413 and 2.365 Å, respectively. The angle formed by the S–Fe–S atom is equal to 105.9°. The total energy is equal to − 42.208 Hartrees. Analysis of the molecular orbitals and the spin densities shows that this system has a d^6 iron atom configuration.

The converged optimized UHF structures for the complexes formed by the N_2 molecule bound to two iron atoms in the monomers are presented in Table 4. They were calculated with the assumption that the iron atoms have oxidation form +2, which yields a high spin multiplicity equal to 9. The end-on trans and the end-on cis structures are not presented, since both of them converge to the end-on linear geometry. The end-on linear structure is the most stable one and its energy is the only one that is lower than the sum of the fragments. However, it is the one which presents the least perturbed N_2 unit.

The other converged structures, side-on and μ-1,1-N_2, have energies higher than the sum of the energies of the fragments. Consequently, these structures are local minima and the global minimum corresponds to dissociated fragments. Both of these structures have a strongly perturbed N_2 unit. These complexes present very similar structures to those presented in Table 3 in which the N_2 molecule binds to monomer I.

We have also calculated the optimized geometry for the end-on linear, side-on and μ-1, 1-N_2 structures at the lower spin multiplicity corresponding to the number of singly occupied orbitals expected in a covalently bound complex, i.e., equal to 7. The spin-up density of the iron is hardly changed by the change in multiplicity, but spin-down density appears on N_2 to give the desired total M_S. Compared to the high spin state, the end-on linear and the side-on structures have higher energy by 52 and 3 kcal/mol, respectively. The μ-1,1-N_2 structure has its energy lowered by 21 kcal/mol, but this is still unbound relative to the high spin monomer.

Table 5. Complexes formed by N_2 molecule and two monomer $Fe(SH)_2$ units in an end-on arrangement. UHF optimized results for a planar molecule[a]

	$2S+1=9$	$2S+1=7$	$2S+1=5$
Binding energy (kcal/mol)	9	− 53	− 66
Geometry			
Fe–S	2.3887 (2.3970)	2.3935 (2.5745)	2.3560 (2.3500)
S–H	1.3530 (1.3540)	1.3544 (1.3557)	1.3530 (1.3530)
Fe–N	2.7133	2.0791	2.7044
N–N	1.0940	1.1664	1.0940
S–Fe–S	172.386	127.121	175.465
Mulliken atomic charge and spin densities (in brackets)			
$Fe_1=Fe_2$	0.701 (4.044)	0.843 (4.006)	0.892 (3.881)
$S_1=S_4$	− 0.442 (− 0.027)	− 0.458 (− 0.018)	− 0.515 (− 0.036)
$S_2=S_3$	− 0.456 (− 0.028)	− 0.252 (− 0.588)	− 0.034 (− 1.095)
$H_1=H_4$	0.058 (0.007)	0.067 (0.008)	0.740 (0.009)
$H_2=H_3$	0.081 (0.008)	0.101 (0.046)	0.130 (0.081)
$N_1=N_2$	0.058 (− 0.005)	− 0.301 (− 0.455)	− 0.547 (− 0.841)
Total	0.000 (8.000)	0.000 (6.000)	0.000 (4.000)

[a] Distances in Å and angles in degrees. Geometry values in parentheses indicate inequivalent S and H on same Fe

3.4 N_2 binding to monomer III (H_2S_2Fe)

Like monomer II, this H_2S_2Fe monomer model was chosen so that the iron atom in the neutral system has oxidation form +2 with spin multiplicity equal to 5. The UHF optimized geometry provides a C_s point group symmetry structure where the S–Fe–S angle is approximately equal to 180°. The S–H and Fe–S bond lengths are equal to 1.354 and 2.389 Å. If the S–Fe–S angle were exactly 180°, the symmetry would be C_{2h} with the z axis out of plane. The total energy is equal to − 42.526 Hartrees.

The complexes formed by the two monomers and the N_2 molecule were calculated at the UHF level. In the high spin multiplicity state, only the planar end-on linear structure converged to a bound geometry. The side-on and μ-1,1-N_2 structures converged to the separated fragments. In a lower spin state (multiplicity equal to 7), we also obtained an optimized μ-1,1-N_2 structure. This multiplicity corresponds to the number of singly occupied orbitals expected if N_2 is covalently bound to each Fe.

Table 5 presents the results obtained at the UHF level for the optimized end-on structures at three different spin states. The high spin structure presents an unperturbed N_2 unit. The states with lower multiplicity have a perturbed N_2 unit with spin-down density on nitrogen and sulfur, but have higher energy. The state with multiplicity equal to 5 has the smallest Fe–N bond length and the most negative net charge on the nitrogen atoms and consequently has the most perturbed N_2 unit. This multiplicity corresponds to the number of singly occupied orbitals expected if the N_2 has a double bond to each Fe.

We also optimized the structures of the three spin states using the MP2 method. The high spin case still has the lowest energy. The results obtained for the high spin state still present an unperturbed N_2 unit, as was obtained at the UHF level.

4 Conclusion

For all the model compounds studied, the iron atom presents oxidation form +2 (d^6) even though we tried clusters such as LiS_2Fe with formal oxidation number +3.

Using the model in which N_2 binds with two iron atoms with formal oxidation number +3, the N_2 molecule prefers to bind in an end-on coordination mode instead of a side-on mode. The μ-1,1-N_2 structure was also investigated. This has weaker net binding between Fe and N_2 than the end-on form, but the N_2 shows partial promotion to a double bond length and has a net spin down of about one electron and a net charge of − 0.67. Except for the slightly larger bond length, this is similar to N_2 in the end-on mode. The MgS_2Fe dimer model binds N_2 much more weakly. The end-on mode gives little change in the N_2 bond length or charge distribution. The μ-1,1 mode gives a local minimum with a shorter Fe–N distance and a high energy. From these results, it would appear that a dimer site of Fe(III) centers with low coordination number might be useful for catalysis of N_2 reductions.

No stable four-iron N_2 cluster was found, even though a number of different binding modes were investigated.

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