Interpretation of the Photoelectron Spectra of FeS_2^- by a Multiconfiguration Computational Approach

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The ground states of FeS_2 and FeS_2^-, and several low-lying excited electronic states of FeS_2 that are responsible for the FeS_2^- photoelectron spectrum, are calculated. At the B3LYP level an open, quasi-linear $[SFeS]^-$ conformation is found as the most stable structure, which is confirmed at the ab initio CASPT2 computational level. Both the neutral and the anionic unsaturated complexes possess high-spin electronic ground states. For the first time a complete assignment of the photoelectron spectrum of FeS_2^- is proposed. The lowest energy band in this spectrum is ascribed to an electron detachment from the two highest-lying $3d_\pi$ antibonding orbitals (with respect to the iron−sulfur bonding) of iron. The next-lowest experimental band corresponds to an electron removal from nonbonding, nearly pure sulfur orbitals. The two highest bands in the spectra are assigned as electron detachments from π and σ bonding mainly sulfur orbitals.

Introduction

The difficulties inherent to wavefunction theoretical investigations of complex iron−sulfur clusters that play catalytic and transportation roles in metalloenzymes are still to be overcome. Although there are theoretical studies on iron−sulfur clusters/complexes of various sizes performed on a more practical but moderate level of theory,[1−3] there is still an unfulfilled demand for higher-level computational studies of these types of relatively large clusters in relation to various biochemical and physical investigations.[4−7] The investigation in a systematic way of smaller iron−sulfur clusters, or more appropriately called unsaturated iron−sulfur complexes, by employing high-level accuracy computational methods, gives us the opportunity to seek insight into the elementary properties of iron−sulfur bonding, serving as a basis for the understanding of the more complicated inorganic or biological systems.[8−10] In a previous paper we investigated the photoelectron spectra (PES) of the simplest iron−sulfur complexes, namely, the diatomic FeS and FeS^- complexes.[11] Indeed, the detailed experimental PES of the FeS_n^- complexes[12] are useful for calibrating present day computational methods. In this respect the present contribution intends to assign for the first time all features of the photoelectron spectra of the FeS_2^- cluster as reported by Zhai et al.[12] The 355 nm spectrum of FeS_2^- exhibits an isolated band X with a vertical detachment binding energy (VDE) at 3.306 eV. On the basis of the low-energy side of this band, an adiabatic detachment energy (ADE) of 3.222 eV has been proposed. Intense bands called A−E were recorded at VDEs of 3.75, 4.01, 4.25, 4.66, and 5.15 eV, respectively. Both Zhai et al.[12] and Schröder et al.[14] have performed density functional theory (DFT) calculations on FeS_2^- and FeS_2 and agree that an open quasi-linear structure $[S-Fe-S]^-$ is to be held responsible for these major spectral features. A very weak feature (X′) that has been identified at the lower binding energy side of the 355 nm spectrum with a VDE of 2.15 eV and a ADE of 2.05 eV has been ascribed to the high-energy closed (cyclic) isomer of FeS_2^-.[12,14] The main purpose of this contribution is to identify by means of the CASSCF/CASPT2 method the electronic states of the neutral species (calculated at the ground-state equilibrium geometry of the anion) that are responsible for all of the observed bands of the aforementioned spectra. In this way we hope to establish a complete assignment of the photoelectron spectra of FeS_2^-.

Computational Details

The first step in an attempt to assign the photoelectron spectra of FeS_2^- is the unambiguous determination of its ground state. The potential energy surfaces of the FeS_2 and FeS_2^- systems were first thoroughly and completely investigated at the B3LYP/SV(P) level by using the TURBOMOLE software.[13] The results confirmed the previous works of Schröder et al.,[14] that the ground-state conformation of the anionic FeS_2^- is an open S−Fe−S configuration such as that in Figure 1(**o**) and not the much higher-lying closed conformation (**c**). Both conformations were reoptimized at B3LYP in combination with the larger QZVP[15] basis sets (Table 1), and the following geometries were found: the open conformation has a Fe−S bond distance of 2.115 Å, the angle between the two FeS bonds being 164.4 degrees. The conformation (**c**) is found higher in energy than (**o**) by 27.92 kcal/mol, with the following parameters: a Fe−S bond of 2.294 Å and an S−S bond of 2.154 Å. Starting from these geometries, more elaborate CASPT2 geometry optimizations have been carried out on the anionic lowest state of conformations **o** and **c** and on the open conformation of the neutral complex. The electron binding energies were calculated subsequently by taking into consideration the Franck−Condon principle, and the calculated vertical detachment energies were tentatively assigned to the experimentally observed bands. The ground state of the anion and neutral complex in their equilibrium geometries in addition to all relevant excited states of the neutral species at the anionic ground-state geometry were calculated at the CASPT2 level by employing the same basis sets as for the CASPT2 geometry optimizations: ANO-RCC

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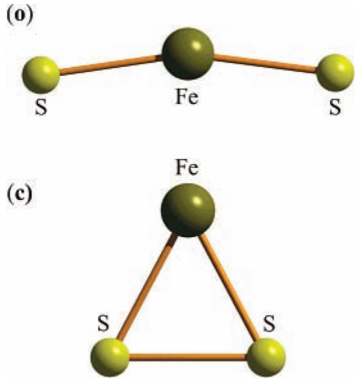

Figure 1. Ground-state open (upper; **o**) and closed (lower; **c**) conformations of the FeS_2^- species. The z-axis of the coordinate system is located along the C_2 axis, both molecules placed in the yz plane.

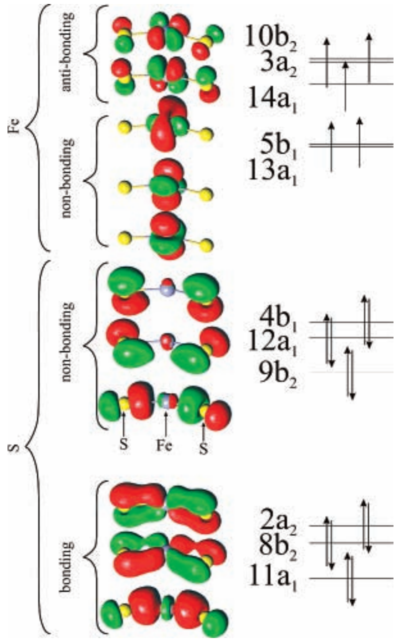

Figure 2. $^6A_1$ anionic ground-state molecular orbitals for the open conformation of FeS_2^- and their occupation in the predominant CASSCF configuration, ordered by CASPT2 orbital energies.

[7s6p4d3f2g1h] for Fe and [6s5p3d2f1g] for S, as implemented in the MOLCAS 6.4 package.[16]

The choice of the active space for the CASSCF calculation is not trivial,[17,18] even though the molecule is a very simple one, just one transition metal and two sulfur atoms. It seems that the valence orbitals of the sulfur atoms have energies relatively comparable to the valence orbitals of the iron atom. Ideally, a CASSCF calculation would require that all 2p electrons of sulfur besides the iron valence 3d electrons are included in the active space. In some geometrical conformations a molecular orbital with strong iron 4s character becomes singly occupied, and consequently this orbital is also required in the active space. This would result in 16 electrons of the neutral molecule (17 for the anion) in 16 (17 with Fe 4s) orbitals, if double shell orbitals are included as well. This size of the active space is not practical, therefore we had to reduce its size. In particular, for configuration **o**, the (16i15) designated active space (17i15 for the anion) comprises the 3p orbitals of the sulfur atoms, the 3d orbitals of iron, and, to account for the double shell effect, one additional orbital per irreducible representation of C_{2v}. For conformation **c** a slightly reduced (16i15) active space was employed. It includes all sulfur 3p orbitals, except the unoccupied σ^* combination, the iron 3d and 4s orbitals plus four double shell orbitals (one per irreducible representation). This approach has previously led to acceptable results.[19,20] Part of the dynamical correlation has been recovered at the CASPT2 level by correlating the valence electrons of all atoms plus the 3p of iron. The vertical detachment energies were obtained by including the scalar relativistic effects according to the so-called Douglas−Kroll transformation and using the default Hamiltonian (IPEA = 0.25) during the CASPT2 calculations, as implemented in MOLCAS.[16,21] By performing test calculations on the VDE of the X feature of the PES, spin−orbit effects are estimated to be of the order of a few thousandths of an electronvolt and therefore can be neglected on the whole.

Results and Discussion

The extensive experimental and B3LYP investigation of the FeS_2 molecule and FeS_2^- ion by Schröder et al.[14] showed that the anion has an open configuration in its ground state with a Fe−S bond of 2.12 Å and S−Fe−S angle of 166.7°. This conformation was also found by Zhai et al. as the most stable geometry for the anion.[12] Our CASPT2 geometry optimization yielded the same C_{2v} open conformation as the global minima of the anion with a Fe−S bond of 2.087 Å, without a bond between the two sulfur atoms (Table 1). It closely resembles a linear structure with the Fe atom placed between two sulfur atoms, the S−Fe−S angle being equal to 158°. An inspection of the electronic structure of the anion, as depicted in Figure 2, reveals that the $^6A_1$ ground state has five unpaired electrons in the predominantly 3d orbitals of iron, and the anion can formally be regarded as $S^{2-}Fe^{3+}S^{2-}$. This means that FeS_2^- possess a high-spin ground state, which is what can be expected for this unsaturated complex. It indicates that the lowest band in the PES is most likely due to electron detachment from one of the 3d orbitals. The rather large angle of 158° between the two Fe−S bonds basically keeps the orbital pattern very close to the one of a linear S−Fe−S molecule: the (10b$_2$, 3a$_2$) pair of orbitals and (5b$_1$, 13a$_1$), (4b$_1$, 12a$_1$), and (2a$_2$, 8b$_2$), as well, are very close in energy, their nature being similar to π or δ orbitals of a linear structured molecule. Also qualitatively in agreement with the results of Schröder et al.[14] our CASPT2 geometry optimization yielded a stable closed conformation (**c**) energetically positioned at 42.22 kcal/mol above the ground-state conformation (**o**). In accordance with the B3LYP (QZVP) results, Table 1 shows that the iron−sulfur bond distance considerably enlarges when **o** transforms into **c**. The obtained CASPT2 value of 2.250 Å resembles reasonable well the B3LYP distance of 2.294 Å. A sulfur bond of 2.147 Å is somewhat larger than what can be expected on the basis of the covalent radius of the element (1.04 Å), but comparable to the bond distance of 2.18 Å that we obtained for S_2^{2-} by optimizing the geometry of this uncoordinated dianion at the CASPT2 level. The third and last conformation that was reoptimized starting from its B3LYP geometry was the open conformation of the neutral FeS_2. Again, as can be deduced from Table 1 the geometric differences between the two computational methods are rather small. So, the CASPT2 optimization confirms that the S−Fe−S bond angle for the neutral system is much smaller. Removal of an electron reduces this bond angle from its more linear value of 158° to an almost rectangular value of 114°. The distance between the two sulfur nuclei is 3.388 Å, which is a clear indication that there is still no bond between them, and we can safely conclude that this structure is best described as an open conformation. The difference in energy between the ground states of the neutral and the anion, both open conforma-

TABLE 1: Optimized Geometries of the Conformations (c) and (o) of the FeS_2^- Anion at B3LYP (QZVP) and CASPT2 Levels

		B3LYP			CASPT2		
	state	r_{Fe-S}, Å	r_{S-S}, Å	θ_{S-Fe-S}, deg	r_{Fe-S}, Å	r_{S-S}, Å	θ_{S-Fe-S}, deg
$SFeS^-$ (**o**)	$^6A_1$	2.115	4.190	164.4	2.087	4.098	158
$Fe(S_2)^-$ (**c**)	$^6A_1$	2.294	2.154	56	2.250	2.147	57
SFeS (**o**)	$^5B_2$	2.012	3.375	114	2.020	3.388	114
$Fe(S_2)$ (**c**)	$^5A_1$	2.168	2.210	61.29			

TABLE 2: CASPT2 Vertical Detachment Energies (VDE) and Predominant Electronic Configuration of the Lowest States of the Neutral FeS_2 Molecule at the Anionic Geometry

			VDE (eV)	
	state CASPT2	predominant configuration CASSCF	expt[12]	CASPT2
X	$^5B_2$	$12a_1^2 13a_1^1 14a_1^1 4b_1^2 5b_1^1 8b_2^2 9b_2^2 10b_2^0 2a_2^2 3a_2^1$	3.306	3.21
	$^5A_2$	$12a_1^2 13a_1^1 14a_1^1 4b_1^2 5b_1^1 8b_2^2 9b_2^2 10b_2^1 2a_2^2 3a_2^0$		3.24
A	1^7A_1	$12a_1^1 13a_1^1 14a_1^1 4b_1^2 5b_1^1 8b_2^2 9b_2^2 10b_2^1 2a_2^2 3a_2^1$	3.75	3.80
	1^7B_1	$12a_1^2 13a_1^1 14a_1^1 4b_1^1 5b_1^1 8b_2^2 9b_2^2 10b_2^1 2a_2^2 3a_2^1$		3.74
B	1^5A_1	$12a_1^2 13a_1^1 14a_1^0 4b_1^2 5b_1^1 8b_2^2 9b_2^2 10b_2^1 2a_2^2 3a_2^1$	4.01	4.05
	2^5A_1	$12a_1^1 13a_1^1 14a_1^1 4b_1^2 5b_1^1 8b_2^2 9b_2^2 10b_2^1 2a_2^2 3a_2^1$		
	1^5B_1	$12a_1^2 13a_1^1 14a_1^1 4b_1^1 5b_1^1 8b_2^2 9b_2^2 10b_2^1 2a_2^2 3a_2^1$		4.10
C	3^5A_1	$12a_1^2 13a_1^0 14a_1^1 4b_1^2 5b_1^1 8b_2^2 9b_2^2 10b_2^1 2a_2^2 3a_2^1$	4.25	-
	2^5B_1	$12a_1^2 13a_1^1 14a_1^1 4b_1^2 5b_1^0 8b_2^2 9b_2^2 10b_2^1 2a_2^2 3a_2^1$		4.40
	1^7B_2	$12a_1^2 13a_1^1 14a_1^1 4b_1^2 5b_1^1 8b_2^2 9b_2^1 10b_2^1 2a_2^2 3a_2^1$		4.22
D	2^7B_2	$12a_1^2 13a_1^1 14a_1^1 4b_1^2 5b_1^1 8b_2^1 9b_2^2 10b_2^1 2a_2^2 3a_2^1$	4.66	4.80
	$^7A_2$	$12a_1^2 13a_1^1 14a_1^1 4b_1^2 5b_1^1 8b_2^2 9b_2^2 10b_2^1 2a_2^1 3a_2^1$		4.65
X		$12a_1^2 13a_1^1 14a_1^1 15a_1^0 4b_1^2 5b_1^1 8b_2^2 9b_2^2 2a_2^2 3a_2^1$	2.15	2.36

tions, amounts to 2.90 eV, which is our CASPT2 estimate for the ADE. The experimental value as tentatively derived from the threshold value of the lowest intense band X in the photoelectron spectrum of FeS_2^- is 3.222 eV.[12] The B3LYP/6-311+G* value of Schröder et al.[14] of 3.30 eV is larger and more in line with the experimental estimate. However, these authors argue that due to the significant difference in bond angles of ground-state structures of the anionic and the neutral complex, the vibrational 0 → 0 transition may have an unfavorable Franck−Condon factor and therefore may not be observable as a threshold of the X band. This means that the current experimentally proposed value is an upper limit of the true ADE. A further and more detailed ab initio investigation comprising a thorough vibrational analysis based on highly accurate potential energy surfaces is needed to settle the matter.

The photoelectron spectroscopy measurements involve the synthesis of the anionic species, which first undergo mass selection, followed by photoelectron extraction using irradiation with different wavelengths.[12] The energy of the detached photoelectrons corresponds to the difference between the energy of the incident irradiation ($h\nu$) and the binding energy of that electron. The peaks of the observed bands correspond to vertical detachment energies (VDE). To calculate the VDEs that correspond to the observed spectra, we remove an electron from the anionic FeS_2^- $^6A_1$ ground state and calculate the various low-lying states of the neutral FeS_2 at the anionic $^6A_1$ equilibrium geometry. If the removed electron is one of the five unpaired electrons in Figure 2, it will result in a neutral FeS_2 state with quintet spin multiplicity. Removing a β spin electron from the lower doubly occupied orbitals produces septet states. In Table 2 we present the CASPT2 results for the VDEs and the predominant electron configuration of the neutral FeS_2 states. As expected, the removal of the highest in energy anionic electron from the $10b_2$ orbital results in a $^5B_2$ ground state for the neutral. The corresponding VDE is computed as 3.21 eV. The almost degenerate $3a_2$ electron ($^5A_2$) yields a detachment at 3.24 eV. Given an experimental value of 3.306 eV, we assign the *X feature* of the spectra to these two detachments from these two d_π antibonding (with respect to the iron−sulfur bond) orbitals. The 355 nm spectrum revealed only a partially resolved vibrational progression for the X feature, which could be an indication that more than one vibrational mode is active. The two concurrent detachments from $3a_2$ and $10b_2$ orbitals, occurring with the same probability, could also explain the irregular vibrational resolution.

Inspection of Figure 2 allows us to classify the *other d orbitals* as mainly nonbonding. They are therefore situated lower in energy than $10b_2$ and $3a_2$. The first orbital underneath the d_π level is the $14a_1$ singly occupied orbital. Although it has σ antibonding capabilities with the sulfur $3p_y$ orbitals by symmetry, it is mostly nonbonding in nature and resembles the $3d_{y^2}$ orbital with a minor variation that is due to the deviation of the molecule from linearity. The removal of the anionic electron from this orbital would result in the neutral FeS_2 1^5A_1 state. This state is calculated at 4.05 eV and is expected to be responsible for the *B feature* of the PES at 4.01 eV. We like to mention the fact that the 266 nm spectrum does not permit one to clearly distinguish the B and C features; there are definitely more states responsible for these features, and they can be anywhere between 3.9 and 4.4 eV. The individual detachments at several positions with different intensities are likely from the experimental recorded broad band in this energy region. With only weak δ interaction capabilities, the $3d_{x^2-z^2}$ and $3d_{xz}$ orbitals of the Fe atom are even lower in energy than the $14a_1$ orbital and nonbonding in nature. One electron detachment from either one of these two orbitals would be expected to occur at energies higher than that of the B feature. Indeed, at CASPT2 the 2^5B_1 state was found at 4.40 eV, but, unfortunately, for the calculation of the 3^5A_1 state the afforded number of roots did not comprise the expected excitation. Nevertheless, the resulting 3^5A_1 and 2^5B_1 states should be almost degenerate, according to orbital symmetry. The photoelectron detachment from the $5b_1$ and $13a_1$ orbitals can therefore be responsible for the intensity of the *C feature* in the PES at 4.25 eV.

On the basis of Figure 2 we can divide the *sulfur 3p orbitals* into three groups: the essentially nonbonding $12a_1$, $4b_1$, and $9b_2$ orbitals, the π bonding $8b_2$ and $2a_2$ orbitals, and finaly the lowest lying σ bonding 11 a_1 orbital. Because the geometry of the ground state of the anionic molecule is almost linear, the detachment of a β electron from almost degenerate ($12a_1$, $4b_1$) or ($2a_2$, $8b_2$) pairs of orbitals will result in two ($^7A_1$, $^7B_1$) and ($^7A_2$, 2^7B_2) quasi-degenerate pairs of states. The ($^7A_1$, $^7B_1$) and

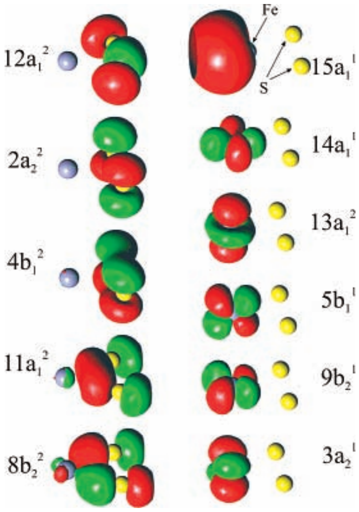

Figure 3. $^6A_1$ anionic ground-state molecular orbitals for the closed conformation of FeS_2^-. Sulfur orbitals at the left-hand side of the figure are all doubly occupied in the leading configuration of the CASCCF wave function. Iron orbitals can be found on the right-hand side; they are all singly occupied except for the $13a_1$ orbital that is doubly occupied as indicated.

($^7A_2$, 2^7B_2) pairs can, according to the results shown in Table 2, be clearly assigned to the *A and D features* of the PES spectra, respectively. The A band therefore originates from the nonbonding sulfur 3p orbitals, while the D band stems from the π bonding orbitals. Photodetachment of an α electron from the nonbonding sulfur will yield quintet spin multiplicity states with six unpaired electrons, one of which formally has a β spin function. In general these quintet states will be somewhat higher in energy than the corresponding septet states. Just as an example, this assumption is confirmed by the 1^5B_1 ($12a_1^2 13a_1^1 14a_1^1 4b_1^1 5b_1^1 8b_2^2 9b_2^2 10b_2^1 2a_2^2 3a_2^1$) state, which is calculated at 4.10 eV, presumably adding some intensity to the B or C features. Several other quintets were calculated in this energy region, probably adding intensity to the bands B and C. The detachment of a β electron from the $9b_2$ orbital (which is of sulfur 3p σ* nature) results in a neutral 1^7B_2 state. At 4.22 eV, this detachment corresponds to the feature C of the photoelectron spectra, but as we can see from Table 2, this is not the only detachment responsible for that feature. With a σ bond for each of the two iron sulfur bonds, the $11a_1$ orbital is the lowest valence orbital with a predominantly sulfur 3p character. Detachment from this orbital is expected to give rise to the *E spectral feature*. Unfortunately the optimization of this specific detachment was problematic, and due to its obviously higher position in the spectra we did not persevere in its calculation.

Conformation **c** of FeS_2^- which has the two sulfurs bound to each other, is about 40 kcal/mol higher than configuration **o**. Despite this fact, Zhai et al. ascribed the recorded very weak X′ spectral feature with VDE = 2.15 eV and ADE = 2.05 eV to this isomer. B3LYP calculations by Schröder et al. yielded a vertical transition to the ground state of the resultant closed neutral species of 1.71 eV. Table 1 and Figure 1 (**c**) present our optimized geometry of the anionic $^6A_1$ ground state of the isomer **c**. From Figure 3 it can be concluded that its electronic structure is quite different from that of isomer **o**: the lowest iron $3d_{x^2-y^2}$ is doubly occupied and an iron sd-hybrid orbital is singly occupied (not so in **o**), and on the sulfur atoms the b_2 combination of the $3p_y$ orbitals is not occupied at all, being a strong antibonding and consequently higher-lying orbital. Formally, its electronic structure on iron can be described as $3d^6 4s,^1$ which corresponds to $Fe^+{-}S_2^{2-}$. Our CASPT2//B3LYP calculations indicate that the lowest electron detachment takes place from the sd-hybrid iron orbital and results in a $^5A_1$ neutral species, with VDE = 2.40 eV and ADE = 2.15 eV. Nevertheless the obtained VDE value has a large discrepancy (0.25 eV) with the experimental value; we can conclude that the assignment of the *X′ feature* to the closed isomer is confirmed at the CASPT2 level of theory.

Conclusions

Detailed investigations of the anionic and neutral species of FeS_2 iron−sulfur cluster have been performed at the CASSCF/CASPT2 level of theory. We have found both at the B3LYP and CASPT2 levels that the most stable geometrical conformation of the FeS_2^- molecule is an almost linear structure with the iron atom between the two sulfur atoms. The major bands in the photoelectron spectrum can be ascribed as electron detachments from the calculated orbitals of this quasi-linear anionic ground-state structure. The electronic structure of the neutral open conformation, calculated at the geometry of the anionic open conformation, revealed the most probable character for the various electronic detachments that are responsible for the observed bands in the photoelectron spectra. Photoelectron detachments from the two highest $3d_\pi$ antibonding orbitals of iron are at the origin of the X band, whereas photodetachments from sulfur 3p nonbonding lone-pair orbitals are computed to be responsible for the A band of the photoelectron spectra. The π bonding 3p sulfur orbitals are accountable for the D band. By elimination the E band is ascribed to an electron detachment from the σ bonding 3p sulfur orbital. The experimental observed electron intensity in the broad region of bands B and C is proposed to have contributions from electron detachments out of the lower 3d nonbonding orbitals of iron and from quintet states of the neutral FeS_2 arising from a loss of an electron from the nonbonding 3p sulfur orbitals. The low-intensity barely observed X′ feature of the photoelectron spectrum at a VDE of 2.15 eV is due to the closed triangular cyclic isomer of FeS_2^- with a bond between the sulfur atoms.

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