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Alkyl radical generation by an intramolecular homolytic substitution reaction between iron (II) and trialkylsulfonium groups

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Abstract: Intramolecular, homolytic substitution reactions between iron (II) species and various trialkylsulfonium groups were directly observed in the gas phase upon collision induced dissociation. In spite of the notoriously low reduction potential of trialkylsulfonium species and the mismatched oxidation potential of iron (II), the reactions proceed at moderate collision energies, forming an alkyl radical as well as a thioether coordinated to the iron. In contrast to classical homolytic substitutions, the attacking radical is a “metalloradical”, namely iron (II) that is oxidized to iron (III) during the reaction. With this process we demonstrate that the conceptually analogous, putative radical generation step in Radical S-Adenosyl Methionine Enzymes is possible and plausible. Further, we show that this kind of reaction only occurs in constrained systems with a defined geometry. Combining experimental measurements with DFT studies and NBO analyses allowed us to gain insights into the reactivity and transition states of these systems. Based on our findings, we challenge the notion of a collinear transition state in the radical generation step of Radical SAM Enzymes and propose it to be bent instead.

Introduction

Reductive cleavage processes of sulfonium groups have been known for a long time.^[1–3] One-electron reduction of a sulfonium cation by chemical or electrochemical means in many cases leads to fragmentation into a sulfide and a radical species. While sulfonium groups with many different substituents have been reductively cleaved,^[1–7] the chemical cleavage of trialkylsulfonium species is challenging because of their low reduction potentials, e.g. for the trimethylsulfonium cation, it has been measured to lie at -1.8 V versus standard calomel electrode.^[8] However, in this work we show that trialkylsulfonium species can easily be cleaved reductively via an intramolecular homolytic substitution reaction. Homolytic substitution reactions are chemical processes where a radical attacks an atom bearing a leaving group that is extruded as a radical in the course of the reaction. They are generally accepted to follow one of three possible mechanisms. Either they go via **1**) a back-side attack similar to an S_N2 reaction, **2**) a front-side attack or **3**) a short-lived intermediate.^[9] For substitutions that take place at silicon, germanium or tin, it has been shown that the reaction can proceed either by back-side (**1**) or front-side (**2**) attack^[10], while reactions involving chalcogens appear to occur

only via backside attack, or through a short-lived intermediate (of minor mechanistic relevance) (**3**) in the case of tellurium.^[11–12] In accordance with Pryor's recommendation^[13] we use the designation “S_H2” for homolytic, direct, one step displacement reactions with backside attack (**1**) in this paper.

Schiesser et al. calculated that S_H2 reactions of alkyl radicals at sulfur and selenium occur as shown in Scheme 1. The attacking radical acts as an electrophile (in contrast to S_N2 reactions) and interacts significantly with the lone pair of the atom at which the substitution takes place. As a result of that interaction with the lone pair, the transition state (TS) is bent instead of linear.

Scheme 1. S_H2 reaction between an alkyl radical and an X=S, Se species according to Schiesser et al.^[14]

A number of homolytic substitution reactions have been discovered to date. While for most cases the central atom is found in groups 14 to 16 in the periodic table, with oxygen, sulfur and selenium dominating^[15–16], the attacking radical is often a carbon radical; other species, among these halogen, oxygen and nitrogen centered radicals, are also known.^[9, 15–17] This is also true for the leaving (radical) group. There are, however, a few reported cases where the leaving group, taken strictly, is not a radical, but rather a transition metal species that takes up an electron. For example, Co(III) species reduced to Co(II)^[9, 18–19] or Ti(IV) reduced to Ti(III) have been observed.^[20]

The biologically relevant radical generation step proposed to occur in Radical S-Adenosyl Methionine Enzymes (RSE) may be regarded as an example of the microscopic reverse of those processes involving a transition metal (Scheme 2). It is an intramolecular S_H2 reaction between a [4Fe-4S] cluster acting as a “metalloradical” and the trialkylsulfonium species, S-Adenosyl methionine (SAM, **1**, Figure 1), forming a highly reactive 5'-deoxyadenosyl radical (dAdo). This carbon based radical then acts as an initiator for a great number of biological radical reactions.^[21–22] The proposed process is remarkable in many ways. First, a metalloradical as attacking species in an S_H2 is unusual, and iron (II) has to the best of our knowledge never been observed in this role outside of biological systems. Second, the normally difficult reductive cleavage of a trialkylsulfonium group is achieved easily in this reaction.

While Holm and coworkers have shown in model studies that site-differentiated [4Fe-4S] clusters are capable of reductively cleaving dialkylarylsulfonium salts, as well as sulfonium species bearing electron-withdrawing groups, in what is a reductive cleavage, (although probably not an S_H2 reaction, since their system's redox potentials match^[4–5]), they did not cleave any

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trialkylsulfonium species, much less SAM itself. To the best of our knowledge this has not been achieved in a classical chemical way so far, only electrochemically^[23] or by the use of solvated electrons in aqueous solutions by radiolysis, or photochemically^[24-26]. The proposed S_H2 reaction in RSE has also never been directly observed either *in vitro* or *in vivo*, given that the formed dAdo radical has not been unambiguously detected^[27] due to its short lifetime. However, evidence for this reaction has been gathered, the most direct by Frey and coworkers.^[28-29] They were able to observe a stabilized form of the proposed dAdo radical by using S-3',4'-anhydroadenosyl-L-methionine, again not a trialkylsulfonium species, instead of SAM as enzyme substrate. In this work we report the direct observation of some examples of intramolecular S_H2 reactions involving an iron (II) metalloradical reductively cleaving trialkylsulfonium groups in the gas phase. Further, we show that these S_H2 processes only occur in geometrically constrained systems, where the sulfonium moiety can approach the iron (II) in an axial way. Lastly, we discuss what impact our findings might have on the TS structure of RSE.

Scheme 2. Proposed formation of the 5'-deoxyadenosyl radical in Radical SAM Enzymes. Adapted from Frey, 2003.^[30]

Results

Gas phase studies on iron (II) compounds with various sulfonium bearing ligands (Figure 1, 2-11) were performed by means of ESI-MS and collision induced dissociation (CID). Mixing equimolar amounts of iron (II) acetate with (S)-N,N'-(2-(dimethylthio)ethyl)ethylene]bis salicylideneimine (S-met-salmet) in degassed methanol under inert atmosphere and electrospraying this mixture showed the formation of complex **2**. This compound, as well as its derivatives **3-6**, underwent an S_H2 reaction upon CID involving the iron (II) center and the sulfonium moiety, yielding a methyl radical for **2**, **3** and **4**, a 2-tetrahydrofuranylmethyl (major) and methyl (minor) radical for **5**, and a benzyl radical for **6** (Scheme 3). Looking at the CID spectrum of **2** (Figure 2 (top), for complexes **3** and **4** see SI Figure 15 and 17), neutral fragments with the mass 15 u, corresponding to a methyl radical, and 62 u, coming from the formation of dimethyl sulfide (SMe₂) by S-C_γ cleavage (bond nomenclature see Figure 1), are seen. To verify that the fragment of 15 u really is a methyl radical formed by a S_H2 reaction, we electrosprayed the uncomplexed ligands (Figure 2, middle, SI Figures 10 and Figure 11 for **3** and **4**), as well as the analogous zinc (II) complexes (Figure 2, bottom, SI Figures 16 and 18 for **3** and **4**). Zinc (II) displays similar coordination chemistry as iron (II), but, in contrast to iron, it does not participate in one-electron chemistry. In line with the proposed mechanism, neither the uncomplexed ligand, nor the zinc complex show any trace of radical formation

under CID conditions over a range of collision offset from 10 V to 100 V. This strongly suggests that the methyl radical formed in the iron system indeed stems from a S_H2 reaction.

Figure 1. SAM, Fe(II)-SAM and Fe(II)-S-R₃-salmet complexes. **1**: SAM, **2-6**: [Fe(S-R₃-salmet)]⁺ and derivatives, **7**: [Fe(OAc)(SAM)]⁺, **8**: [Fe(Gly)(SAM)]⁺, **9**: [Fe(SAM)(Tm-Me)]⁺, **10**: [Fe(SAM)(Tp*)]⁺ and **11**: [Fe(SAM)(Tp-Me,Ph)]⁺. dAdo=5'-deoxyadenosyl.

Due to the apparent similarity of the reaction happening in complex **2** with the process proposed to form dAdo radicals in RSE (Scheme 2), namely an iron species reductively cleaving a trialkylsulfonium moiety by S_H2, complexes **5** and **6** where synthesized to investigate the regioselectivity of the S_H2 process. Here, instead of two indistinguishable methyl groups, the sulfonium moiety bears only one methyl group, the second methyl having been exchanged for a 2-tetrahydrofuranylmethyl group (**5**), or a benzyl group (**6**), respectively. The 2-tetrahydrofuranylmethyl group was chosen for its similarity to the ribose unit in SAM; the benzyl group was chosen because of the expected weak S-C_{benzyl} bond strength.

Scheme 3. Collision-induced dissociation of [Fe(II)(S-R₃-salmet)]⁺ initiates an S_H2 reaction forming a penta-coordinate [Fe(III)](salmet)⁺ species and an R₃ radical.

Since the sulfonium moiety can rotate, we would expect selectivity in radical formation to be determined by the homolytic S-C bond strengths during CID for these complexes^[31]. Indeed, for complex **5** we observe a small peak stemming from the loss of the less stable methyl radical and a bigger peak stemming from the formation of the somewhat more stable 2-tetrahydrofuranylmethyl radical (Figure 3, top). However, the dominating fragmentation channel is again the S-C_γ cleavage forming methyl-2-

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tetrahydrofuranylmethyl sulfide (MTS). For complex **6**, we observe homolytic cleavage of the weak S-C_{benzyl} bond, as expected, and neither methyl radical formation, nor S-C_V cleavage (Figure 4, top). It appears that benzyl radical formation is energetically favored enough to out-compete these other two processes.

Figure 2. Top: CID spectrum of [Fe(II)(S-met-salmet)]⁺ (**2**); For higher collision offsets see SI Figure 12. Middle: uncomplexed S-met-salmet. Bottom: [Zn(II)(S-met-salmet)]⁺. For higher collision offsets see SI Figure 13. Insets left: Experimental (black) and calculated (red) isotope pattern of the ions; Insets right: Zoom at 396 (top) and 404 (bottom) where fragment peaks from methyl loss should appear. All spectra have been measured at at 0.1 mTorr and collision offset of 25 V.

The formation of any radicals, at all, in systems **2-6** is remarkable, since most sulfonium species sprayed alone are not cleaved in a homolytic way in CID experiments (not true for methyl groups). This is the case, not only for SAM itself (Figure 5) with its 2-tetrahydrofuranylmethyl-like ribose moiety, but also for benzyl groups (see SI Figure 9).

CID spectra of the uncomplexed ligands (Figure 3, middle for S-tet-salmet and Figure 4, middle for S-bn-salmet) again showed no traces of radical formation at all. The same is true for the corresponding one-electron chemistry inactive zinc (II) complexes (Figure 3, bottom and Figure 4, bottom), indicating that it is indeed an S_H2 that occurs for the iron complexes. The [Zn(II)(S-bn-salmet)]⁺ complex does not form significant fragments at all during CID with a collision offset of 25 V and gas pressure of 0.1 mTorr. Looking at the energetics, it becomes obvious that these reactions cannot proceed in a two-step process where an electron is transferred from the iron (II) to the sulfonium group by an outer sphere mechanism, followed by fragmentation of the formed sulfuranly radical. We computed a vertical electron transfer (without optimization of products) from **2** to a trimethylsulfonium cation, as an estimate for the general intramolecular outer-sphere

electron transfer, to cost 573 kJ/mol (M06-L/cc-pVDZ). Upon allowing the structures, e.g. the unstable trimethylsulfuranly radical in the hypothetical two-step process, to relax geometrically, this value drops to a still too-high 325 kJ/mol. In contrast, the S_H2 reaction in [Fe(S-met-salmet)]⁺, which corresponds to an inner-sphere mechanism, appears in our calculations to be endothermic by 48.3 kJ/mol, with an activation energy of 50.2 kJ/mol, which is clearly preferable to the outer-sphere alternative.

Figure 3. Top: CID spectrum of [Fe(II)(S-tet-salmet)]⁺ (**5**). Middle: uncomplexed S-tet-salmet. Bottom: [Zn(II)(S-tet-salmet)]⁺. Insets left: Experimental (black) and calculated (red) isotope pattern of the ions; Insets right: Zoom at 466 (top) and 474 (bottom) where fragment peak from methyl loss should appear. Inset middle: Zoom at 404 (bottom) where a fragment peaks from 2-tetrahydrofuranylmethyl radical loss would appear. MTS = methyl tetrahydrofuranylmethyl sulfide. All spectra have been measured at at 0.1 mTorr and collision offset of 25 V.

The computed structure of the TS for this process can be seen in Figure 6. The Fe-S-CH₃ angle in the TS is not linear, but rather 159°. The Fe-S bond distance is 2.57 Å and the S-CH₃ bond distance 2.52 Å (Table 2).

For the main channel in all these systems except **6**, the cleavage of the S-C_V bond, we compute a reaction barrier of 51.5 kJ/mol (SI Figure 24). The resulting intermediate, where the dimethyl sulfide is coordinated to iron but not the CH₂ moiety (Scheme 4), lies 20 kJ/mol above the starting material. Interestingly, according to Mulliken spin densities, the CH₂ moiety has radical character and is therefore probably also the product of an S_H2 reaction, even though the Fe-S-C_V angle of only 103° is unfavorable. This intermediate can be stabilized by coordination of the CH₂ group to the iron to form a pseudo-octahedral iron (IV) complex (-34 kJ/mol). However, we could not find a TS leading directly to this stable conformation, namely an oxidative addition TS. Dissociation of dimethyl sulfide from this complex then leads to the -62 fragment measured in the CID experiment. A S_N2 TS where iron attacks C_V and extrudes SMe₂ could also not be found.

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In the uncomplexed ligand the S-C_V bond cleavage fragment is also formed, but by heterolytic S-C_V cleavage. Also in the zinc complexes heterolytic S-C_V bond cleavage is the only channel observed, since an S_H2 reaction is not possible (as is also seen by the lack of formation of radicals). This also explains why the daughter peak stemming from S-C_V cleavage is more pronounced for the iron than for the zinc complexes, since heterolytic as well as homolytic S-C_V bond cleavage are probably present at the same time.

Looking at the S-met-salmet derivatives **3** and **4**, we found that a donating group, as in complex **3**, decreases both the activation and the reaction endothermicity, while an electron withdrawing group, like in complex **4**, increases them both. For the influence of the substituents on the TS geometry, no significant statements can be made, since the differences between the structures are very small and probably within the margin of error of the calculation.

Figure 4. Top: CID spectrum of $[\text{Fe}(\text{II})(\text{S-bn-salmet})]^+$ (**6**). Middle: uncomplexed S-bn-salmet. Bottom: $[\text{Zn}(\text{II})(\text{S-bn-salmet})]^+$. Insets left: Experimental (black) and calculated (red) isotope pattern of the ions; Insets right: Zoom at 472 (top) (the small peak is located at 471 and does not stem from methyl radical loss) and 480 (bottom) where fragment peaks from methyl loss should appear. Inset middle: Zoom at 404 (bottom) where a fragment peak from benzyl radical loss would appear. All spectra have been measured at 0.1 mTorr and collision offset of 25 V.

To investigate what kind of prerequisites are necessary for the S_H2 reactions we observe to proceed, we also investigated a variety of iron (II) complexes with non-salen-type ligands. While the salen-type complexes are geometrically rather constrained we decided to move to complexes where the sulfonium group bearing moiety, like in RSE, binds in a bidentate instead of a tetradentate manner. SAM itself was chosen as the sulfonium bearing ligand together with a variety of space-holder ligands allowing different electronic as well as steric properties (complexes **7-11**). As seen in Figure 5, SAM alone does not cleave an S-C_{alkyl} bond

homolytically in CID experiments. To the contrary, the favored bond breaking is heterolytic at the S-C_S site, forming methionine and an adenosyl cation. A second observed channel results from the heterolytic cleavage of the S-C_V bond. Neither homolytic nor heterolytic cleavage of the S-C_{methyl} bond could be observed at all. Moving to complexes **7** to **11**, all CID studies led to qualitatively similar results, in spite of the complexes' apparent differences. The most important observation is the fact that **no** homolytic cleavage of SAM, and therefore **no** dAdo formation, was observed (Figure 7, SI Figures 5-8). All relevant decay channels stem from two-electron-processes over the entire investigated range of collision energies from 10 V up to 100 V. Moreover, complexed SAM behaves differently than the free molecule. In uncomplexed SAM, heterolytic cleavage of the S-C_S bond and the S-C_V bond occur simultaneously, with S-C_S breakage dominating. In SAM complexes with iron (II), the S-C_S cleavage channel is shut down.

Figure 5. CID Spectrum of SAM (**1**) at 0.1 mTorr and collision offset 50 V. No dAdo formation was observed. HSL: homoserine lactone, met: methionine. Inset: Experimental (black) and calculated (red) isotope pattern of ions.

Figure 6. DFT-optimized TS structure of the S_H2 reaction in **2**.

Further investigations of this phenomenon showed that the preference for selective S-C_V bond cleavage in these complexes is unchanged, even if the adenosyl moiety is exchanged by a benzyl (S-benzyl methionine, SBM) or a methyl group (S-methyl

Scheme 4. Mechanism for homolytic S-C_V cleavage and the formation of the SMe₂ fragment (-62).

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methionine, SMM), or if the iron is replaced by zinc (SI Figures 1-4). In other words, iron- and zinc complexed SAM derivatives in these systems have an inherent propensity for breaking the S-C_V bond under CID conditions, even if the S-C_{5'} bond is formally weaker. We suspect this to be a result of an intramolecular S_N2 5-exo-tet reaction, wherein the carboxylate attacks C_V and extrudes the sulfide (Scheme 5). To demonstrate the energetic feasibility, reaction mechanism a) in (Scheme 5) has been calculated for the SMM equivalent of complex **8** to have an activation barrier of only 13.5 kJ/mol.

Figure 7. CID spectrum of [Fe(OAc)(SAM)]⁺ (**5**) at 0.1 mTorr and collision offset 50 V. No dAdo formation was observed. HSL: homoserine lactone, MTA: Methylthioadenosine. Inset: Experimental (black) and calculated (red) isotope pattern of ions. The discrepancy between calculated and experimental spectrum at *m/z*=512 stems from a background artifact.

To investigate the origin of the different behaviors of the salen-type complexes **2-6** (radical formation) versus the complexes **7-11** (no radical formation), several additional experiments and computations were performed. The most important difference concerning this subject are the structural discrepancies between the complexes (Figure 8 for [Fe(S-met-salmet)]⁺, Figure 9 for [Fe(OAc)(SMM)]⁺). The almost perfectly planar structure of the salen moiety in complexes **2-6** places the sulfonium group beautifully above the iron core of the complex allowing an attractive interaction of the sulfonium moiety's lone pair with the high spin iron, worth 53.9 kJ/mol in **2** (Table 2). This is not astonishing, since sulfonium groups are known to interact with metals.^[32-33] The geometric arrangement in this case is very similar to the one in RSE where the sulfonium group also adopts a pseudo-axial position.^[34-37] In the complexes [Fe(OAc)(SMM)]⁺, **7** (SI, Figure 22) and **8** the sulfonium group does not coordinate (Fe-S distance: 4.01 Å for [Fe(OAc)(SMM)]⁺). The ground state of [Fe(OAc)(SMM)]⁺ has a distorted tetrahedral coordination sphere which hinders the iron-sulfur interaction. Even if the geometry optimization is started from a pseudo-square-pyramidal geometry resembling [Fe(S-met-salmet)]⁺, with the sulfonium group occupying the pseudo-axial position, the complex relaxes to the known pseudo-tetrahedral geometry. TS searches on this compound for an S_H2 process comparable to the one happening in the salen-type complexes proved unsuccessful.

Another obvious difference between the two classes of systems (**2-6** versus **7-11**) is the fact that **7-11** have a 5'-deoxyadenosyl group on the sulfonium group instead of a methyl, benzyl or 2-tetrahydrofuranylmethyl group.

Replacing this adenosyl group by a second methyl group for complex **8**, forming [Fe(Gly)(SMM)]⁺, or by a benzyl group for complex **7**, forming [Fe(OAc)(SBM)]⁺, did not lead to radical formation (SI Figure 4, SI Figure 2).

Further, we also investigated if the different behavior could be an issue of redox potentials. Even though we do not assume the reaction to be a simple electron transfer, redox potentials can still tell us something about reactivity, since iron is formally oxidized

in the radical formation process, while the sulfonium group is reduced.

Scheme 5. Mechanisms for the selective cleavage of the S-C₇ bond in complexes **5-9**, leading to formation of a) methyl thioadenosine (MTA) and b) homoserine lactone (HSL).

A cyclic voltammetry study on our complexes failed due to irreversibility of the oxidation process in the non-salen complexes (SI Figure 19, 20). As an alternative, which might, in fact, be more appropriate as an indicator for the gas-phase dissociations observed in this study, we considered ionization potentials (IP) of the iron (II) complexes. We calculated the adiabatic and the vertical IPs of every class of complexes that we had measured by ESI-MS and CID.

Complex	adiabatic IP/eV	vertical IP/eV	radicals
[Fe(SAM)(Tm-Me)] ⁺ , 9	7.05	7.36	×
[Fe(SAM)(Tp-Me,Ph)] ⁺ , 11	7.40	7.61	×
[Fe(SAM)(Tp*)] ⁺ , 10	7.40	7.69	×
[Fe(S-met-OMe-salmet)] ⁺ , 4	8.28	8.42	✓
[Fe(S-met-salmet)] ⁺ , 2	8.70	8.83	✓
[Fe(S-met-F-salmet)] ⁺ , 3	8.80	8.92	✓
[Fe(OAc)(SAM)] ⁺ , 7	8.96	9.51	×
[Fe(Gly)(SAM)] ⁺ , 8	9.29	9.33	×

Table 1. Calculated ionisation potentials (M06-L, cc-pVDZ)

The quintet state was hereby found to be the ground state for iron (II) and the sextet state for the oxidized iron (III) species (SI, Table 1).

Figure 8. DFT-optimized structure of **2** (M06-L/cc-pVDZ).

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Complex	ΔE_{act}	ΔE_{react}	$\Delta E_{\text{coord, sulfonium}}$	$\Delta E_{\text{coord, sulfide}}$	React $\angle_{\text{Fe-S-CH}_3}$	$\angle_{\text{Fe-S-CH}_3}$ (TS)	React $d_{\text{Fe-S}}$	TS $d_{\text{Fe-S}}$	Prod $d_{\text{Fe-S}}$
3	45.9	38.8	59.3	79.4	118.3°	158.7°	2.60 Å	2.57 Å	2.53 Å
2	50.2	48.3	53.9	89.1	122.8°	158.9°	2.63 Å	2.57 Å	2.50 Å
4	51.6	50.8	50.2	90.3	123.3°	159.1°	2.64 Å	2.56 Å	2.52 Å

Table 2. Energies (in kJ/mol) for S_H2 the reaction of $[\text{Fe}(\text{S-met-salmet})]^+$ and derivatives and structure parameters for the reactant the TS and the product. ΔE_{act} : activation energy; ΔE_{react} : reaction energy; $\Delta E_{\text{coord, sulfonium}}$: coordination energy of the sulfonium group in the reactant structure; $\Delta E_{\text{coord, sulfide}}$: coordination energy of the sulfide in the product structure.

Figure 9. DFT-optimized structure of $[\text{Fe}(\text{OAc})(\text{SMM})]^+$ (M06L/cc-pVDZ).

The values, obtained using the M06-L functional, which has been used for iron complexes previously [38–39], can be seen in Table 1. In addition, we performed the same calculations with three other functionals, namely M06, B3LYP and TPSS (see SI Table 2). All of these functionals afforded the same trend. The iron (II) (S-met-salmet) complexes exhibit somewhat lower adiabatic potentials than the $[\text{Fe}(\text{OAc})(\text{SAM})]^+$ and $[\text{Fe}(\text{Gly})(\text{SAM})]^+$, but higher than the adiabatic potentials for **7**, **8** and **9** (7.40 eV). The vertical IPs display analogous trends.

To better understand the TS of the radical formation process of $[\text{Fe}(\text{S-met-salmet})]^+$ in general, we performed Natural Bond Orbital (NBO) analyses at the M06-L/cc-pVDZ level. Figure 10 shows the visualization of NBO calculations.

Figure 10. Open shell NBOs and orbital interactions of the TS of $[\text{Fe}(\text{s-met-Salmet})]^+$. Bonds are defined for orbital interactions to describe the microscopic reverse of the S_H2 reaction measured.

The bonds were specified to represent a methyl radical attacking a thioether coordinated to iron (III). One can hereby think of this

as the microscopic reverse of the reaction observed in the CID experiment.

In agreement to the Hammond postulate, this choice is justified by the very product-like TS for the forward reaction, as indicated by our computed 50.2 kJ/mol activation energy and 48.3 kJ/mol endothermicity in that forward direction. Compared to the standard S-C bond length of approximately 1.8 Å, the S-CH₃ bond with a length of 2.52 Å in the TS is not yet formed to a significant extent.

Moreover, the incoming CH₃ radical is still almost planar (Figure 6). This direction of the reaction can be directly compared to Schiesser's systems (see Discussion), and it is also easier to treat from a practical point-of-view. Using the "second order perturbation theory analysis of Fock matrix in NBO basis" we found several significant orbital interactions for the geometry of the TS. The SOMO $\rightarrow \sigma^*(\text{Fe-S})$ interaction found in the β spin set amounts to 47 kJ/mol. In the α spin set a LP_s $\rightarrow \text{SOMO}^*$ interaction of 6 kJ/mol and a $\sigma(\text{Fe-S}) \rightarrow \text{SOMO}^*$ interaction of 105 kJ/mol were found.

Figure 11. DFT optimized structure of the $[\text{Fe}(\text{S-met-salmet})]^+$ linear TS with an Fe-S-CH₃ bond angle of 180°.

To obtain information about how much the bent TS differs from the linear TS in terms of energy, we calculated the TS of **2** with the Fe-S-CH₃ angle constrained to be 180° (Figure 11). We found the linear TS to lie 13 kJ/mol higher in energy than the bent TS. An NBO analysis of the linear TS (Figure 12) gave a $\sigma(\text{Fe-S}) \rightarrow \text{SOMO}^*$ interaction worth 125 kJ/mol in the α spin set and a SOMO $\rightarrow \sigma^*(\text{Fe-S})$ interaction worth 57 kJ/mol in the β spin set. No LP_s $\rightarrow \text{SOMO}^*$ interaction was found, which is expected based on symmetry. In Figure 13, a Fe-S-CH₃ angle scan can be seen. Starting at the bent TS (159°), the angle was decreased in one scan and increased in a second in steps of 2.5° each. The

¹ In a closed-shell calculation, SOMO stands for singly occupied molecular orbital, which is characteristic for radicals. Since we are dealing with open-shell calculations, we split this "SOMO" into an

occupied spin-orbital called "SOMO" and an unoccupied spin-orbital with corresponding spatial component "SOMO*".

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structures were optimized at each point with the respective Fe-S-CH₃ angles fixed. In this graph energies are given as pure electronic energies without zero-point energy correction.

Figure 12. Open shell NBOs and orbital interactions of the linear TS of [Fe-(S-met-salmet)]⁺ (Fe-S-CH₃ bond angle: 180°). Bonds are defined for orbital interactions to describe the microscopic reverse of the S_H2 reaction measured.

Discussion

An S_H2 reaction involving a “metalloradical”

Electrosprayed iron (II) (S-met-salmet) complexes (**2-4**) undergo an S_H2 reaction during CID, forming iron (III) (salmet) and methyl radicals. Iron (II) (S-tet-salmet) (**5**) complexes form preferentially 2-tetrahydrofuranylmethyl radicals, and, in a second channel, methyl radicals and iron (II) (S-bn-salmet) (**6**) forms benzyl radicals exclusively. The fact that no radicals are formed at all if the salen-type ligands are electrosprayed either uncomplexed, or as the one-electron-chemistry inactive zinc (II) complexes, is a very strong indication that we are actually observing S_H2 processes. In these S_H2 processes, the iron is formally oxidized and the sulfonium group formally reduced.

What makes the presented reaction stand out from classical S_H2 reactions is the fact that a “metalloradical” takes the role of the attacking species. Although paramagnetic metal ions like iron (II) are, strictly speaking, not radicals, their similarity to classical radicals is apparent, given the “isolobal” analogy^[40].

A further interesting point that distinguishes the S_H2 reactions presented here from classical S_H2 reactions like the ones described by Schiesser is the fact that the sulfonium group is interacting with iron already before the start of the reaction (Figure 8). One could ask the question if the electron transfer already happens to a certain extent when the sulfonium moiety is interacting with the iron in the ground state. However, this can be excluded, given that the Mulliken spin density on the sulfur does not change significantly upon coordination.

The TS is not reached by the attacking radical approaching its reaction partner, but by rotation of the sulfonium group around the S-C_γ bond to the “backside attack conformation” needed for optimal orbital overlap (Figure 6). This ability of the sulfonium group to rotate also has an influence on the regioselectivity of the reaction. Not the Fe-S-C_γ angle but the other two Fe-S-C angles can easily reach the optimum value of 159°. Therefore the choice between the two possible radicals is given by the bond energies, i.e. radical stabilization. The 2-tetrahydrofuranylmethyl radical is

preferred moderately over the methyl radical in **5**, and the benzyl radical exclusively over the methyl radical in **6**.

The conceptually identical chemical process has been proposed to occur in RSE with the difference that the electron donor species is an iron-sulfur cluster instead of a simple iron (II) atom, and that dAdo radicals are formed exclusively.

The concomitant cleavage of the S-C_γ bond that is not observed in RSE but observed in **2-4** and **6** also shows radical formation is not by default. According to the Mulliken spin density on C_γ in the TS, the S-C_γ bond is cleaved homolytically, indicating that this process is also an S_H2 process, even though the Fe-S-C_γ bond angle of 103° is far away from the optimum of 159° calculated for methyl cleavage (Figure 13, SI Figure 24). Why this process is still competitive in spite of such a small bond angle can be explained by the sulfur-lone-pair-iron interaction that is not lost in the TS as it is the case for the TS of the homolytic cleavages of the other two bonds. Furthermore, no bond rotation is needed to reach the TS; the ground state structure is perfectly preorganized for this reaction. While, in terms of activation energies, radical formation and S-C_γ bond cleavage are very similar, thermodynamically the latter is preferred. In order to allow selective radical formation, RSE have to control the TS of the radical generation step tightly. How S-C_γ bond cleavage is prevented in RSE is not known. It could have something to do with the fact that the iron-sulfonium moiety distance in the ground state in RSE is longer than in our systems, as crystal structures reveal^[34-37]. This would then not allow for the TS stabilization by sulfur-lone-pair-iron interaction for the S-C_γ bond cleavage TS and therefore disfavor this process and uniquely cleave the S-C_δ bond. Interestingly, in a recently published paper, Dong et al.^[41] revealed deep insights into the mechanism of diphthamide biosynthesis by a diphthamide-biosynthesis-protein-1-diphthamide-biosynthesis-protein-2-heterodimer by means of EPR experiments and crystal structures. This enzymatic system cleaves the S-C_γ bond in SAM and produces methyl thioadenosine (which is the chemical equivalent of SMe₂ in the reaction of **2**). In what way their observation is related to ours is yet to be investigated. It is, however, exciting that our simple model systems shows both type of reactivities, namely radical cleavage of the S-C_δ bond as well as cleavage of the S-C_γ bond. With this work, we could demonstrate that an iron species can reductively cleave even trialkylsulfonium groups with their extremely negative reduction potentials via a S_H2 reaction, supporting the mechanistic proposal for the radical generation step in the 5' deoxyadenosyl radical generating enzymes.

Why do only the iron (II) salen-type complexes form radicals?

One might ask how we can claim that we observe a conceptually analogous reaction to what is proposed to occur in RSE for our salen-type complexes **2-6**, when complexes **7-11** do not show any radical formation at all, even though, at first sight, they might look more similar to the active site of RSE. It is noteworthy that, in RSE, none of the reactivity found for **7-11** is found. The fact that we do not observe any S_H2 process or radical formation for those complexes, as well as their SMM- and SBM-bearing derivatives, suggests that the radical generation reaction needs more than just the presence of iron and a sulfonium group to occur. One could explain the difference in reactivity in three different ways: First, one could argue, that, only for the S-met-salmet complexes and

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derivatives **2-6**, the radical formation process is feasible in terms of energetics. Second, the different architectures of the compounds, especially the keto group that is present in **7-11**, could lead to different processes dominating the CID spectrum, meaning that S_H2 is only observed if competing, otherwise more favorable, processes are suppressed. Third, the geometric arrangement of the ligands and the sulfonium group around the iron core could be decisive for the occurrence of an S_H2 reaction. The first proposition was addressed by calculation of IPs of the complexes. In Table 1 (SI Table 1) it is seen that IPs are heavily influenced by the nature of the ligands. However, no radical generation is observed in any of the non-salen-type complexes, regardless of low or high IPs. One could now argue that IPs are still decisive and that the S_H2 reaction in the low IP complexes **9-11** is only hindered by steric constraints. Even if steric issues are likely to have an influence, they are nevertheless not a sufficient explanation. During CID, homoserine lactone (HSL) is formed in all of these three compounds, leaving methylthioadenosine (MTA) coordinated to the iron center (Scheme 5, SI Figures 5-8). This observation indicates that the iron and the sulfonium group can come in proximity to each other, in spite of their steric bulk. Using the SAM derivative SMM, that can only coordinate via the amino group and the carboxylate, we found that HSL formation is also not the product of SAM coordinating through the adenine moiety. It occurs for SMM complexes as well (SI Figure 4). In addition, the HSL loss in the analogous Zn (II) complexes shows that this product channel does not derive from an one-electron process. We can therefore exclude IPs as the decisive factor for the lack of S_H2 reactions in the compounds **5-9**.

Figure 13. TS Fe-S-CH₃ angle scan for compound **2** in steps of 2.5° (except for last step which was chosen to be 180°). The curve's minimum corresponds to the bent TS (159°). Going to the right side leads to the linear TS (180°). Energies in this graph are not zero-point corrected.

The second and the third propositions, however, might indeed be more relevant. The imino group in the S-met-salmet ligand is the functional analog to the carboxylate moiety in SAM that participates in the bidentate binding of an amino acid to the metal center. The process shown in Scheme 5 is therefore not possible, since the imino group is geometrically constrained against

engaging in an intramolecular S_N2 displacement to form homoserine lactone. In RSE, where the reaction happens with SAM, and the keto group is present, side reactions are probably suppressed by the enzymatic scaffold that helps control SAM reactivity. Recent studies on Pyruvate Formate-Lyase Activating Enzyme^[42] revealed, in addition, a monovalent cation, most likely K⁺, bound to the carboxylic acid moiety of SAM. Possibly it helps to decrease the carboxylic acid's reactivity.

In our opinion, the most important factor for the inability of the non-salen complexes **7-11** to form radicals is found in their geometry. Only the salen-type complexes exhibit a pseudo-square pyramidal structure, allowing the axial iron-sulfonium group interaction (Figure 8) like in RSE. This means that, even in the ground state, the sulfonium group is placed beautifully above the dz^2 orbital on the iron, only a bond rotation away from the S_H2 transition state. In [Fe(OAc)(SMM)]⁺ (Figure 9), **7** and **8** the complex geometry is much more distorted, inhibiting this iron-sulfonium group interaction and therefore probably the S_H2 process. In **9-11** the axial placement of the sulfonium group is hindered by the tridentate nature and geometry of the space holder ligands. As shown by crystal structures,^[34-37] in RSE we have a pseudo octahedral arrangement around the unique iron with the sulfonium moiety of SAM in one of the axial positions. This situation is geometrically close to our salen-type complexes and allows for this direct iron-sulfonium moiety interaction.

Energetic considerations and the geometry of the TS

Orbital interactions and the attendant geometric constraints are the origin of stereoelectronic effects in two-electron chemistry. We consider that comparable constraints may apply for the S_H2 reactions as well. The literature available on the radical generation step in RSE, in general, gives the impression that the S_H2 reaction is seen as an analog to an S_N2 reaction, just lacking an electron. Based on the work of Kampmeier^[43] and Beckwith^[44] who showed the necessity for a backside attack in S_H2 reactions, it has sometimes been explicitly or implicitly assumed that the TS needed collinear arrangement of iron, the sulfonium's sulfur atom and the departing radical. However, as Schiesser^[14] and coworkers have shown, an S_H2 reaction on a sulfur center does not go via a collinear, but rather a bent, TS because of sulfur lone pair involvement in the TS (Scheme 1). As stated by Renaud et al.^[45], this S_H2 mechanism shown for reactions at sulfur and selenium might be generally applicable, even for reactions involving non-carbon-based radicals^[11]. We propose to generalize our findings on orbital interactions and TS geometry in our systems on RSE. This means that, looking at the microscopic reverse of the reaction, an adenosyl radical also reacts mainly as an electrophile, via a bent TS.

This finding bears importance for the understanding of RSE and how they control the generation of a highly reactive 5'-deoxyadenosyl radical. Radical generation has to happen in a highly controlled manner to avoid damage to the enzyme and other nearby molecules by unspecific reactions of the radical. On the basis of our findings, we *speculate* that there may be stereoelectronic control of release of the radical.

For **2**, thinking about going from the starting structure with the sulfur atom's lone pair pointing towards the iron with an Fe-S-CH₃ bond angle of 123° to the TS with its bent structure, the sulfonium group has to rotate around the S-C_γ bond (36° for **2** (57° if the TS

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were linear)). In RSE, having a bent TS structure means less rotation for the bulky adenosyl group to reach the TS. It is known, that RSE, even with the iron sulfur cluster being in the reduced state, as is required for the reaction, can bind SAM in the absence of substrate in a relatively stable state.^[46] No, or only very slow, SAM cleavage is observed under these circumstances. Given our results, it is reasonable to propose that the enzyme could control SAM cleavage by controlling the Fe-S-C bond angle (Figure 14). As is known from the plethora of crystal structures of RSE, SAM does interact and form hydrogen bonds with the enzymatic scaffold that holds the molecule in place in the resting state. Binding of the substrate causes structural changes in the enzyme. This might now allow the previously “fixed” bulky adenosine moiety to move, and the S-C γ bond to rotate to reach an angle around 159° needed for the lowest energy TS. If we take the approximate 14 kJ/mol difference in TS energy from our model system between a TS that keeps the Fe-S-C bond angle of the resting state (123°) and a TS that adopts the lowest energy angle of 159°, using the Arrhenius equation, we can estimate a relative rate difference of almost 300 at room temperature. The difference in rates between the two TS is therefore big enough to be relevant for reaction control. If true, our proposition could explain the enzyme inactivity in absence of substrate, and shows how the enzyme stereoelectronically modulates its reactivity by controlling the Fe-S-C angle.

Figure 14. Speculative mechanism of stereoelectronic reaction control in RSE. In the resting state before the reaction, rotation of the S-C γ bond is inhibited by the enzyme. Substrate binding causes a conformational change in the enzyme and enables rotation around this bond to make the TS accessible. E depicts enzymatic side chains.

However, it should be stated, that the Fe-S-C bond angle of the resting state in RSE crystal structures is generally higher than 123°. The crystal structures are often resolved at an accuracy of 1.5 Å or worse, leaving some uncertainty for the actual bond angle. Independent of this, turning of the S-C γ bond is expected to cost energy in either case and can therefore be used to control reactivity.

Conclusions

In this study we describe the intramolecular chemical reductive cleavage of a trialkylsulfonium species by iron (II) in iron(II) (S-met-salmet), iron (II) (S-tet-salmet) and iron (II) (S-bn-salmet) complexes and derivatives in the gas phase. Extremely mismatched redox potentials and comparison to related analogous complexes with zinc(II) as a one-electron-chemistry-inactive species indicate that the process follows a homolytic substitution reaction (S_H2) mechanism. In the S_H2 reaction, which

goes through a three-center, three-electron TS, iron (II) is formally oxidized to iron (III), and the sulfonium's sulfur atom formally reduced, leading to the formation of an alkyl radical and a thioether coordinating to the iron(III). In contrast to classical S_H2 reactions, we deal here with the unusual case of a high spin “metalloradical” (iron (II)) in the role of the attacking radical.) In addition the reaction does not proceed by the radical approaching its reaction partner from the back to reach the TS; the reaction partners are already interacting with each other in the ground state. The “back-side-attack” TS geometry is reached by rotation of the sulfonium group coordinated to the iron in the ground state. What makes this reaction especially interesting is the conceptual similarity to the proposed radical generation step in RSE. In both of processes an iron species with the function of an electron reservoir reductively cleaves a trialkylsulfonium species, producing an alkyl radical via a S_H2 reaction. Geometrically the systems are also related, because both systems contain a trialkylsulfonium bearing ligand that interacts with the metal center via an intramolecular bridge of the same length and orientation and in a similar geometric coordination environment.

The failure to reproduce the observed radical formation via S_H2 reaction in iron (II) complexes bearing an S-Adenosyl Methionine molecule and more general space holder ligands showed that geometric constraints are necessary for the reaction to occur. Especially the axial placement of the sulfonium moiety over the iron seems to be crucial. With the help of DFT calculations and NBO analyses we also looked at reactant and TS geometries of our complexes involved in the S_H2 process. We found evidence that the S_H2 proceeds via a TS exhibiting a bent (159°) instead of a collinear Fe-S-CH₃ angle. The bent TS is hereby significantly favored over the linear TS by 13 kJ/mol. From the insights we gained with our model systems, we speculate that the TS in Radical SAM Enzymes is reached from the ground state via a specific rotation around the S-C γ bond to achieve the optimum “bent” Fe-S-C angle, potentially facilitating stereoelectronic control of radical production, triggered by substrate binding.

Experimental Section

ESI-MS studies were performed on a Thermo Finnigan TSQ Quantum instrument with a flow rate of 5 μ l/min. The measurements were conducted at spray voltages from 4500 V to 5000 V at a capillary temperature of 473 K. Argon was used as collision gas for CID studies with a pressure of 0.1 mTorr.

Full density functional theory (DFT) structure optimizations were performed using the Gaussian 09^[47] program. The functionals employed were M06,^[48] M06-L,^[49] B3LYP,^[50-53] and TPSS^[54-55] using the cc-pVDZ^[56-57] basis set for the IP calculations and M06-L with cc-pVDZ for all further studies. M06-L is known to be adequate for transition metal complexes and has been used for iron (II) before.^[38-39] For the numerical integration of the calculations an ultrafine grid was chosen. Frequency analyses were performed for each optimized structure to verify the absence of imaginary frequencies and to obtain zero-point corrected energies. All the energies reported are zero-point corrected electronic energies (except for the angle scan were electronic energies are reported). Iron (II) complexes were calculated in the quintet state and iron (III) species in the sextet state, because those states were energetically most favorable (SI, Table 1). The angle scan was performed starting at the bent TS and going into both directions by increasing or decreasing the Fe-S-CH₃ angle in

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steps of 2.5° (except for the largest bond angle which was set to be 180°) with subsequent optimization of the structure at that fixed angle. NBO analyses were performed using the NBO 6 program.^[58] Desired resonance structures were defined using the \$CHOOSE keyword (see SI for input file).

Selected Synthetic Procedures

All reactions were done under inert atmosphere, unless stated otherwise. S-(5'-Adenosyl)-L-methionine p-toluene sulfonate (SAM-pTs, ~90%), S-(5'-Adenosyl)-L-methionine iodide (SAM-I, >=80%) and S-(5'-Adenosyl)-L-methionine chloride dihydrochloride (SAM-Cl*2HCl, >=75%) were commercially available at Sigma-Aldrich. Solvents were degassed and dried using standard distillation procedures. Water was degassed by three freeze-pump-thaw cycles. [Fe(Gly)₂]^[59] (crystal structure: SI Figure 21), (S)-N,N'-[(2-(methylthio)ethyl)ethylene]bis(salicylideneimine) (salmeth₂), 2-Amino-5-thiahexylamine (= S-methionamine, SI, S8)^[60] and homocysteineamide hydrochloride^[61-62] (SI, scheme 1, S3) were synthesized according to literature procedures. The labels S3-S10 refer to compound names in scheme 1 in the SI.

S-(2-tetrahydrofuranylmethyl)-homocysteineamide hydrochloride (SI, S4):

Homocysteineamide hydrochloride (2g, 11.76 mmol) was dissolved in 25 ml of isopropanol together with 1 eq. of potassium *tert*-butoxide (1.319 g, 11.76 mmol). After stirring for 1 h 15 min the potassium chloride that had formed was filtered off and washed copiously with isopropanol. To the filtrate was then added another equivalent of potassium *tert*-butoxide (1.319 g, 11.76) and (2-tetrahydrofuranylmethyl) bromide (1.2 eq., 14.1 mmol, 2.33 g, 1.605 ml) was added. Immediately the solution became turbid. The suspension was stirred at r.t. overnight leading to a slightly yellowish color. The mixture was neutralized by addition of a few drops a conc. hydrochloric acid. Then the formed potassium bromide was filtered off and more HCl added to make the solution acidic in order to protonated the amine and stored at -20°. The white to yellow precipitate was filtered off and the filtrate concentrated and allowed again to crystallize (1.206 g, 4.7 mmol, 40 %). Mixture of diastereomers. ¹H NMR (400 MHz, MeOD-d₄) δ 4.09-4.00 (m, 2H) δ 3.91-3.85 (m, 1H) δ 3.79-3.33 (m, 1H) δ 2.79-2.65 (m, 4H) δ 2.23-2.03 (m, 3H) δ 2.01-1.85 (m, 2H) δ 1.71-1.61 (m, 1H). ¹³C-NMR (101 MHz, MeOD-d₄) δ 171.93 δ 171.89 δ 80.50 δ 80.38 δ 69.22 δ 69.19 δ 53.51 δ 53.45 δ 37.67 δ 37.58 δ 32.73 δ 32.65 δ 31.92 δ 28.60 δ 28.55 δ 26.69. High resolution ESI-MS, MeOH, positive mode, [M]⁺ calculated m/z = 219.1162 u/e, measured m/z = 219.1162 u/e.

S-(2-tetrahydrofuranylmethyl) homocysteine amine (SI, S5):

Lithium aluminium hydride (214 mg, 5.63 mmol) was suspended in 5 ml of dry THF. Then S-(2-tetrahydrofuranylmethyl) homocysteine amide (SI, S4) hydrochloride was added (500 mg, 1.962 mmol) portion wise (H₂ evolution) and the suspension was heated to 55°C for 17 h. Then the suspension was cooled in an ice bath and cautiously quenched by adding water (0.21 ml) dropwise, followed by 15% NaOH (0.21 ml) and the again water (0.64 ml). The suspension was filtered and the filter cake washed with hot THF and then extracted with boiling THF (3 x 3 ml). The combined filtrates were mixed and the solvent evaporated on the rotary evaporator. The resulting oily substance was purified by flash column chromatography (MeOH:DCM:NEt₃ = 15:84:1)

yielding a colorless liquid (280 mg, 1.37 mmol, 70 %). Mixture of diastereomers. ¹H NMR (400 MHz, MeOD-d₄) δ 4.08-4.00 (m, 1H) δ 3.90-3.83 (m, 1H) δ 3.78-3.70 (m, 1H) δ 2.86-2.77 (m, 1H) δ 2.76-2.59 (m, 5H) δ 2.53-2.46 (m, 1H) δ 2.11-2.01 (m, 1H) δ 2.00-1.83 (m, 2H) δ 1.78-1.63 (m, 2H) δ 1.63-1.51 (m, 1H). ¹³C-NMR (101 MHz, MeOD-d₄) δ 80.47 δ 80.41 δ 69.15 δ 53.33 δ 53.29 δ 48.28 δ 37.80 δ 37.78 δ 35.75 δ 35.70 δ 31.92 δ 31.91 δ 30.21 δ 30.19 δ 26.67. High resolution ESI-MS, MeOH, positive mode, [M]⁺ calculated m/z = 205.1369 u/e, measured m/z = 205.1371 u/e.

S-(2-tetrahydrofuranylmethyl) homocysteinesalen (SI, S6):

Done under air. S-(2-tetrahydrofuranylmethyl) homocysteine amine (SI, S5) (56 mg, 0.274 mmol) was dissolved in 1 ml of benzene and salicylaldehyde was added (2. eq, 67.2 mg, 58.4 µl). The mixture immediately turned yellow. It was refluxed for 5 minutes. A spatula tip of sodium sulfate was added to remove water and the mixture was filtered. The filtrate was dried in vacuo yielding 108 mg (0.261 mmol, 95%) of the product as a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.37 (s, 1H) δ 8.30 (s, 1H) δ 7.32-7.26 (m, 2H) δ 7.25-7.18 (m, 2H) δ 6.97-6.91 (m, 2H) δ 6.89-6.81 (m, 2H) δ 4.03-3.95 (m, 1H) δ 3.95-3.88 (m, 1H) δ 3.88-3.80 (m, 1H) δ 3.80-3.66 (m, 3H) δ 2.77-2.49 (m, 4H) δ 2.10-1.95 (m, 3H) δ 1.94-1.78 (m, 2H) δ 1.65-1.53 (m, 1H). ¹³C-NMR (101 MHz, CDCl₃) δ 166.77 δ 166.21 δ 161.12 δ 132.65 δ 132.57 δ 131.84 δ 131.64 δ 118.90 δ 118.80 δ 118.71 δ 118.60 δ 117.08 δ 117.04 δ 78.88 δ 78.72 δ 68.58 δ 68.52 δ 68.38 δ 68.37 δ 64.69 δ 37.36 δ 37.25 δ 33.60 δ 33.52 δ 31.19 δ 31.17 δ 29.47 δ 29.43 δ 25.92 δ 25.88. High resolution ESI-MS, MeOH, positive mode, [M]⁺ calculated m/z = 413.1883 u/e, measured m/z = 413.1893 u/e.

S-methyl-(2-tetrahydrofuranylmethyl) homocysteinesalen iodide (S-tet-salmet, SI, S7):

S-(2-tetrahydrofuranylmethyl) homocysteinesalen (10 mg, 0.024 mmol) was dissolved in dry DMF (1 ml). Iodomethane (200 eq., 4.84 mmol, 688 mg, 302 µl) was added and the solution was stirred at r.t. for 3h 30 min. Then all volatiles were evaporated in vacuo at r.t. and the yellow residue was washed several times with diethyl ether. ¹H-NMR: Mixture of 8 isomers (4 diastereomers), ca. 60% pure, ¹H-NMR (400 MHz, DMF-d₇): δ 8.75 δ 8.74 (s, 1H) δ 8.67 (s, broad, 1H) δ 7.50-7.44 (m, 2H) δ 7.41-7.32 (m, 2H) δ 7.00-6.87 (m, 4H) δ 4.44-4.35 (m, 1H) δ 4.13-4.02 (m, 1H) δ 4.01-3.65 (m, 8H) δ 3.25 (s, broad, 3H) δ 2.58-2.48 (m, 1H) 2.48-2.36 (m, 1H) δ 2.20-2.12 (m, 1H) δ 1.98-1.86 (m, 2H) δ 1.79-1.69 (m, 1H). ¹³C NMR (101 MHz, DMF-d₇): δ 168.96 δ 168.81 δ 162.08 δ 162.01 δ 133.81 δ 133.65 δ 133.26 δ 133.02 δ 120.05 δ 119.99 δ 119.90 δ 119.78 δ 117.64 δ 117.59 δ 75.40 δ 75.31 δ 74.90 δ 74.75 δ 69.44 δ 69.41 δ 69.36 δ 69.24 δ 69.23 δ 64.45 δ 64.42 δ 64.40 δ 47.37 δ 47.31 δ 47.17 δ 40.29 δ 40.20 δ 40.18 δ 32.20 δ 32.17 δ 32.04 δ 32.00 δ 29.10 δ 29.08 δ 29.02 δ 28.99 δ 26.37 δ 26.36 δ 26.27 δ 26.26 δ 24.62 δ 24.54 δ 24.12 δ 24.06. High resolution ESI-MS, DCM/MeOH, positive mode, [M]⁺ calculated m/z = 427.2050 u/e, measured m/z = 427.2038 u/e. ESI-MS-CID spectrum see Figure 3 (middle). No further purification was performed.

S-benzyl-methionamine sulfate (SI, S9):

Done under air. 2-Amino-5-thiahexylamine (= S-methionamine, SI, S8, 100 mg, 0.74 mmol) was dissolved in TFA (3ml). To this solution conc. sulfuric acid (0.14 ml) was added slowly. Then benzyl bromide (1. eq, 88 µl) was added and the solution was

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stirred at r.t. for 46 h. Then another 0.5 eq. of benzyl bromide were added (0.44 μ l) was again stirred for 24 h and one more equivalent of benzyl bromide (88 μ l) was added. After stirring for another 26 hours the white suspension was filtered and the resulting white powder washed with diethyl ether resulting in a white powder that was dried in vacuo (130 mg, 0.403 mmol, 55%). Two diastereomers. $^1\text{H-NMR}$ (400 MHz, D_2O) δ 7.59-7.48 (m, 5H) δ 4.83-4.65 (m, 2H) δ 3.83 (p, J = 6.3 Hz, 1H) δ 3.59-3.34 (m, 2H) δ 3.39 (d, J = 6.1, 2H) δ 2.85 (s, 3H) δ 2.40-2.21 (m, 2H). ^{13}C NMR (101 MHz, D_2O) δ 130.79 δ 130.41 δ 129.69 δ 126.28 δ 48.18 δ 45.95 δ 45.87 δ 40.49 δ 40.44 δ 36.38 δ 36.33 δ 25.34 δ 25.30 δ 21.49 δ 21.45.

S-benzyl-methyl-homocysteinesalen hemisulfate (SI, S10):

20 mg of *S*-benzyl-methionamine sulfate (0.062 mmol) were suspended in 1 ml of MeOH (1N in NH_3) and salicylic aldehyde (2 eq., 0.124 mmol, 15.2 mg, 13.2 μ l) were added. After 40 minutes of stirring the remaining white powder was filtered off and the filtrate was concentrated in vacuo at r.t.. The resulting yellow oil was washed with diethyl ether and dissolved in DCM and filtered. The filtrate was dried in vacuo to yield a yellow oil. (24 mg crude product).

Diastereomers. The compound could not be isolated in a pure form. However, newly emerging $^1\text{H-NMR}$ (400 MHz, CDCl_3) signals at δ 5.22-4.90 (m, 2H, SCH_2Bn) and δ 3.00 and δ 2.98 (2 x s for each diastereomer, SCH_3) and $^{13}\text{C-NMR}$ (101 MHz, CDCl_3) signals at δ 22.14 and δ 22.03 (SCH_3) and δ 45.43 and δ 45.40 (SCH_2Ph) together with high resolution mass spectrometry and CID studies (Figure 4, middle) unambiguously confirmed the compounds identity. High resolution ESI-MS, MeOH, positive mode, $[\text{M}^+]$ calculated m/z = 433.1944 u/e, measured m/z = 433.1950. The compound was used without further purification.

(*S*)-*N,N'*-[(2-(dimethylthio)ethyl)ethylene]bis(salicylideneimine) iodide (*S*-met-*L*-salmet):

Done under air, protected from light. salmet- H_2 (103 mg, 0.3 mmol) was dissolved in 6 ml of methanol and an excess of iodomethane (20 eq. 852 mg, 375 μ l). The solution was stirred over the weekend. All volatiles were removed in vacuo. The residue was dissolved in DCM and was precipitated by addition of hexane. The compound was then put onto silica gel and washed with (EtOAc /hexane: 20/80) and then eluted with DCM/MeOH 90:10 yielding 67% of the yellow oily product pure enough for electrospray experiments. Alternatively the crude product can be washed with Et_2O twice to give a yellow oil which then is dissolved in DCM and dried again in vacuo, yielding a yellow solid. $^1\text{H-NMR}$ (400 MHz, MeOD-d_4) δ 8.57 (s, 1H), δ 8.47 (s, 1H), δ 7.39-7.26 (m, 4H), δ 6.91-6.81 (m, 4H), δ 4.04-3.98 (m, 1H), δ 3.89-3.76 (m, 2H), δ 3.53-3.36 (m, 2H), δ 2.97 (s, 3H) δ 2.95 (s, 3H) δ 2.44-2.24 (m, 2H). ^{13}C NMR (101 MHz, MeOD-d_4) δ 169.29, δ 169.06, δ 162.65, δ 161.98, δ 133.99, δ 133.83, δ 133.35, δ 133.03, δ 120.13, δ 119.94, δ 119.89, δ 119.77, δ 117.82, δ 117.65, δ 69.72, δ 64.39, δ 41.70, δ 29.12, δ 25.58, δ 25.33. High resolution ESI-MS, DCM/MeOH, positive mode, $[\text{M}]^+$ calculated m/z = 357.1631 u/e, measured m/z = 357.1631 u/e. ESI-MS-CID spectrum see Figure 2 (middle).

ESI-MS studies

$[\text{Fe}(\text{OAc})(\text{SAM})]^+$: m/z = 513 u/e, a 5×10^{-4} M solution of $\text{Fe}(\text{OAc})_2$ in methanol was mixed in a 1:1 ratio with a 5×10^{-4} M solution of SAM-pTs in methanol and then electro sprayed immediately.

$[\text{Fe}(\text{S-met-salmet})]^+$: m/z = 411 u/e, a 10^{-5} M solution of $\text{Fe}(\text{OAc})_2$ and S-met-*L*-salmet in methanol was electro sprayed after 15 minutes of stirring.

$[\text{Fe}(\text{S-tet-salmet})]^+$: m/z = 481 u/e, a 10^{-5} M solution of $\text{Fe}(\text{OAc})_2$ and S-tet-salmet in methanol was electro sprayed after 15 min of stirring.

$[\text{Fe}(\text{S-bn-salmet})]^+$: m/z = 487 u/e, a 10^{-5} M solution of $\text{Fe}(\text{OAc})_2$ and S-bn-salmet in methanol.

$[\text{Zn}(\text{S-met-salmet})]^+$: m/z = 419 u/e, a 10^{-5} M solution of $\text{Zn}(\text{OAc})_2$ and S-met-*L*-salmet in water was electro sprayed after 15 minutes of stirring.

$[\text{Zn}(\text{S-tet-salmet})]^+$: m/z = 489 u/e, a 10^{-5} M solution of $\text{Zn}(\text{OAc})_2$ and S-tet-salmet in water was prepared and electro sprayed immediately.

$[\text{Zn}(\text{S-bn-salmet})]^+$: m/z = 495 u/e, a 10^{-5} M solution of $\text{Zn}(\text{OAc})_2$ and S-bn-salmet in water was prepared and electro sprayed immediately.

Further experimental procedures are found in the SI.

Acknowledgements

We are very thankful to Prof. B. Jaun for help with the cyclic voltammetry studies, to Michael Solar and Nils Trapp from Small Molecule Crystallography Center at ETH Zürich for crystal structure determination and Joël Gubler for providing R scripts. Financial support from the ETH Zürich and the Swiss National Science Foundation are also gratefully acknowledged.

Keywords: homolytic substitution • S-Adenosyl methionine • electrospray ionisation mass spectrometry • trialkylsulfonium group • collision induced dissociation • transition state geometry • radical SAM enzymes

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Entry for the Table of Contents (Please choose one layout)

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Stefan Jungen, Peter Chen*

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Homolytic substitutions closely related to the proposed radical generation step in Radical SAM Enzymes

Electrospray ionisation mass spectrometry investigations of $[\text{Fe}(\text{S-R-salmet})]^+$ complexes showed homolytic substitution reactions involving iron (II) and a trialkylsulfonium or a benzylsulfonium group, forming an alkyl or benzyl radical, respectively. The setting of an iron (II) "metalloradical" reductively cleaving a trialkylsulfonium species via a homolytic substitution reaction is closely related to the proposed radical generation step in Radical S-Adenosyl Methionine Enzymes.

Supporting Info

Alkyl radical generation by an intramolecular homolytic substitution reaction between iron (II) and trialkylsulfonium groups

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Experimental

Synthetic details

All reactions were done under inert atmosphere unless stated otherwise. Ortho-vanillin was commercially available. Benzyl dimethyl sulfonium bromide¹, (2S)-2-Amino-5-thiahexylamine (S8)², S-Benzyl-L-methionine (SBM) bromide³, [Fe(Tp-Me,Ph)(Cl)]⁴, [Fe(Tp*)(OAc)]⁵, [Fe(Tm-Me)(Cl)]⁶, N,N'-Bis(5-sulfonatosalicylidene)-1,2-diaminoethane disodium salt (salenSO₃)Na₂⁷⁻¹⁰, the complex Na₂[Fe(salenSO₃)]¹¹ and were synthesized according to literature procedures.

Scheme 1. Synthesis of S-tetrahydrofuranylmethyl-met-salmel iodide

Scheme 2. Synthesis of S-benzyl-salmel hemisulfate

(S)-N,N'-[(2-(methylthio)ethyl)ethylene]bis(3-methoxysalicylideneimine)(3,3'-OMe-L-salmeth₂):

Done under air. (2S)-2-Amino-5-thiahexylamine (120 mg, 0.89 mmol) was dissolved in ethanol (8 ml). Two equivalents of ortho-vanillin (272 mg, 1.79 mmol) were added together with 10 ml of ethanol. The light yellow solution was stirred at r.t. for 3 hours. The ethanol was partially removed in vacuo and water was added dropwise. The solution was stored at -20°C overnight. The yellow oil that separated was decanted. 242 mg, 67%. ¹H-NMR (400 MHz, CDCl₃) δ 13.52 (br, 2H) δ 8.33 (s, 1H) δ 8.27 (s, 1H) δ 6.93-6.74 (m, 6H), 3.99-3.93 (m, 1H), δ 3.88 (d, J = 1.9 Hz, 6H), δ 3.79-3.66 (m, 2H), δ 2.64-2.55 (m, 1H), δ 2.50-2.41 (m, 1H), δ

2.11-1.99 (m, 5H). ¹³C NMR (101 MHz, CDCl₃) δ 166.92 δ 166.30 δ 151.53 δ 151.47 δ 148.41 δ 148.39

δ 123.47 δ 123.30 δ 118.51 δ 118.40 δ 118.34 δ 118.22 δ 114.37 δ 114.24 δ 68.36 δ 64.49 δ 56.23 δ 56.19 δ 33.06 δ 30.71 δ 15.56. High res ESI-MS, DCM/MeOH, positive mode, $[M+H]^+$, calculated m/z = 403.1692 u/e, measured m/z = 403.1698 u/e.

(S)-N,N'-[(2-(Dimethylthio)ethyl)ethylene]bis(3-methoxysalicylideneimine)(S-met-3,3'-OMe-L-salmeth₂ iodide):

Done under air, protected from light. 3,3'-OMe-L-Salmeth₂ (20 mg, 0.05 mmol) were dissolved in 2 ml of MeOH. Then 0.1 ml of methyl iodide (228 mg, 1.6 mmol) were added. The solution was stirred over the weekend. The yellow precipitate formed was filtered off and washed with Et₂O. The yellow powder was dried in HV. 19 mg, 70%. ¹H-NMR (400 MHz, DMSO-d₆) δ 13.35 (s, 1H) δ 13.03 (s, 1H) δ 8.59 (s, 1H) δ 8.54 (s, 1H) δ 7.09-6.97 (m, 4H) δ 6.87-6.76 (m, 2H) δ 3.98-3.90 (m, 1H) δ 3.86-3.68 (m, 2H) δ 3.77 (s, 3H) δ 3.75 (s, 3H) δ 3.39-3.26 (m, 2H) δ 2.89 (s, 3H) δ 2.88 (s, 3H) δ 2.29-2.08 (m, 2H) ¹³C NMR (101 MHz, DMSO-d₆) δ 167.56 δ 167.19 δ 150.99 δ 150.54 δ 147.88 δ 147.86 δ 123.26 δ

123.09 δ 118.39 δ 118.30 δ 118.25 δ 117.98 δ 115.04 δ 114.75 δ 67.51 δ 62.55 δ 55.79 δ 55.64 δ 39.18 δ 27.31 δ 24.32 δ 24.21. High res ESI-MS, MeOH, positive mode, $[M]^+$, calculated m/z = 417.1843 u/e, measured m/z = 417.1847 u/e.

(S)-N,N'-[(2-(methylthio)ethyl)ethylene]bis(4-fluorosalicylideneimine)(4,4'-F-L-salmeth₂):

Done under air. (2S)-2-Amino-5-thiahexylamine (120 mg, 0.89 mmol) was dissolved in Ethanol (8ml). Two equivalents of 4-fluoro-2-hydroxybenzaldehyde (249 mg, 1.78 mmol) in ethanol (10 ml) were added and the mixture was refluxed for 2.5 hours. The ethanol was partially removed in vacuo then water was added and the solution was stored at -20° over the weekend yielding a yellow precipitate that was filtered off (87% yield). ¹H-NMR (400 MHz, CDCl₃) δ 13.55 (br, 2H) δ 8.31 (s, 1H) δ 8.25 (s, 1H) δ 7.23-7.13 (m, 2H) δ 6.65-6.51 (m, 4H) δ 3.94-3.85 (m, 1H) δ 3.76-3.65 (m, 2H) δ 2.65-2.57 (m, 1H) δ 2.50-2.41 (m, 1H) δ 2.09 (s, 3H) δ 2.07-2.00 (m, 2H). ¹³C-NMR (151 MHz, CDCl₃) (remark: splittings in the signals of the aromatic carbons caused by fluorine are in the same order as the differences of the chemical shift due to the asymmetry of the molecule. Those two effects were distinguished by measuring the carbon spectrum at 101 MHz and at 151 MHz considering that the splittings in Hertz do not change in higher fields but the splittings measured in ppm do. δ 165.89 δ 165.36 δ 165.51 (d, J = 252.1 Hz) δ 165.47 (d, J = 252.0 Hz) δ 163.68 (d, J = 25.0 Hz) δ 163.59 (d, J = 25.0 Hz) δ 133.51 (d, J = 11.6) δ 133.30 (d, J = 11.6) δ 115.40 (d, J = 2.3 Hz) δ 115.30 (d, J = 2.3 Hz) δ 106.68 (d, J = 106.68) δ 106.54 (d, J = 22.9) δ 104.28 (d, J = 23.9) δ 104.23 (d, J = 24.0) δ 68.13 δ 64.06 δ 32.77 δ 30.76 δ 15.50 ¹⁹F-NMR (282 MHz, CDCl₃) δ -105.25 δ -105.34. High res ESI-MS, DCM/MeOH, positive mode, $[M+H]^+$, calculated m/z = 379.1286 u/e, measured m/z = 379.1294 u/e.

(S)-N,N'-[(2-(Dimethylthio)ethyl)ethylene]bis(4-fluorosalicylideneimine)(S-met-4,4'-F-L-salmeth₂ iodide):

Done under air, protected from light. 4,4'-F-L-Salmeth₂ (20 mg, 0.053 mmol) was dissolved in 2 ml MeOH. Methyl iodide (228 mg, 1.6 mmol, 100 μ l) was added and the solution was stirred for seven days at r.t..

The volatiles were removed in vacuo and the resulting yellow oil was washed twice with Et₂O to give a yellow oil in 88% yield. ¹H-NMR (600 MHz, MeOD-d₄) δ 8.58 (s, 1H) δ 8.45 (s, 1H) δ 7.42 (dd, J = 8.6, 6.6 Hz, 1H) δ 7.33 (dd, J = 8.7, 6.8 Hz, 1H) δ 6.65 – 6.57 (m, 2H) δ 6.54 – 6.46 (m, 2H) δ 4.05-4.00 (m, 1H) δ 3.90-3.80 (m, 2H) δ 3.54-3.48 (m, 1H) δ 3.46-3.39 (m, 1H) δ 3.00 (s, 3H) δ 2.99 (s, 3H) δ 2.42-2.35 (m, 1H) δ 2.34-2.26 (m, 1H).

¹³C NMR (151 MHz, MeOD-d₄) δ 168.63 δ 168.20 δ 167.82 (d, J = 252.1 Hz) 167.11 (d, J = 251.2 Hz) δ 168.39 (d, J = 14.0 Hz) δ 165.01 (d, J = 13.8 Hz) δ 135.74 (d, J = 12.4 Hz) δ 135.64 (d, J = 11.8 Hz) δ 116.76 (d, J = 2.2 Hz) δ 116.28 (d, J = 1.9 Hz) δ 107.49 (d, J = 23.2 Hz) δ 106.80 (d, J = 23.7 Hz) δ 105.21 (d, J = 22.6 Hz) 104.64 (d, J = 24.2 Hz) δ 69.02 δ 62.24 δ 41.53 δ 28.94 δ 25.64 δ 25.38. High res ESI-MS, DCM/MeOH, positive mode, [M]⁺, calculated m/z = 393.1443 u/e, measured m/z = 393.1452 u/e.

Preparation of Complexes for ESI-MS

[Fe(OAc)(SBM)]⁺:

m/z = 354 u/e, a 10⁻⁴ M solution of Fe(OAc)₂ and SBM bromide was prepared in degassed MeOH and electrosprayed.

[Zn(OAc)(SBM)]⁺:

m/z = 362 u/e, a 10⁻⁴ M solution of Zn(OAc)₂ and SBM bromide was prepared in degassed MeOH and electrosprayed.

[Fe(Gly)(SAM)]⁺:

m/z = 528 u/e, a 1:1 water-methanol mixture 10⁻⁴ M in [Fe(Gly)₂] and 10⁻³ M in SAM iodide was electrosprayed after stirring for 1.5 hours at room temperature.

[Fe(SAM)(Tp*)]⁺:

$m/z = 751$ u/e, a 10^{-5} M solution of $[\text{Fe}(\text{Tp}^*)(\text{OAc})]$ in methanol was mixed with a $2 \cdot 10^{-5}$ M solution of SAM-Cl $\cdot$ 2HCl in methanol and sprayed after stirring for 10 minutes at room temperature.

[Fe(SAM)(Tp-Me,Ph)]⁺:

$m/z = 937$ u/e, $[\text{Fe}(\text{Cl})(\text{Tp-Me,Ph})]$ (2mg, 0.0035 mmol) was dissolved in DCM together with NaBARF (1eq., 3.1 mg, 0.0035 mmol) and stirred overnight. After filtering off the NaCl that had formed, DCM was evaporated in vacuo. A part of the residue was dissolved in methanol to form a ca. 10^{-5} M solution. This solution was mixed 1:1 with a $2 \cdot 10^{-5}$ M solution of SAM-Cl $\cdot$ 2HCl in methanol and electrosprayed after stirring for 10 minutes at room temperature.

[Fe(SAM)(Tm-Me)]⁺:

$m/z = 805$ u/e, $\text{Fe}(\text{Cl})(\text{Tm-Me})$ (1,1 mg, 0.0025mmol) and NaBARF (1.eq, 2.2 mg) were dissolved in MeOH and stirred for 30 minutes. The solution was filtered and a little bit of it added to a solution of 10^{-5} M SAM-Cl $\cdot$ 2HCl in MeOH/H $_2$ O 1:1. Then the solution was electrosprayed after 10 minutes of stirring at room temperature.

[Fe(Gly)(SMM)]⁺:

$m/z = 293$, analogous to **[Fe(Gly)(SAM)]⁺**. Alternatively a procedure published in Izvestiya Akademii Nauk Kirgizskoi SSR¹² can be followed. However, with this procedure we were able to see the complex in ESI-MS with good intensity, but we were not able to reproduce the purification procedure.

[Fe(S-met-4,4'-F-L-salmet)]⁺:

$m/z = 447$ u/e, a 10^{-5} M solution of $\text{Fe}(\text{OAc})_2$ and S-met-4,4'-F-L-salmetH₂ iodide in methanol was electrosprayed after 15 minutes of stirring.

[Zn(S-met-4,4'-F-L-salmet)]⁺:

$m/z = 455$ u/e, a 10^{-5} M solution of $\text{Zn}(\text{OAc})_2$ and S-met-4,4'-F-L-salmetH₂ iodide in water was electrosprayed after 15 minutes of stirring.

[Fe(S-met-3,3'-OMe-L-salmet)]⁺:

$m/z = 471$ u/e, a 10^{-5} M solution of $\text{Fe}(\text{OAc})_2$ and S-met-3,3'-OMe-L-salmet iodide in methanol was electrosprayed after 15 minutes of stirring.

[Zn(S-met-3,3'-OMe-L-salmet)]⁺:

$m/z = 479$ u/e, a 10^{-5} M solution of $\text{Zn}(\text{OAc})_2$ and S-Met-3,3'-OMe-L-salmet iodide in water was electrosprayed after 15 minutes of stirring.

Crystallization procedure for $[\text{Fe}(\text{Gly})_2(\text{H}_2\text{O})_2]$

Some milligrams of $[\text{Fe}(\text{Gly})_2]$ were dissolved in as little freeze-pump-thaw degassed HPLC water as possible. By vapor diffusion technique degassed acetonitrile was added leading to X-Ray quality crystals after some days.

Selective bond cleavage in S-Adenosyl-methionine complexes and derivatives

In the paper it was shown that in free SAM both $\text{S-C}_{\text{alkyl}}$ bonds are cleaved during CID, while when complexed to iron(II) only the S-C_γ bond is cleaved selectively. To investigate this phenomenon the SAM derivative S-Benzyl-methionine (SBM) was synthesized. In SBM there should be preference for $\text{S-C}_{\text{benzyl}}$ bond cleavage since a benzylic bond is generally weaker than an $\text{S-C}_{\text{alkyl}}$ bond. As can be seen in **Error! Reference source not found.** in free SBM this preference is observed. However, if complexed to iron(II) (Figure 2) only S-C_γ cleavage is observed. In other words complexation overrules the propensity to break the weaker bond and even reverses it. To address the question if this selectivity has something to do with one electron redox chemistry the analogous zinc(II) complex (Figure 3) was synthesized. Zn(II) is known not to participate in one electron chemistry. However, the zinc complex behaves exactly the same as the iron complex. As with SAM, exchanging the space holder ligand acetate for glycine did not change anything (data not shown). The reason for this selectivity is most likely an intramolecular 5-exo-tet- reaction where the complexed carboxylate attacks the C_γ and extrudes the sulfide.

Figure 1. Left: CID of S-Benzyl-Methionine(SBM) at 0.1 mTorr at various collision offsets. Main bond cleavage happens at $\text{S-C}_{\text{Benzyl}}$, in a minor channel the S-C_γ bond is broken releasing benzyl methyl sulfide (BMS). Inset: Experimental (black) and calculated (red) isotope pattern of ions. Right: Structure of parent ion and fragments.

Figure 2. Left: CID of $[\text{Fe}(\text{OAc})(\text{SBM})]^+$ at 0.1 mTorr at various collision offsets. Remarkably S-C_γ cleavage forming BMS happens almost exclusively. Inset: Experimental (black) and calculated (red) isotope pattern of ions. The peak at 353 is a background artifact. Right: Structure of parent ion and fragments.

Figure 3. Left: CID of $[\text{Zn}(\text{OAc})(\text{SBM})]^+$ at 0.1 mTorr at various collision offsets. As in the Iron complex S-C_γ cleavage forming BMS happens almost exclusively. Inset: Experimental (black) and calculated (red) isotope pattern of ions. Right: Structure of parent ion and fragments.

$[\text{Fe}(\text{Gly})(\text{SMM})]^+$

To prove that the appearance of homoserine lactone (HSL) in the CID spectra of SAM does not come from alternative coordination of SAM via the adenine instead of the amino acid moiety, $[\text{Fe}(\text{Gly})(\text{SMM})]^+$ was electro sprayed (Figure 4). The reason for the lower intensity of the HSL formation channel in this system compared to the corresponding SAM complex can be explained by the fact that in the latter coordination of the nascent MTA in a bidentate fashion leads to a fourfold coordinated complex, while in the former coordination of SMe_2 leads to a three coordinated iron complex.

Figure 4. CID Spectrum of $[\text{Fe}(\text{Gly})(\text{SMM})]^+$ at 0.1 mTorr and collision offset 30 V. No radical formation was observed. HSL: homoserine lactone. Inset: Experimental (black) and calculated (red) isotope pattern of ions.

Iron(II)-SAM complexes with various space holder ligands

Figure 5. CID Spectrum of $[\text{Fe}(\text{Gly})(\text{SAM})]^+$ at 0.1 mTorr and collision offset 50 V. No adenosyl radical (dAdo[•]) formation was observed. HSL: homoserine lactone, MTA: Methylthioadenosine, Gly: glycine. Inset: Experimental (black) and calculated (red) isotope pattern of ions.

Figure 6. CID Spectrum of $[\text{Fe}(\text{SAM})(\text{Tp}^*)]^+$ at 0.1 mTorr and collision offset 25 V. No dAdo- formation was observed. HSL: homoserine lactone, MTA: Methylthioadenosine. Inset: Experimental (black) and calculated (red) isotope pattern of ions.

Figure 7. CID Spectrum of $[\text{Fe}(\text{SAM})(\text{Tp-Me,Ph})]^+$ at 0.1 mTorr and collision offset 50 V. No dAdo- formation was observed. HSL: homoserine lactone, MTA: Methylthioadenosine. Inset: Experimental (black) and calculated (red) isotope pattern of ions.

Figure 8. CID Spectrum of $[\text{Fe}(\text{Tm-Me})(\text{SAM})]^+$ at 0.1 mTorr and collision offset 50 V. No dAdo-formation was observed. HSL: homoserine lactone, MTA: Methylthioadenosine. Inset: Experimental (black) and calculated (red) isotope pattern of ions.

SMe₂Bn

Figure 9. CID of Benzyl dimethyl sulfonium bromide at 0.1 mTorr and collision offset of 20 V. No benzyl radical formation is observed.

Non-complexed S-met-Salmet and derivatives

Figure 10. CID Spectrum of S-methyl-3,3'-methoxy-salmet at 0.1 mTorr and collision offset 25 V. No methyl radical formation was observed. Inset: Experimental (black) and calculated (red) isotope pattern of ions.

Figure 11. CID Spectrum of S-methyl-4,4'-fluoro-salmeterol at 0.1 mTorr and collision offset 25 V. No methyl radical formation was observed. Inset: Experimental (black) and calculated (red) isotope pattern of ions.

Iron-salmeterol and zinc-salmeterol complexes at a collision offset of 40 V

Figure 12. CID Spectrum of $[\text{Fe(II)}(\text{S-met-salmeterol})]^+$ at 0.1 mTorr (top) and collision offset of 40 V. Inset left: Experimental (black) and calculated (red) isotope pattern of the ions.

Figure 13. CID Spectrum of $[\text{Zn(II)(S-met-salmet)}]^+$ at 0.1 mTorr and collision offset of 40 V. Inset: Experimental (black) and calculated (red) isotope pattern of the ions. Inset right: Zoom to 404, the mass-to-charge ratio where a fragment peak would appear if methyl radicals were formed.

Iron-S-met-salmet-derivative and zinc-S-met-salmet-derivative complexes

Figure 14. Substituted $[\text{Fe(II)(S-met-salmet)}]^+$ complexes **3** and **4**.

Figure 15. CID Spectrum of $[\text{Fe}(\text{S-met-3,3'-methoxy-salmet})]^+$ at 0.1mTorr and collision offset of 25V. Inset: Experimental (black) and calculated (red) isotope pattern of ions.

Figure 16. CID Spectrum of $[\text{Zn}(\text{S-met-3,3'-methoxy-salmet})]^+$ at 0.1mTorr and collision offset of 25V. No methyl radical formation is observed. Inset: Experimental (black) and calculated (red) isotope pattern of ions.

Figure 17. CID Spectrum of $[Fe(S\text{-met-4,4'-fluoro-salmet})]^+$ at 0.1mTorr and collision offset of 25V. Inset: Experimental (black) and calculated (red) isotope pattern of ions.

Figure 18. CID Spectrum of $[Zn(S\text{-met-4,4'-fluoro-salmet})]^+$ at 0.1mTorr and collision offset of 25V. No methyl radical formation is observed. Inset: Experimental (black) and calculated (red) isotope pattern of ions.

Cyclic voltammetry

The REDOX potentials of the iron(II)-salmet and the iron amino acid complexed were planned to be compared to have an estimation of how easily the iron(II) is stripped of an electron in these complexes. For this reason the two model compounds [Fe(S-met-5,5'-sulfonato-salen)] and [Fe(Gly)₂] were synthesized. The sulfonate group on the salen ligand were necessary to make the salen complex water soluble. Measurements in organic solvents were not possible since iron amino acid complexes are insoluble in all common organic solvents almost independent of the side chain.

The [Fe(S-Met-5,5'-Sulfonato-Salen)] complex gave a reversible potential wave with $E_p = -237$ mV (Figure 19). The [Fe(Gly)₂] complex gave an irreversible potential wave (Figure 20) most likely due to adsorptive effects on the working electrode. However, this potential wave stayed approximately the same during multiple cycles, indicating that the adsorption process is reversible. Varying the sweep rate or exchanging the glassy carbon electrode by a platinum electrode did not solve this problem. Furthermore, the redox processes for complexes of iron (II) with Tp and an amino acid show irreversible results due to structural changes.¹³

Cyclic voltammograms were obtained with a BAS-100 W apparatus. The sample cell (volume 1 ml) was equipped with a glassy carbon working electrode (2 mm diameter), a normal calomel reference electrode (1M KCl) and the counter electrode consisting of a curled platinum wire. MOPS (recrystallized twice from a water-ethanol mixture) buffered water (20mM, milli-Q, adjusted to pH=7 with NaOH), degassed by argon bubbling, with KClO₄ (100mM, 99.99% trace metals basis, Sigma Aldrich) or KCl (100mM, 99.995% trace metals basis) as electrolyte was used as solvent.

Figure 19. Cyclic voltammogram of 1mM [Fe(S-met-5,5'-sulfonato-salen)] in MOPS buffered H₂O containing 0.1M KClO₄ measured with a sweep rate of 100 mV/s at a glassy carbon electrode. Potential is given relative to a 1M KCl calomel electrode. $E_p = -237$ mV.

Figure 20. Cyclic voltammogram of 1mM $[\text{Fe}(\text{Gly})_2]$ in MOPS buffered H_2O containing 0.1M KClO_4 measured with a sweep rate of 100 mV/s at a glassy carbon electrode. Potential is given relative to a 1M KCl calomel electrode. The irreversible behavior is most likely coming from adsorption effects on the electrode surface.

Crystal structure of $[\text{Fe}(\text{Gly})_2(\text{H}_2\text{O})_2]$

Figure 21. Thermal ellipsoid (50% probability) representation of $[\text{Fe}(\text{Gly})_2(\text{H}_2\text{O})_2]$. Selected bond distances [Å]: $\text{Fe}_1\text{-O}_1$ 2.134, $\text{Fe}_1\text{-O}_2$ 2.139, $\text{Fe}_1\text{-N}_1$ 2.187, selected torsion angles [°]: $\text{Fe}_1\text{-N}_1\text{-C}_2\text{-H}$ -89.3 and 152.4.

XYZ-Coordinates of X-Ray structure of $[\text{Fe}(\text{Gly})_2(\text{H}_2\text{O})_2]$

Fe	2.135695	0.000000	4.329904	O	2.260360	-1.867913	3.304670
O	2.011030	1.867913	5.355139	O	2.108668	-0.944790	6.248831
O	2.162723	0.944790	2.410977	H	1.704318	-1.753015	6.226403
H	2.567072	1.753015	2.433406	H	2.895144	-1.103021	6.668053
H	1.376247	1.103021	1.991756	O	3.672663	-3.411486	2.525027
O	0.598728	3.411486	6.134782	N	4.295457	-0.325654	4.221657
N	-0.024066	0.325654	4.438152	H	4.741791	-0.013131	4.979390
H	-0.470401	0.013131	3.680419	H	4.624880	0.118181	3.489903
H	-0.353489	-0.118181	5.169906	C	3.407956	-2.399070	3.214521
C	0.863435	2.399070	5.445288	C	4.536396	-1.765490	4.018151
C	-0.265005	1.765490	4.641658	H	5.393238	-1.891484	3.539221
H	-1.121847	1.891484	5.120588	H	4.607037	-2.215050	4.897269
H	-0.335647	2.215050	3.762540				

Spin states of complexes

Compound	2S+1	Energy+ZPE			2S+1	Energy+ZPE
[Fe(II)(S-met-Salmat)] ⁺ (2)	1	-2697.2403		[Fe(II)(SAM)(Tp*)] ⁺	1	-3888.7538
	3	-2697.2628			3	-3888.7641
	5	-2697.2754			5	-3888.7888
[Fe(III)(S-Salmat)] ⁺	2	-2657.4250		[Fe(III)(SAM)(Tp*)] ²⁺	2	-3888.4658
	4	-2657.4496			4	-3888.4853
	6	-2657.4583			6	-3888.5104
[Fe(III)(S-met-Salmat)] ²⁺	2	-2696.9265		[Fe(II)(SAM)(Tm)] ⁺	1	-4965.5061
	4	-2696.9517			3	-4965.5244
	6	-2696.9525			5	-4965.5563
				[Fe(III)(SAM)(Tm)] ²⁺	2	-4965.2466
[Fe(II)(Gly)(SMM)] ⁺	1	-2386.8996			4	-4965.2753
	3	-2386.9155			6	-4965.2952
	5	-2386.9695				
[Fe(III)(Gly)(SMM)] ²⁺	2	-2386.5655				
	4	-2386.6014				
	6	-2386.6235				

Table 1. Energies for spin states of iron (II) and iron (III) complexes (in Hartree) with lowest energy states marked in red. [†]not entirely converged, one negative frequency at -7.44 cm⁻¹.

Remark to the calculated Ionization potentials (IPs)

The trends and the interpretation of the IPs for the iron (II) complexes is independent of the functional used. However, there was one universal trend that was found. The more Hartree-Fock exchange is included in a functional the higher the IP that is calculated with it. TPSS and M06L having no Hartree-Fock exchange give the lowest values, followed by B3LYP and then M06 (27% HF exchange).

		adiabatic IP/eV	vertical IP/eV	radical formation
[Fe(Tm-Me)(SAM)]⁺	M06L/cc-pVDZ	7.05	7.36	×
	M06/cc-pVDZ	7.38	7.73	×
	B3LYP/cc-pVDZ	7.46	7.78	×
	TPSSTPSS/cc-pVDZ	6.97	7.24	×
[Fe(Tp-Me,Ph)(SAM)]⁺	M06L/cc-pVDZ	7.40	7.61	×
	M06/cc-pVDZ	7.80	8.09	×
	B3LYP/cc-pVDZ	7.96	8.33	×
	TPSSTPSS/cc-pVDZ	7.45	7.63	×
[Fe(Tp[*])(SAM)]⁺	M06L/cc-pVDZ	7.40	7.69	×
	M06/cc-pVDZ	7.94	8.26	×
	B3LYP/cc-pVDZ	8.10	8.42	×
	TPSSTPSS/cc-pVDZ	7.54	7.73	×
[Fe(ome-salmet)]⁺	M06L/cc-pVDZ	8.28	8.42	✓
	M06/cc-pVDZ	8.68	8.86	✓
	B3LYP/cc-pVDZ	8.59	8.80	✓
	TPSSTPSS/cc-pVDZ	8.24	8.36	✓
[Fe(salmet)]⁺	M06L/cc-pVDZ	8.70	8.83	✓
	M06/cc-pVDZ	8.99	9.17	✓
	B3LYP/cc-pVDZ	8.98	9.16	✓
	TPSSTPSS/cc-pVDZ	8.71	8.83	✓
[Fe(f-salmet)]⁺	M06L/cc-pVDZ	8.80	8.92	✓
	M06/cc-pVDZ	9.11	9.29	✓
	B3LYP/cc-pVDZ	9.10	9.29	✓
	TPSSTPSS/cc-pVDZ	8.79	8.91	✓
[Fe(OAc)(SAM)]⁺	M06L/cc-pVDZ	8.96	9.51	×
	M06/cc-pVDZ	9.33	9.97	×
	B3LYP/cc-pVDZ	9.33	9.89	×
	TPSSTPSS/cc-pVDZ	8.60	9.39	×
[Fe(Gly)(SAM)]⁺	M06L/cc-pVDZ	9.29	9.33	×
	M06/cc-pVDZ	9.75	10.03	×
	B3LYP/cc-pVDZ	9.56	9.82	×
	TPSSTPSS/cc-pVDZ	9.08	9.49	×

Table 2. Calculated IPs

Spin state of the iron complexes

DFT calculated structure of $[\text{Fe}(\text{OAc})(\text{SAM})]^+$

Figure 22. DFT-optimized structure of $[\text{Fe}(\text{OAc})(\text{SAM})]^+$. The sulfonium does not coordinate to iron.

DFT calculated structure of $[\text{Fe}(\text{Tp}^*)(\text{SAM})]^+$

Figure 23. DFT-optimized structure of $[\text{Fe}(\text{SAM})(\text{Tp}^*)]^+$. The sulfonium does not coordinate to iron.

DFT calculated structure of S-C_γ bond cleavage transition state in [Fe(S-met-salmet)]⁺

Figure 24. DFT-optimized structure of S-C_γ bond cleavage transition state in [Fe(S-met-salmet)]⁺

NBO input file

```
%chk=file.chk
%mem=16GB
%nprocshared=8
#P M06L/cc-PVDZ Pop=(NBO6read, savenbos) geom=checkpoint guess=checkpoint Test
```

NBO analysis of product like TS of complex 2

1 5

\$NBO E2pert=1

\$END

\$CHOOSE

ALPHA

LONE 6 1 7 1 32 3 33 5 34 3 41 1 END

BOND S 1 2 S 1 3 S 1 7 S 1 35 S 3 4 S 3 5 S 3 6 D 6 8 D 7 10 S 8 9 S 8 12

S 10 11 S 10 22 D 12 13 S 12 14 S 13 15 S 13 32 D 14 16 S 14 17 D 15 18

S 15 19 S 16 18 S 16 20 S 18 21 D 22 23 S 22 24 S 23 25 S 23 34 D 24 26

S 24 27 D 25 28 S 25 29 S 26 28 S 26 30 S 28 31 S 35 36 S 35 37 S 35 38

S 38 39 S 38 40 S 38 41 S 33 41 S 41 46 S 42 43 S 42 44 S 42 45 S 46 47 S 46 48

S 46 49 END

END

BETA

LONE 6 1 7 1 32 3 34 3 41 1 42 1 END

BOND S 1 2 S 1 3 S 1 7 S 1 35 S 3 4 S 3 5 S 3 6 D 6 8 D 7 10 S 8 9 S 8 12

S 10 11 S 10 22 S 12 13 S 12 14 S 13 15 D 13 32 D 14 16 S 14 17 D 15 18

S 15 19 S 16 18 S 16 20 S 18 21 S 22 23 S 22 24 S 23 25 D 23 34 D 24 26

S 24 27 D 25 28 S 25 29 S 26 28 S 26 30 S 28 31 S 35 36 S 35 37

S 35 38 S 38 39 S 38 40 S 38 41 S 33 41 S 41 46 S 42 43 S 42 44 S 42 45 S 46 47

S 46 48 S 46 49 END

END

\$END

Geometries of calculated species (M06I/cc-pVDZ)

[Fe(II)(S-met-salmel)]⁺ (sulfonium moiety coordinated to iron (II)) (quintet state)

C	0.697625238215	-2.667295494663	-0.984725974723
H	1.345458523743	-3.355198808764	-1.557360437379
C	-0.594268404541	-2.446337577572	-1.770176319658
H	-0.331211116608	-2.291426462916	-2.829512512295
H	-1.243749601383	-3.339169455924	-1.729866517402
N	-1.266719947607	-1.256677031189	-1.263392320900
N	1.347978980738	-1.366814120236	-0.831854291588
C	-2.575233680169	-1.221918999022	-1.311433479486
H	-3.110747798983	-2.092894041917	-1.730285354785
C	2.660410738381	-1.332657535051	-0.844703946350
H	3.210937097457	-2.271611233380	-1.040962637286
C	-3.399996411797	-0.152920140751	-0.850295263727
C	-2.863118977968	1.060027599905	-0.298363307843
C	-4.806105429069	-0.305793097844	-0.947398267136
C	-3.774140225980	2.052550895374	0.133552930122
C	-5.670096520973	0.679189125303	-0.519255913842
H	-5.197591327718	-1.231450297631	-1.378458230360
C	-5.139731781998	1.865325527738	0.023022006653
H	-6.748372025953	0.546317778472	-0.605271968533
H	-5.816529080207	2.654279669541	0.357775899640
C	3.460296463910	-0.176492575938	-0.627298497995
C	2.890384595562	1.111275610025	-0.332215817537
C	4.871082970931	-0.310022610090	-0.705625713676
C	3.775813347302	2.196799187316	-0.130411769930
C	5.706525636384	0.765908431659	-0.505545603969
H	5.286321624296	-1.294906524609	-0.936784651632
C	5.143959646202	2.025919563597	-0.217117683315
H	6.787847231050	0.648660832780	-0.573837813427
H	5.800467152336	2.884513012555	-0.061257705859

O	-1.577561169706	1.269145327070	-0.169958583855
Fe	0.018903855531	0.285459900020	-0.593995386169
O	1.602825413638	1.304280921989	-0.226253018384
C	0.499312051746	-3.326427386900	0.390170306396
H	1.484606936424	-3.440439930546	0.870769082174
H	0.126635455088	-4.353760284145	0.246156732951
C	-0.475193957648	-2.685016519516	1.364529105420
H	-0.494148345874	-3.212134514767	2.330216666508
H	-1.500922801760	-2.643401290424	0.969994351004
S	-0.122411011841	-0.921041603363	1.743551928581
C	-1.398512897841	-0.547790357450	2.960495737011
H	-1.218881168908	0.476148246662	3.306819854301
H	-2.355421317106	-0.581909422293	2.425551803123
H	-1.373435413128	-1.264581624891	3.789336194444
C	1.402300560048	-0.975912287525	2.697613729018
H	1.326400019593	-1.700511362455	3.516664031363
H	2.203782283936	-1.235592434308	1.995011403283
H	1.575715612930	0.038998270333	3.074019950533
H	-3.359451628193	2.975194803905	0.541800216706
H	3.337914027517	3.171485981835	0.087559069810

[Fe(II)(S-met-salmet)]⁺ transition state for methyl radical generation (quintet state)

C	-0.690455803531	1.722172785022	-1.952972238405
H	-1.337488667493	2.042776758754	-2.788501705791
C	0.617201785244	1.178386738340	-2.527649566840
H	0.383800246570	0.560814075536	-3.410619210758
H	1.271623122821	1.996718095364	-2.873707342761
N	1.274463078101	0.344033897185	-1.525213744796
N	-1.325659288158	0.628222995997	-1.221131109470
C	2.564391126443	0.156828096663	-1.623773650780
H	3.105306748868	0.669952992523	-2.438476892581

C	-2.610917673481	0.444093104328	-1.331595709591
H	-3.176789538180	1.085239067587	-2.032029561708
C	3.369394780703	-0.655360395606	-0.773126421943
C	2.821415898483	-1.428639316749	0.303887054001
C	4.761594387645	-0.709296446851	-1.025496998772
C	3.699333410305	-2.218783790577	1.075704945943
C	5.600046845874	-1.486199998374	-0.253309354724
H	5.163716683988	-0.120597353669	-1.854078435886
C	5.055498740347	-2.242468960644	0.800667088003
H	3.272639679378	-2.807555562744	1.887810887892
H	6.669631209597	-1.518789008841	-0.458791865151
H	5.712854818630	-2.863355813085	1.412554232199
C	-3.377876419381	-0.517383395865	-0.604181549606
C	-2.792290813584	-1.383831353562	0.377305538988
C	-4.767293427628	-0.595520479155	-0.856186090840
C	-3.633893641050	-2.283584904199	1.062502209883
C	-5.570234273909	-1.488368909911	-0.174738003204
H	-5.198475339008	0.069276652922	-1.609154046814
C	-4.990782498258	-2.332484070558	0.788155314483
H	-3.179914369685	-2.939620169677	1.805444994689
H	-6.638920736099	-1.540049269003	-0.380983766287
H	-5.618821116905	-3.042607332961	1.329636002025
O	1.543112354292	-1.424847419920	0.583203487911
Fe	0.016712142404	-0.491663308477	-0.038816882542
O	-1.510027339140	-1.359959955595	0.659685045472
C	-0.519138529871	2.940315117834	-1.036372690209
H	-1.508417038889	3.216692798095	-0.637129684015
H	-0.212612627359	3.795524811502	-1.661270271569
C	0.494475726465	2.873220706381	0.094558569427
H	0.533026063317	3.840553861133	0.615250664555
H	1.511992956645	2.664162750715	-0.265532608914

S	0.243913196060	1.616743842409	1.413345938109
C	1.075183922124	3.125539437901	3.249649646207
H	0.870849268190	2.485279637196	4.109932173866
H	2.120771613672	3.224281508194	2.951660351124
H	0.434275947888	4.000858479480	3.118104709603
C	-1.479099757891	1.892724114741	1.902136543700
H	-1.634343848714	2.952662786879	2.134550424651
H	-2.164957944230	1.559466811113	1.114837483189
H	-1.644074061918	1.291483218670	2.804023756897

[Fe(II)(S-met-salmet)]⁺ linear transition state for methyl radical generation (quintet state)

C	0.658559232003	1.583876211291	2.042208997666
H	1.304915192646	1.866452596938	2.891816752012
C	-0.648527855515	1.007419315496	2.587480832393
H	-0.413706766161	0.334105523002	3.428241700204
H	-1.300687846898	1.803549578659	2.985320854199
N	-1.307128338231	0.242984152088	1.530784131658
N	1.291407968279	0.532187362793	1.254159748194
C	-2.594240190732	0.034658869162	1.622675456525
H	-3.132390312036	0.464486825775	2.485806944078
C	2.561132111799	0.279977866745	1.407286391580
H	3.119265903560	0.840834619634	2.178677907713
C	-3.399582602615	-0.696409233528	0.702162860908
C	-2.856175497460	-1.337082822786	-0.460394345369
C	-4.788182952520	-0.793150836595	0.961063704671
C	-3.734830987138	-2.040950305242	-1.309953505323
C	-5.627511046201	-1.487104279288	0.114288130806
H	-5.186680767279	-0.304967163727	1.854179161031
C	-5.087641748548	-2.111136525701	-1.024935399871
H	-3.312208978771	-2.527858544224	-2.188846936553
H	-6.694331847698	-1.554720077296	0.325382639780

H	-5.745848806293	-2.664839387406	-1.697418454621
C	3.317067472334	-0.660217594947	0.643741390402
C	2.732718914832	-1.437012352382	-0.411598315173
C	4.693059611337	-0.811687713213	0.937067959561
C	3.563790688987	-2.322121958897	-1.128306292132
C	5.484324245969	-1.688812284582	0.223719815298
H	5.121878144743	-0.216195827088	1.747167930118
C	4.907000357355	-2.442708963316	-0.813288710737
H	3.112031410845	-2.909325498561	-1.927974423226
H	6.542196829143	-1.798076945233	0.460803673164
H	5.526623106163	-3.139940462609	-1.380677971546
O	-1.579653815440	-1.291451868264	-0.746665539538
Fe	-0.049182813017	-0.451310548074	-0.021120172820
O	1.463026286870	-1.343365584025	-0.731121732200
C	0.479215892594	2.836786297082	1.178573275357
H	1.468166206574	3.149948938568	0.806475437695
H	0.148979846321	3.655847231692	1.839005740233
C	-0.523216389422	2.813485585977	0.035931695628
H	-0.644536262268	3.832674060376	-0.350360424716
H	-1.517691729763	2.475555764843	0.358911830246
S	-0.194063295702	1.762347770564	-1.461892126156
C	-0.328566813347	3.817445435800	-2.799466547978
H	-0.013947570565	3.468291732159	-3.785669007868
H	-1.386438048534	4.070886058913	-2.700948210740
H	0.379221780919	4.453692887300	-2.262493494037
C	1.603472927189	1.887641842145	-1.730276805976
H	1.766943966167	1.583127801103	-2.771040938719
H	1.937740700457	2.922727963547	-1.603504263202
H	2.152172185070	1.213585135331	-1.064683802617

[Fe(III)(salmet)]⁺ (sulfide moiety coordinated to iron (III)) (sextet state)

Fe	-0.158542403549	-1.285462121742	0.823849931866
N	0.338683358466	0.760637171157	0.788909558695
N	-0.783543435589	-0.669383066541	-1.109127444724
C	0.476659443898	1.543264490831	1.821524392106
H	0.749660208330	2.599310348734	1.647183311547
C	-1.323548747883	-1.441252507410	-2.010825940823
H	-1.559276381379	-1.006759083999	-2.998226716564
C	0.295560269440	1.162358447990	3.185638564070
C	0.475114178891	2.145764009338	4.184665115957
C	-0.070125708141	-0.168549275913	3.571631731162
C	0.307064712909	1.846786587635	5.522976078391
H	0.751722127687	3.157328347760	3.877159647200
C	-0.241331170343	-0.449149193709	4.940986060449
C	-0.053380092302	0.540363372356	5.892829495803
H	0.449538537791	2.614643165303	6.282746886400
H	-0.522503598359	-1.463848563132	5.222458493721
H	-0.190606621656	0.297406007623	6.948172902555
O	-0.247117806613	-1.130009340363	2.693942428018
C	-1.648838859789	-2.824750745027	-1.858123362095
C	-2.229409184145	-3.496278937240	-2.958334517548
C	-1.421743257408	-3.545342449024	-0.640388576814
C	-2.577474424480	-4.831519587270	-2.881941802222
H	-2.403938751053	-2.934439398122	-3.879413750059
C	-1.786908908079	-4.904818953332	-0.584251425082
C	-2.351793204199	-5.530486374341	-1.684832362421
H	-3.025620188618	-5.335296478242	-3.737831592135
H	-1.615316069930	-5.441202579490	0.349174602269
H	-2.628322271517	-6.584240082112	-1.615468916893
O	-0.883743700212	-2.977846564168	0.413743691301
C	0.579710381441	1.282206187275	-0.556329233435

C	-0.543216470527	0.734908563198	-1.440481236649
H	-1.462920376817	1.307308034705	-1.236893949568
H	-0.311203488321	0.866296541587	-2.510693542873
C	1.994801265380	0.924268587027	-1.031906035978
H	2.182006195954	1.467944208732	-1.971692144552
H	2.718291566762	1.328676519119	-0.306749997152
C	2.302470492273	-0.537181206968	-1.308216888066
H	1.612715265317	-0.974513043019	-2.045316597209
H	3.320466407347	-0.632100525789	-1.711949860235
S	2.259961078484	-1.608136633072	0.188619766772
C	2.327137047920	-3.237013492748	-0.601286860042
H	1.517592605571	-3.348021403310	-1.333633529573
H	3.303581729059	-3.368552603848	-1.082300137210
H	2.208442785411	-3.983847038148	0.191391535687
H	0.513974202572	2.383974087708	-0.549015124046

[Fe(II)(S-met-salmet)]⁺ (sulfonium moiety not coordinated to iron (II)) (quintet state)

C	-2.882002492543	0.887227059948	-0.250744571294
H	-2.403100307239	0.923809457280	-1.247091042515
C	-1.870977519309	1.293684275580	0.841936609605
H	-1.023247178259	0.593285471656	0.793243805803
H	-1.459607690574	2.309604818297	0.690789282403
N	-2.581391947148	1.160278233715	2.099325630147
N	-3.301268131450	-0.460732911673	0.107393046592
C	-2.725391241593	2.214397470331	2.856773273152
H	-2.099316192643	3.104682964540	2.643862656463
C	-3.059576676468	-1.459604367139	-0.700972967624
H	-2.671347333797	-1.241245341815	-1.712680270968
C	-3.652992844821	2.345688211397	3.931033822979
C	-4.713672266381	1.395750383637	4.151239054144
C	-3.566325042943	3.498591065370	4.752586386138

C	-5.625280364304	1.669519193680	5.202201295767
C	-4.460101773402	3.725928421888	5.775285053278
H	-2.749970297857	4.203938005999	4.567870183426
C	-5.494196992666	2.793337536942	5.994067270459
H	-6.426573897914	0.948694570297	5.369783366903
H	-4.367963664127	4.607315676689	6.410254171512
H	-6.206771323230	2.960829491835	6.804827553407
C	-3.238200658455	-2.834920761038	-0.379247551714
C	-3.533902362998	-3.287685487908	0.955697043894
C	-3.057997757199	-3.788517812229	-1.413722956320
C	-3.646580536869	-4.683183113995	1.163866213666
C	-3.183073723605	-5.139381044539	-1.179366544260
H	-2.818605761055	-3.423566562872	-2.416479749977
C	-3.481672106550	-5.578639057324	0.125531288032
H	-3.866220807175	-5.022497669256	2.176488995705
H	-3.047089733984	-5.858524005547	-1.986994823429
H	-3.577591816569	-6.648441948670	0.323993282661
O	-4.890763666941	0.335432115265	3.412877125580
Fe	-3.759785831536	-0.593192984912	2.162784437102
O	-3.677210125192	-2.483391334692	1.973988148839
C	-4.157198778035	1.752969831553	-0.224177995522
H	-4.708330665234	1.471782621392	0.692153172771
H	-4.796514922627	1.465709518919	-1.071952233327
C	-3.920728023252	3.251549865415	-0.216589816003
H	-3.702391467733	3.691478673544	-1.201618051047
H	-3.126074175910	3.547127413906	0.485212340791
S	-5.391373755024	4.108319222645	0.463670390243
C	-5.008379519791	5.841719841954	0.159745528642
H	-5.885438071620	6.428731866368	0.454078406404
H	-4.165062785796	6.104675177683	0.808110463385
H	-4.761594637235	6.004579380762	-0.895623430035

C	-6.649584078194	3.776545631386	-0.782260382904
H	-6.276522380766	4.023720138128	-1.783319721133
H	-6.912313546597	2.715578031975	-0.705873189094
H	-7.526964175388	4.381483233637	-0.527386102727

[Fe(S-met-salmet)]⁺ (transition state for S-C_γ bond cleavage) (quintet state)

C	-0.755119193605	2.362327725852	-1.219793543392
H	-1.409289734268	2.851191933133	-1.962209620940
C	0.573668817564	2.040386577628	-1.904615539846
H	0.364246032757	1.738801047640	-2.944183758635
H	1.221240787683	2.932478026383	-1.959967922525
N	1.240277135904	0.927794340468	-1.234657478693
N	-1.363197862038	1.088881756470	-0.822219262276
C	2.541001987926	0.855297932303	-1.319381932390
H	3.078390033854	1.671507357513	-1.834746235549
C	-2.660813784483	0.973968381420	-0.924794798364
H	-3.234634606525	1.839513027509	-1.303782384609
C	3.365850099299	-0.197398704373	-0.817749366958
C	2.829882024015	-1.372668093569	-0.194047552159
C	4.766495198784	-0.081929256267	-0.986215374319
C	3.729315566940	-2.376782013781	0.224554901238
C	5.626099479406	-1.074001564801	-0.559984153847
H	5.159475507758	0.815457612743	-1.471411112099
C	5.093879736914	-2.226114425173	0.045741312773
H	6.702063449168	-0.971004937375	-0.698074195255
H	5.766465926034	-3.019162169215	0.378676721412
C	-3.435263943178	-0.181345132974	-0.606387306379
C	-2.845042956933	-1.410360181309	-0.159861416218
C	-4.839506346979	-0.109701907536	-0.773297858169
C	-3.695792499583	-2.507416248515	0.096264220162
C	-5.650128608582	-1.194010186443	-0.508704025653

H	-5.274405389921	0.830752320280	-1.121876392367
C	-5.064555860123	-2.396698376856	-0.072549469507
H	-6.729430749649	-1.123520714899	-0.641266256351
H	-5.699340323498	-3.260713213868	0.133705630459
O	1.545377890716	-1.536767239170	0.002476161421
Fe	-0.012399768286	-0.471266319292	-0.234695232892
O	-1.554754473834	-1.542345373847	0.020521694171
C	-0.648954128515	3.362422669005	-0.046393846284
H	-1.632827169482	3.435033564507	0.445499510883
H	-0.501897399803	4.359624210842	-0.511665346415
C	0.427724906943	3.211981543523	0.960237254500
H	0.330423776205	3.748932868819	1.907836226290
H	1.458075692935	3.047630843568	0.626469893126
S	0.168141678365	0.822567509473	1.822211853138
C	1.571166078066	0.522956571045	2.912018779833
H	1.489486623738	-0.478320996187	3.351422567941
H	2.471199916534	0.574698108950	2.288121594852
H	1.612608615651	1.291012835972	3.693270302750
C	-1.264662045963	0.763105793876	2.913013872595
H	-1.193235526414	1.546786852002	3.676504320442
H	-2.146148136770	0.929788387715	2.282574286337
H	-1.332866615097	-0.228262189821	3.376805872402
H	3.312065704608	-3.271581026993	0.687281599721
H	-3.236981971809	-3.439078762306	0.428052279874

[Fe(S-met-salmet)]⁺ (cleaved S-C_ν bond, dimethyl sulfide coordinated to iron (II)) (quintet state)

Fe	0.499899679231	0.073922031476	0.551487591228
O	0.688266742517	-1.226635594547	1.903244843094
O	-1.224261701306	-0.300506267171	-0.135509365162
N	2.582505692789	0.327753855693	0.670306119221
N	1.010529788542	0.780781645757	-1.390114758170

C	3.117766049216	1.278555572749	-0.284741024386
H	4.210219356443	1.184034330778	-0.394073123446
H	2.918797852729	2.303011086910	0.079695512285
C	2.431137141559	1.108166437709	-1.638932823513
H	2.877478663962	0.232396112003	-2.143299304100
C	0.176880549095	0.858016326104	-2.391473224363
H	0.553260396001	1.221026862376	-3.362601435639
C	-1.209101590685	0.508863257402	-2.390808754305
C	-1.948020884127	0.721863129719	-3.577136553101
C	-1.861174672948	-0.075833958745	-1.258476547396
C	-3.287203624147	0.390438831087	-3.657958825227
H	-1.436665354824	1.157234646860	-4.439529352282
C	-3.224826456710	-0.415913087224	-1.365464075276
C	-3.919868970959	-0.181351042581	-2.541544552349
H	-3.844421059732	0.563056837189	-4.578222962608
H	-3.707597798003	-0.870332475784	-0.499815403054
H	-4.975595818197	-0.452860520962	-2.600534725141
C	3.399628783945	-0.328514213009	1.447712378370
H	4.480225819127	-0.121600456346	1.359409431273
C	2.661744812414	2.356255719194	-2.504964332198
H	3.745894488375	2.543145980697	-2.524668180256
H	2.403256477781	2.125735217421	-3.555154475065
C	3.032340317926	-1.312267664194	2.413722510090
C	4.053333858764	-1.902527043039	3.192740387102
C	1.676226476805	-1.733401720416	2.601397927537
C	3.764491416574	-2.868577400608	4.137048855040
H	5.084712975966	-1.577451811366	3.034750525900
C	1.405325852442	-2.724683190089	3.565271473892
C	2.431192214678	-3.274565634765	4.316942205053
H	4.560493797683	-3.313677381295	4.733278047333
H	0.370215308702	-3.039376343385	3.697157034108

H	2.196748888424	-4.040153473868	5.058972793357
C	1.930012484469	3.561923978688	-2.038256738264
H	0.835654115120	3.578838811360	-2.039346563795
H	2.430766413170	4.528592390309	-1.953373136362
S	-0.313786564207	2.069105622435	1.864064841092
C	-1.611888484590	2.730139456982	0.788395075534
H	-1.257049149771	2.830827113581	-0.245914191913
H	-2.448763362677	2.024250710789	0.825530502329
H	-1.937352543004	3.702266946112	1.177271055130
C	0.940408147558	3.365675417681	1.704379670430
H	1.181728944511	3.555095544887	0.647949934369
H	0.566935434187	4.282582372796	2.176448114747
H	1.833158305185	3.026624982649	2.242844678857

[Fe(S-met-salmet)]⁺ (SMe₂ abstracted) (quintet state)

C	-0.664270929155	2.440136189936	-0.998532268074
H	-1.309147043859	3.230969827916	-1.414049997464
C	0.381662029514	2.009971347230	-2.035429530460
H	-0.136415849142	1.689973104639	-2.953710402936
H	1.058152286133	2.840060181054	-2.293894317905
N	1.088723406322	0.879303142813	-1.454147903996
N	-1.420813427194	1.222885890681	-0.691207526372
C	2.383189485065	0.791403465716	-1.546161670577
H	2.918515906032	1.516242893427	-2.183351879949
C	-2.710020304196	1.109723931554	-0.832837673933
H	-3.275265703840	1.991302353350	-1.176255664322
C	3.202476821184	-0.155385942551	-0.853043725984
C	2.682512500104	-1.062270061919	0.127828058271
C	4.590802570203	-0.152335762766	-1.110588917725
C	3.573038487277	-1.914286307863	0.808920628398
C	5.446541400642	-1.008905827095	-0.443469786452

H	4.981260227419	0.543831497336	-1.856599214420
C	4.927424367412	-1.890197987224	0.519185569073
H	6.514505904372	-0.998420369372	-0.659453911662
H	5.598804923022	-2.567569567890	1.049715355377
C	-3.446451879497	-0.081466811115	-0.580160879890
C	-2.790166848818	-1.290689523399	-0.168443868264
C	-4.848411494514	-0.077212673195	-0.761778736132
C	-3.574727419418	-2.444701109382	0.036775665244
C	-5.593886208692	-1.218456821064	-0.549104397130
H	-5.333279872912	0.849386785256	-1.077834319468
C	-4.945007289451	-2.401899393112	-0.148440076827
H	-6.673946257187	-1.206909225252	-0.692258099475
H	-5.533112547702	-3.306122103554	0.019079845343
O	1.397258363282	-1.141852794594	0.402396107359
Fe	-0.078611874223	-0.097848583054	0.026028141902
O	-1.494190381762	-1.354973058798	0.015562167124
C	-0.003431583482	2.833881900444	0.331748174174
H	-0.707631682267	3.446876656172	0.914187063299
H	0.882901182907	3.456243920808	0.141188087203
C	0.362324134596	1.592830768315	1.128391740122
H	-0.288451297729	1.369802959434	1.989287204321
H	1.420829714955	1.471011722197	1.391339962988
H	3.160386939271	-2.595150224690	1.553099252863
H	-3.068359574672	-3.358360040391	0.347120476356

[Fe(S-met-4,4'-fluoro-salmet)]⁺ (sulfonium moiety coordinated to iron (II)) (quintet state)

C	0.697684533182	-2.668168500413	-0.972737690448
H	1.345488365912	-3.353598500031	-1.548324086507
C	-0.595896925464	-2.447423993771	-1.756042428774
H	-0.334565426143	-2.293565324713	-2.816060191846
H	-1.244486787053	-3.340835294495	-1.714194782396

N	-1.268849831692	-1.258008875348	-1.249078899872
N	1.346385414991	-1.367261133193	-0.817279992603
C	-2.577098149560	-1.217761611916	-1.309642751007
H	-3.111834158845	-2.085895377468	-1.734865461052
C	2.658809244985	-1.328131236380	-0.844820720863
H	3.210093773750	-2.263984591816	-1.052449344837
C	-3.401258628647	-0.146829606487	-0.857838207734
C	-2.866143724022	1.066622665783	-0.298015434593
C	-4.806481636277	-0.290257946432	-0.973986038849
C	-3.772190070394	2.062652697307	0.126113839191
C	-5.678614893294	0.691176250423	-0.560145044427
H	-5.200135131303	-1.211397706247	-1.410822036375
C	-5.130030011696	1.861242441455	-0.013024156740
H	-6.758718679361	0.590386945600	-0.650469623961
C	3.456376368802	-0.171974005572	-0.631039135143
C	2.886279994233	1.116122437906	-0.323390459455
C	4.866211684894	-0.298643787814	-0.727765812303
C	3.764677591456	2.203483127025	-0.124816546419
C	5.708065452742	0.771100007740	-0.534239308377
H	5.285036392233	-1.278772336774	-0.968903174682
C	5.125944351428	2.014389480240	-0.233808264633
H	6.790523654075	0.685999460896	-0.611142770160
O	-1.583955873037	1.270166581426	-0.155281480090
Fe	0.015144133620	0.282410738025	-0.575509189881
O	1.601790570943	1.303782639599	-0.203214718898
C	0.502346487189	-3.331452882611	0.400315630661
H	1.488118388807	-3.444806101390	0.880047948130
H	0.131619844489	-4.359177586570	0.254104341995
C	-0.472678091030	-2.694737523993	1.377231075565
H	-0.489743871523	-3.224471825605	2.341508473453
H	-1.498809378762	-2.653694891317	0.983660066559

S	-0.122720613443	-0.931447941640	1.761332031812
C	-1.388500995460	-0.567322710867	2.992136269954
H	-1.209220246943	0.455698342038	3.341385560510
H	-2.350981642789	-0.603865165085	2.467664685642
H	-1.351976431730	-1.287593286618	3.817530672934
C	1.409721825085	-0.983430749237	2.703083637485
H	1.343351959760	-1.712825676037	3.518688229902
H	2.206958538383	-1.235630071032	1.993063727209
H	1.580568875921	0.030205926720	3.084126919239
F	5.938683615156	3.056597624955	-0.043445021516
F	-5.967954059620	2.819786326855	0.392590847141
H	3.358551785423	3.187574563047	0.103564273559
H	-3.390974089367	2.993712153828	0.543007743501

[Fe(S-met-4,4'-fluoro-salmet)]⁺ transition state for methyl radical generation (quintet state)

C	-0.692932744631	1.728620731746	-1.949932191529
H	-1.336025106668	2.043064688480	-2.790777771937
C	0.626390122140	1.201526535994	-2.513591870567
H	0.409868365341	0.589608757301	-3.404766992377
H	1.276854958151	2.029238610325	-2.844515794529
N	1.280332357131	0.366148326206	-1.509197344068
N	-1.321529782656	0.625991197098	-1.225702576343
C	2.571569116972	0.175547909311	-1.608104239743
H	3.112480662530	0.689303922907	-2.422008675229
C	-2.604547181407	0.424167162856	-1.349166094633
H	-3.170527291126	1.056215942849	-2.057269815184
C	3.373379228300	-0.639755933751	-0.762971631922
C	2.824271154510	-1.415788979609	0.315632367260
C	4.765340241131	-0.702267671123	-1.017099961475
C	3.693197975104	-2.210528361220	1.085561872195

C	5.608128676987	-1.480785704800	-0.256183835516
H	5.171947275698	-0.115248661231	-1.843792525377
C	5.042814365447	-2.225992449881	0.789960909738
H	6.678994077483	-1.537674448330	-0.442601303279
C	-3.364757156751	-0.543666348278	-0.629338751337
C	-2.777553547163	-1.402291307903	0.362328283261
C	-4.751316092191	-0.643027837150	-0.892129921748
C	-3.607372249836	-2.308235835026	1.045900011515
C	-5.556018660199	-1.537755320052	-0.220742256446
H	-5.187648216620	0.011325585071	-1.650280958326
C	-4.956223208829	-2.358311400977	0.744844192914
H	-6.623304770605	-1.624141421422	-0.416191169295
O	1.548656334928	-1.406245751553	0.596092653624
Fe	0.021959419831	-0.471414251774	-0.034609724999
O	-1.500339000919	-1.362000094970	0.654966417432
C	-0.544144931617	2.946887239730	-1.029771435473
H	-1.539588374062	3.210177579072	-0.637175802711
H	-0.243336506503	3.807466557746	-1.650065084052
C	0.462277678741	2.889936616104	0.108195199659
H	0.486213392489	3.856525891818	0.631102551504
H	1.484659159741	2.693040004141	-0.245174555485
S	0.218062078335	1.628381170474	1.424481575394
C	1.019433364533	3.152349285242	3.281978293460
H	0.818268282559	2.502703745755	4.135870983101
H	2.064556121474	3.267115175755	2.988471988687
H	0.363673018411	4.015841894472	3.146457700802
C	-1.511502099439	1.882480053923	1.901619236230
H	-1.679569518238	2.939221536658	2.139455588136
H	-2.187350884905	1.547732273098	1.106261516188
H	-1.677297233722	1.273880980766	2.798424482447
H	-3.182048275269	-2.969030622135	1.799267233150

H	3.296682113102	-2.810005706617	1.903055506868
F	-5.725442287561	-3.225292446959	1.400853279501
F	5.851096749846	-2.983672810136	1.529480860513

[Fe(II)(4,4'-fluoro-salmec)]⁺ (sulfide moiety coordinated to iron (II)) (sextet state)

Fe	-0.074348149063	-0.294943896446	0.032503454203
N	-1.423152822979	1.145494496287	-0.676486025519
N	1.143408805744	0.937691489305	-1.176074512659
C	-2.716956040417	1.012891944035	-0.787339837112
H	-3.300766349662	1.870731564784	-1.165086634061
C	2.422468452085	0.771981587479	-1.384541790996
H	2.949401788672	1.514972478129	-2.008057787155
C	-3.462619176536	-0.158366322610	-0.472014128944
C	-4.864086261844	-0.135279638203	-0.661279076883
C	-2.844510952270	-1.359675312346	0.016147782240
C	-5.652078222084	-1.231960843149	-0.386621028310
H	-5.326052406727	0.781059492543	-1.035170812847
C	-3.652929485263	-2.475135474021	0.288365894279
C	-5.019280450155	-2.389649384057	0.087161516774
H	-6.731368746825	-1.225360739920	-0.527125091489
H	-3.202044783365	-3.395241850539	0.655569240253
O	-1.551513384819	-1.447894914251	0.217456154648
C	3.232508627085	-0.286861187490	-0.880650697437
C	4.607174666043	-0.294744341152	-1.214767109735
C	2.708458539076	-1.344989117680	-0.063245187256
C	5.457185975755	-1.286261512631	-0.773623968893
H	4.997244961756	0.509535623504	-1.842503761124
C	3.580029067717	-2.352699826710	0.382346694343
C	4.916148843912	-2.304081499227	0.023629493987
H	6.515803397100	-1.302565272550	-1.026150526391

H	3.199818898704	-3.166754723546	0.997099095333
O	1.445137386384	-1.392751732605	0.280631219819
C	-0.791267481682	2.420681769569	-1.015113734677
C	0.475438612038	2.078800239903	-1.802614981191
H	0.188782897327	1.801531461465	-2.830191932545
H	1.147166646934	2.950232328996	-1.878741952380
C	-0.547195241510	3.258130803382	0.248316466333
H	-0.217268688023	4.260230476792	-0.069138580434
H	-1.512125277665	3.411356529306	0.756509271938
C	0.485994658277	2.757064407103	1.242222890505
H	1.472229268720	2.609249232511	0.777750015896
H	0.608360010550	3.489964470788	2.052286421857
S	0.025727024483	1.177858598211	2.069663826137
C	1.603045501739	0.780690427843	2.867240349346
H	2.416240908233	0.760070331613	2.130960867335
H	1.810300870228	1.519533436200	3.650339755545
H	1.493822522934	-0.210135932974	3.321653318159
H	-1.460185062049	3.010197912132	-1.665560729571
F	-5.770600539315	-3.454831231100	0.352866643102
F	5.726800020757	-3.267020268669	0.453934035576

[Fe(S-met-4,4'-fluoro-salmet)]⁺ (sulfonium moiety not coordinated to iron (II)) (quintet state)

C	0.326936667297	-2.107576160146	-0.532562225394
H	0.773503755340	-3.002775460233	-1.000037135836
C	-0.634242549151	-1.453889938780	-1.529283392600
H	-0.126960091149	-1.356529252629	-2.502776887098
H	-1.543750341835	-2.056899522192	-1.675245741940
N	-0.949420465393	-0.123034684152	-1.018961443313
N	1.365506757866	-1.100747286830	-0.274461244188
C	-2.186652156762	0.299275425189	-1.049127654157
H	-2.942977364930	-0.348106758283	-1.518949620820
C	2.623276581392	-1.450145332259	-0.259946463072

H	2.870701330256	-2.511806853363	-0.431258561432
C	-2.663935930424	1.525297957966	-0.498554875231
C	-1.817364034721	2.446010762702	0.202663446003
C	-4.038157226355	1.825427367971	-0.625092496568
C	-2.373341612910	3.615465506167	0.741528605003
C	-4.582497238864	2.979322522075	-0.097636267467
H	-4.680429775535	1.119301665319	-1.155456018773
C	-3.728556233846	3.857192974412	0.580593671745
H	-1.741650183135	4.322589140874	1.276109463772
H	-5.640120455311	3.219407101878	-0.190900659997
C	3.732162037988	-0.576760829213	-0.059180987965
C	3.579142707325	0.836572362347	0.135961178560
C	5.033346344032	-1.127865058457	-0.067991045650
C	4.722586116324	1.630334231496	0.310238089916
C	6.155399610529	-0.344473058017	0.107418613848
H	5.145471160175	-2.203754452607	-0.217836626477
C	5.972038342459	1.031535371009	0.294348717178
H	4.622220797490	2.704013021774	0.458656299804
H	7.161796168336	-0.759170933155	0.102630881949
O	-0.527175201788	2.230128516287	0.346684845990
Fe	0.634929489602	0.842196948331	-0.098314632232
O	2.395634544097	1.408597808496	0.166409103942
C	-0.310210092956	-2.500180039989	0.803524172131
H	-0.605790137759	-1.587616177191	1.353449630021
H	0.478545077728	-2.960646110432	1.417862916632
C	-1.493585957570	-3.454931358579	0.709526624077
H	-1.386556509461	-4.137057460319	-0.151307650052
H	-1.545240467179	-4.083630479989	1.610129581407
S	-3.076917480911	-2.551310328681	0.574482901508
C	-4.202922774652	-3.957835283841	0.431985481998
H	-5.219528501026	-3.553801744443	0.372789148355

H	-4.000058748281	-4.545884000230	-0.472604972604
H	-4.131987647119	-4.600150551884	1.319470188299
F	7.045917184775	1.795492240082	0.461936654328
F	-4.241697353987	4.970014071518	1.094467486402

[Fe(S-met-3,3'-methoxy-salmet)]⁺ (sulfonium moiety coordinated to iron (II)) (quintet state)

C	0.233902281650	1.897923234979	2.100216540479
H	0.759996970908	2.512036416375	2.853531868080
C	-0.636506254554	0.873616927086	2.827909991346
H	-0.039340640097	0.432060240709	3.642651234732
H	-1.513194847432	1.355122726081	3.296996904178
N	-1.024403586343	-0.172277926282	1.889179203175
N	1.195761238123	1.154064254080	1.289870908424
C	-2.193235163617	-0.741184941118	2.050277820691
H	-2.820374882178	-0.425667597496	2.903130527904
C	2.400443343001	1.656381181420	1.148258783111
H	2.654019288861	2.580769679815	1.699698570956
C	-2.773146432274	-1.722037673336	1.189609490975
C	-2.087943255190	-2.212689704989	0.035432512518
C	-4.082458062810	-2.185553784156	1.487788619144
C	-2.782282827262	-3.127584897094	-0.819239076983
C	-4.708753400049	-3.091462398057	0.664574494670
H	-4.580946549027	-1.809109969359	2.383859208394
C	-4.060409542183	-3.559603382775	-0.496041150178
H	-5.710650322676	-3.451718177460	0.898104763352
H	-4.576287371108	-4.271484808583	-1.140811797169
C	3.438457466908	1.113474596070	0.340779136988
C	3.235280768729	-0.060551682393	-0.452315198346
C	4.701153767284	1.767578027355	0.334731247139
C	4.334072284977	-0.538946874404	-1.237576446990
C	5.734891002361	1.279146935050	-0.426373491938

H	4.834422925097	2.658279139945	0.952790484460
C	5.551857381927	0.123192701401	-1.214330494317
H	6.705266040709	1.775696852235	-0.426743390516
H	6.386027936049	-0.248945036596	-1.809416359456
O	-0.877451306884	-1.852880103714	-0.292271358139
Fe	0.434864960671	-0.638912522467	0.426311344959
O	2.103583398222	-0.701276468305	-0.510221878239
C	-0.548724716279	2.892392521084	1.224683010692
H	0.170088967736	3.577060113646	0.745983379983
H	-1.168294388266	3.531681703978	1.874776565836
C	-1.509078253041	2.342602589039	0.180950300630
H	-1.971370093746	3.144070445685	-0.414706123605
H	-2.309473100901	1.734459724551	0.626575007429
S	-0.739939994884	1.174064363954	-1.012076760212
C	-2.144726270739	0.681916647109	-2.025694032818
H	-1.766570304897	-0.043821163359	-2.755360723015
H	-2.844482232063	0.170773849821	-1.352098019363
H	-2.607817206929	1.550474648190	-2.507739381784
C	0.251613938454	2.229117536545	-2.082389652784
H	-0.339772012291	3.067506955899	-2.468289675761
H	1.103312750417	2.572925594587	-1.483009940793
H	0.623052311342	1.592084751898	-2.893511773951
O	4.056602654311	-1.646895005540	-1.961255858068
O	-2.083576447963	-3.495925580107	-1.920562541319
C	5.118532478406	-2.191594477387	-2.723209638200
H	4.714467760341	-3.080659533864	-3.215742194861
H	5.475346277806	-1.483435652883	-3.488600771746
H	5.966478862973	-2.485230312466	-2.084251326626
C	-2.681086702691	-4.473233889529	-2.753882297848
H	-3.625582820398	-4.113512140929	-3.194068841436
H	-1.962903923033	-4.670880042691	-3.554976391707

H	-2.876544845455	-5.407593591247	-2.204629832077
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[Fe(S-met-3,3'-methoxy-salmet)]⁺ transition state for methyl radical generation (quintet state)

C	0.711203986782	-2.946716877630	-1.130941720619
H	1.360555515034	-3.600344313349	-1.740180059150
C	-0.594069360137	-2.708652295431	-1.889914653859
H	-0.355084334941	-2.530323355805	-2.951445103123
H	-1.244540289612	-3.599589035565	-1.853805684350
N	-1.258265616342	-1.526974776835	-1.348623914246
N	1.346038798086	-1.643679712193	-0.945733552789
C	-2.551691829779	-1.419171131320	-1.498559988993
H	-3.090154589310	-2.245112946501	-1.996184443715
C	2.633264463106	-1.531079166602	-1.111564726211
H	3.199475581199	-2.414503208915	-1.459216150505
C	-3.368682521001	-0.328203147936	-1.077932191721
C	-2.815010337623	0.835630839041	-0.463547152439
C	-4.765006825787	-0.414001545714	-1.309151120492
C	-3.702690367733	1.893053510629	-0.091846450804
C	-5.596520211519	0.619512353047	-0.939863227923
H	-5.166504761310	-1.309272020418	-1.788268394059
C	-5.066325583815	1.772187708675	-0.331913378339
H	-6.669896036336	0.556133236114	-1.117766467043
H	-5.741429633061	2.580304919092	-0.049908040475
C	3.407184214869	-0.354400969040	-0.862526753115
C	2.811941973599	0.837999802131	-0.351024280483
C	4.799396120750	-0.401867919591	-1.116710820983
C	3.657246243278	1.961978172508	-0.098804578537
C	5.590037738206	0.700623155210	-0.872178817276
H	5.233400921912	-1.322819582711	-1.511328511500
C	5.020745927817	1.880324218340	-0.363592354702
H	6.661052123214	0.667445632812	-1.071256350241

H	5.662395075422	2.741767310506	-0.177998461607
O	-1.540882174200	0.978569476841	-0.232437407961
Fe	-0.001920085100	-0.114289623630	-0.382668608204
O	1.534598256990	0.948654821850	-0.096917248804
C	0.534548285664	-3.642888764448	0.224606494035
H	1.521935266806	-3.715303761288	0.708779490275
H	0.230390191186	-4.685697120852	0.034741413116
C	-0.484034257606	-3.090594527578	1.208936566553
H	-0.522877312267	-3.732708996690	2.100348603225
H	-1.500077145039	-3.064122043664	0.789927405495
S	-0.241996605509	-1.382565667070	1.843479499569
C	-1.070751026842	-1.923371516476	4.113794908347
H	-0.880104137950	-0.971502251959	4.613715356356
H	-2.115614866672	-2.151412370386	3.893197188856
H	-0.431820628245	-2.763860542287	4.397028289705
C	1.479541407456	-1.406868147373	2.406851680190
H	1.638981874083	-2.254327438662	3.083620730796
H	2.165774659636	-1.450915903988	1.553249867904
H	1.638221018004	-0.467208920167	2.949041246390
O	3.019977279537	3.042095754641	0.393335993931
O	-3.099420271374	2.952446507320	0.483433272189
C	3.805827046967	4.197824668571	0.637262743604
H	3.116543001793	4.955981256128	1.018671288506
H	4.586426465442	4.004139804678	1.389670090784
H	4.276867685171	4.567077186112	-0.286908010170
C	-3.928226281812	4.043975486085	0.847232049720
H	-4.677020514467	3.750247624787	1.599729798573
H	-3.262991520054	4.798475687105	1.275953654380
H	-4.442998563105	4.469083231926	-0.028535114235

[Fe(III)(4,4'-fluoro-salmet)]⁺ (sulfide moiety coordinated to iron (III)) (sextet state)

Fe	-0.091823251059	-0.338130264765	-0.031291303597
N	-1.441109656274	1.154003616167	-0.675574348953
N	1.129980104584	0.947546604984	-1.213932872774
C	-2.732223441919	1.036740227911	-0.787225387412
H	-3.311124255729	1.907138406681	-1.144722827003
C	2.407410191028	0.798867214269	-1.419635551469
H	2.934911591427	1.560362294173	-2.020834946240
C	-3.494642126074	-0.137361749711	-0.492832949139
C	-4.893085881567	-0.090445391031	-0.695550443300
C	-2.881151882291	-1.332090105646	-0.011720649554
C	-5.675260773124	-1.197041712747	-0.430597087180
H	-5.342996684662	0.832931380015	-1.065519543496
C	-3.712729538339	-2.463063298039	0.252915179666
C	-5.087511651336	-2.379843791108	0.041860209044
H	-6.753070520861	-1.161118010772	-0.587571404528
O	-1.597359443411	-1.440114861969	0.205923032537
C	3.230502810335	-0.264810532876	-0.927909391191
C	4.607183918255	-0.240324197620	-1.252410259949
C	2.703286654444	-1.327121149340	-0.135470707360
C	5.450610301900	-1.235859803795	-0.800497686582
H	4.990602308323	0.575329827555	-1.868726384501
C	3.599312470567	-2.337466610563	0.330153284069
C	4.949339249237	-2.280709213848	-0.009447194738
H	6.510418885881	-1.217906697290	-1.053624756849
O	1.441582535812	-1.414809082401	0.189040886894
C	-0.797984355643	2.431027239919	-0.981453567087
C	0.453108324223	2.103124893648	-1.800480087691
H	0.143712633144	1.847355346694	-2.827206638526
H	1.124224221309	2.975581152769	-1.873013944310
C	-0.525092134655	3.223329899821	0.305495444517

H	-0.198792988549	4.234555915906	0.013988255612
H	-1.480120024650	3.362009661741	0.836323058995
C	0.525756188753	2.688076203773	1.263465273402
H	1.500570401542	2.551453612960	0.772039653488
H	0.670057360990	3.400074940254	2.088522957943
S	0.077099148545	1.086756409430	2.050841864289
C	1.677633964281	0.647359690223	2.775606501345
H	2.467734745530	0.677650962928	2.014275504531
H	1.910899785828	1.332678565369	3.599114426342
H	1.585560276539	-0.373706634447	3.162558229057
H	-1.468937476566	3.051097014428	-1.601506628591
H	-5.720703245270	-3.243836560736	0.243387053440
H	5.630751172099	-3.056452009647	0.339908287802
O	-3.057996090970	-3.548007875773	0.703268419943
O	3.024923239919	-3.287273542273	1.091288958941
C	-3.834004456321	-4.703403269075	0.983735543132
H	-3.128042498854	-5.461999570727	1.331863342738
H	-4.576505598134	-4.507502984128	1.772612607184
H	-4.347943915776	-5.071249638977	0.082349729430
C	3.859011892016	-4.340525522181	1.551883419611
H	3.210710045515	-5.008547074262	2.125069816302
H	4.303612443359	-4.896563722659	0.712425099273
H	4.661436546645	-3.963266193212	2.204687792495

[Fe(S-met-3,3'-methoxy-salmet)]⁺ (sulfonium moiety not coordinated to iron (II)) (quintet state)

C	0.316806459691	-2.111864903371	-0.581286150370
H	0.752515636975	-3.001920193944	-1.069412711387
C	-0.671309655408	-1.452748122339	-1.546203846065
H	-0.184414971856	-1.337339262620	-2.528369659556
H	-1.576379841508	-2.065152942484	-1.682853104268

N	-0.988818769884	-0.129428824250	-1.021463021198
N	1.359236661072	-1.109445524393	-0.328865333925
C	-2.221531929433	0.287632180525	-1.042541158770
H	-2.987926740479	-0.365480976136	-1.489339336122
C	2.609351019572	-1.466404781129	-0.306938102092
H	2.857871300838	-2.526378269638	-0.491141404409
C	-2.693619191190	1.532881816660	-0.508887229534
C	-1.824928380847	2.464462578801	0.130058430862
C	-4.070059866318	1.817296096529	-0.618205616566
C	-2.381397766274	3.675010969986	0.648002424038
C	-4.588027104532	2.998808654273	-0.112161564751
H	-4.722060572011	1.091409202988	-1.107751526341
C	-3.749362432510	3.924284332910	0.517397512809
H	-5.652805110870	3.213781945397	-0.199664108059
C	3.726477668844	-0.598506589616	-0.073619300239
C	3.560466568748	0.795694720587	0.173042303000
C	5.020660857342	-1.161110592121	-0.093088759364
C	4.725436323041	1.594144222207	0.391504209000
C	6.134698865333	-0.368710013433	0.124576709714
H	5.130222203338	-2.230795545654	-0.281775520486
C	5.989365236540	1.002496718937	0.365738209366
H	7.132433313157	-0.806721661897	0.108301186902
O	-0.538343129962	2.268574149223	0.256102718413
Fe	0.626413758414	0.854325503825	-0.112884513384
O	2.390657565963	1.377531961621	0.220861725934
C	-0.289348298186	-2.523743646167	0.763734034551
H	-0.582471634177	-1.619995471744	1.328868021181
H	0.516696651775	-2.983233745285	1.356211303281
C	-1.464430987521	-3.490227175760	0.684223326176
H	-1.363615461767	-4.166243377451	-0.182383972829
H	-1.492086966844	-4.124681123220	1.581997376340

S	-3.061076601970	-2.605761537150	0.583303690654
C	-4.171502687681	-4.029639547811	0.502895567291
H	-5.194935733337	-3.640410672745	0.463210102295
H	-3.987016209082	-4.633751288700	-0.395219638423
H	-4.068631016178	-4.653919619792	1.400261669097
H	-4.173419165866	4.847828699243	0.911007752745
H	6.877428651055	1.611560422542	0.533489897576
O	4.481191241861	2.894887763099	0.610463856621
O	-1.496910554581	4.492768493886	1.237348692265
C	-1.988009355153	5.718014652807	1.766333336877
H	-2.732744845922	5.541902589032	2.557035000529
H	-1.120468222297	6.228478528463	2.192071936877
H	-2.430334394436	6.344928194927	0.977611700374
C	5.600087075442	3.740892640980	0.842454733767
H	6.277683102890	3.754814657641	-0.024532801129
H	5.190333891017	4.742043550670	0.998310950181
H	6.157026725175	3.430515461092	1.739329630548

[Fe(II)(OAc)(SAM)]⁺ (quintet state)

O	0.866789337780	2.076435426065	1.917076874673
C	0.554911966365	3.307276596938	2.037518146479
Fe	-0.020985359318	2.260727036006	-0.120241509116
N	1.877064561426	2.653554753023	-1.315560375904
C	2.504284038013	1.315859012576	-1.351414259188
C	1.397425012893	0.255482001522	-1.514614325264
O	0.192552277545	0.663846453094	-1.303614216523
H	2.538242772742	3.354722262747	-0.976114862790
H	1.648646519312	2.945723071746	-2.267626814412
H	3.187208677320	1.195296700192	-2.208228938221
O	1.731802304463	-0.907157338927	-1.751836394665
C	3.302509123162	1.121728284084	-0.044596187069

H	4.334340269956	1.476215099320	-0.187693464811
H	2.862572556911	1.762671220305	0.737078803512
C	3.389711649623	-0.299542150841	0.483400176009
H	3.610131218963	-1.027078881584	-0.307877835877
H	4.124321341851	-0.394144336192	1.294004335436
S	1.755843865639	-0.819815011040	1.168148749044
C	2.019426965544	-0.717429384565	2.945323408389
H	1.124248936639	-1.136670011911	3.419140618770
H	2.919815739982	-1.266493386269	3.244131596212
H	2.085325406093	0.353169071302	3.174431423907
O	0.038739435339	3.924249859208	1.042432233271
C	0.753712021410	4.035199375883	3.322827772416
H	-0.210939006072	4.095073120027	3.845271664779
H	1.466583563194	3.521291487111	3.974671337527
H	1.075081780405	5.065731924978	3.137098951877
C	1.757591223780	-2.605853531695	0.827216765688
H	2.691530257620	-3.042394788368	1.208279020805
H	1.775643852016	-2.621273159277	-0.273239654116
C	0.504093267616	-3.279164587584	1.409672134638
H	0.750259710259	-3.842814815529	2.320052253779
O	-0.483098876005	-2.288669328053	1.783851607756
C	-0.182055288647	-4.169471590588	0.388640736571
C	-1.580706614973	-2.349725033149	0.887777782115
H	0.540980660382	-4.629410358717	-0.311848012686
C	-1.106062370921	-3.178297261000	-0.319055712586
O	-0.937773677987	-5.121294393650	1.084316895558
H	-2.442149230551	-2.836001381895	1.375390014100
N	-1.939295276318	-0.977507735069	0.534899284631
H	-0.525198791405	-2.513461693231	-0.993588337360
O	-2.109611277684	-3.886599951975	-0.968569192828
H	-1.649732313132	-5.387901373535	0.478969513003

C	-1.524835299155	0.161364176186	1.158816130261
C	-2.632723701252	-0.574294566729	-0.594130712404
H	-2.685885824463	-3.215494718603	-1.395622030758
H	-0.940735522946	0.138474534590	2.073391320497
N	-1.887347093080	1.272529393938	0.527687822321
C	-2.602663642365	0.814984742410	-0.565274527752
N	-3.156550880860	-1.334933917462	-1.561344331586
C	-3.108711076025	1.476908680247	-1.694017704709
C	-3.647191299450	-0.581784144379	-2.559270898883
N	-2.971823935797	2.826501615935	-1.848906380801
N	-3.647785079514	0.750189111730	-2.682914919727
H	-4.100671397746	-1.132471638672	-3.386922531628
H	-3.502229976574	3.219114841106	-2.620397340693
H	-3.001419983440	3.382352357510	-1.000264094737

[Fe(III)(OAc)(SAM)]²⁺ (sextet state)

O	0.581137399522	2.666981572982	1.682343923423
C	0.171499426102	3.885023795711	1.647307608559
Fe	-0.293968429436	2.383564311188	-0.175723243480
N	1.778592561790	2.758471159274	-1.001625928355
C	2.427805498893	1.432445790879	-1.147573446723
C	1.337176959142	0.397395062702	-1.443963249753
O	0.114111687324	0.818541957661	-1.247667632343
H	2.359279365912	3.393860347987	-0.448829920343
H	1.704920309848	3.204925875760	-1.919977529180
H	3.115525707923	1.420581696385	-2.007284045523
O	1.628868396425	-0.740906381421	-1.769925606105
C	3.222498952365	1.095537649431	0.131977940330
H	4.226789943595	1.536985877340	0.052291662639
H	2.746298509087	1.594084436022	0.993291456546
C	3.403610321141	-0.384897757022	0.440992093721

H	3.599011171952	-0.991004545525	-0.452574172713
H	4.201917170052	-0.552302426192	1.175292910883
S	1.845357424279	-1.046027900728	1.183738739163
C	2.295026441464	-1.273498657253	2.916350842511
H	1.416011437818	-1.688830426890	3.422981106380
H	3.157608361625	-1.944212996332	3.006582037645
H	2.524047751957	-0.282854712799	3.326748464959
O	-0.421342363735	4.251788284822	0.567280573123
C	0.343636263755	4.811168734367	2.782707863503
H	-0.612661680261	4.878647322821	3.321110137081
H	1.107182926539	4.456428392271	3.479973215247
H	0.571863655933	5.820410882886	2.423443708951
C	1.698630836423	-2.755980086767	0.561287975040
H	2.656752257656	-3.271825242802	0.717547900643
H	1.546682406298	-2.604873731436	-0.517746642045
C	0.525860981289	-3.470880178226	1.249018344411
H	0.873426102361	-4.066222709409	2.104114392978
O	-0.424895555527	-2.506472448561	1.773039479431
C	-0.270257825292	-4.331236841750	0.282824512062
C	-1.605464760776	-2.528330033183	0.997107962528
H	0.363270844606	-4.761654546825	-0.515804346316
C	-1.275827797046	-3.322297573802	-0.283721665463
O	-0.926040901906	-5.296450155048	1.047623941485
H	-2.431349749488	-2.998336886485	1.553987509367
N	-1.952974674163	-1.122766737863	0.714883967888
H	-0.773745042340	-2.639225368702	-1.001493790658
O	-2.344399906159	-4.008776641246	-0.834206335110
H	-1.614714494323	-5.690920588270	0.488450231782
C	-1.453711523599	-0.043256524681	1.374263078826
C	-2.644537510375	-0.632135737463	-0.386670968454
H	-2.899048410740	-3.361677782961	-1.306579613273

H	-0.865658657563	-0.146470911225	2.280856818040
N	-1.754243141678	1.117034572610	0.791623159577
C	-2.516670546648	0.748227732794	-0.296189198897
N	-3.160884075436	-1.275684223800	-1.432839526258
C	-2.746359456518	1.469165126777	-1.458679468910
C	-3.487172290998	-0.445934017166	-2.436252911727
N	-2.178997202908	2.779289212063	-1.494117127742
N	-3.251419176569	0.882169376741	-2.526212376373
H	-3.951605046446	-0.905735734770	-3.310201140338
H	-2.171952176704	3.132064355323	-2.455999319642
H	-2.731291157879	3.446408719100	-0.942452546069

[Fe(II)(Gly)(SAM)]⁺ (quintet state)

O	3.894186042737	-0.223309109378	-0.997683243958
C	3.855511053783	0.438800785181	-2.127365607547
O	3.940968031130	1.651635015079	-2.242142097063
C	3.630601928411	-0.421929910785	-3.371136419514
N	3.599797284647	-1.873903009575	-3.039780772651
Fe	2.811958986427	-1.891358253199	-1.054521021063
N	2.947155415324	-2.401115588309	1.072374020306
C	2.009705292364	-1.422776306486	1.686042808311
C	0.834906456104	-1.170487228189	0.719365718806
O	0.974871312047	-1.631310379361	-0.487072164751
H	4.553407354018	-2.243246518195	-3.062420955962
H	3.108013730900	-2.383358791363	-3.776850857872
H	3.858438680969	-2.351420639319	1.532941702521
H	2.613039056095	-3.348979384052	1.257634871138
H	1.563869006503	-1.821613423733	2.611502728112
O	-0.123423422407	-0.522440398016	1.127766274199
H	4.386669354512	-0.179918582595	-4.132282751758
H	2.656038809858	-0.149293652432	-3.802612749793

C	2.798821014775	-0.143680114873	2.025933136547
H	3.251778335821	-0.255739224638	3.022660357009
H	3.633700175950	-0.038860642851	1.314079562071
C	2.000854391706	1.147498717219	2.033945383585
H	1.017420346699	1.034895112675	2.505746426149
H	2.554610389664	1.961843266013	2.518511655946
C	2.805723713798	3.078489013255	0.131962647180
H	2.615325943003	3.518341079992	-0.852258565346
H	2.645755268951	3.797259767719	0.944398243656
H	3.814200533605	2.649923153447	0.129883743652
S	1.670148395338	1.692060190531	0.300322159715
C	0.016531785352	2.476351124853	0.413881457687
H	0.131590165210	3.446201721859	0.916758359821
H	-0.574764557232	1.788183955848	1.032125338434
C	-0.590885506646	2.615669833223	-0.965110438820
H	-1.585572922784	3.077496517772	-0.840561333323
O	0.259755955252	3.484748517865	-1.738735656586
C	-0.757002126089	1.325019644223	-1.772819274989
C	0.369697416311	2.944108131263	-3.046596413044
H	-0.659199516997	0.422291225330	-1.140091737165
C	0.358046596765	1.427066261429	-2.815095407679
O	-2.010101864454	1.394051272294	-2.409370014867
H	-0.493005774448	3.240961023842	-3.672592847611
N	1.597682628708	3.470506770180	-3.604866458503
H	1.334939918393	1.169394606718	-2.353365871310
O	0.051953901729	0.616494607642	-3.906114910990
H	-1.942895869887	0.809738943193	-3.182131944097
C	2.254509300366	4.638724991150	-3.247313390009
C	2.329035599469	2.935032849096	-4.637111924100
H	0.670240390032	0.882302212098	-4.632807298222
H	1.854045455196	5.275375053512	-2.462711089682

N	3.340190077820	4.871540062214	-3.943893915463
C	3.396470526418	3.812175510935	-4.821533783006
N	2.082786154731	1.813728519553	-5.336875871294
C	4.316787739268	3.463535476175	-5.830178716279
C	3.023984065612	1.612948563563	-6.275169955431
N	5.420900883733	4.190547493808	-6.084377584421
N	4.102116009853	2.343401314621	-6.554357955777
H	2.883233993915	0.723483795063	-6.897844931441
H	5.947368879824	3.983205874400	-6.922232468826
H	5.509473591849	5.107332872519	-5.668761014634

[Fe(III)(Gly)(SAM)]²⁺ (sextet state)

O	-2.569596911377	1.868861774785	-0.848286162549
C	-1.384182976786	2.119986022939	-0.339814312362
O	-0.332409693264	1.846802363932	-0.895872748713
C	-1.388773479069	2.734078378322	1.056222974137
N	-2.770655769833	3.044364593830	1.514615477285
Fe	-3.958445114047	1.616577993769	0.470375763437
N	-5.434980692377	0.380632154890	-0.471289287118
C	-4.705417395227	-0.915902427629	-0.630221803065
C	-3.758285567473	-1.118576213539	0.564631488401
O	-3.551662970067	-0.062335806455	1.311781073755
H	-2.997492886564	4.014290200246	1.277370917431
H	-2.809134811995	3.017255920028	2.536879577097
H	-5.834344774329	0.669870068637	-1.369128966200
H	-6.250843727974	0.232489788007	0.130297336930
H	-5.411341590149	-1.760730792799	-0.624512380215
O	-3.216519079626	-2.200926165935	0.716203981707
H	-0.737075741042	3.618514815853	1.074614339066
H	-0.948767790600	1.999812460008	1.748241486671
C	-3.956502780346	-0.892598974710	-1.974422734131

H	-4.670917240430	-1.123979776106	-2.778978476869
H	-3.590801926156	0.127892393182	-2.175369640680
C	-2.804111714517	-1.873098842669	-2.103152607855
H	-3.024189882779	-2.846251065555	-1.646828684181
H	-2.521154293485	-2.022272869046	-3.152908635020
C	-0.262658652509	-0.724514773034	-2.623146317591
H	0.727696439382	-0.519155887059	-2.205076252166
H	-0.213633006761	-1.513604257493	-3.382408374561
H	-0.699710737500	0.203718389437	-3.008566418742
S	-1.291526549967	-1.247594404405	-1.239057495486
C	-0.496982849698	-2.799033879619	-0.666711711148
H	-0.101376336506	-3.324275082666	-1.546729780527
H	-1.316624327003	-3.374461502664	-0.216314247091
C	0.569365318344	-2.518868392663	0.363106875916
H	0.945969709524	-3.497916866911	0.709248344524
O	1.635195024618	-1.774194286023	-0.256895433525
C	0.139849884210	-1.722673819131	1.610045107141
C	2.184259031952	-0.962825938217	0.779072649180
H	-0.954306752424	-1.556772962529	1.646378485325
C	0.924237475865	-0.416533260386	1.443201297180
O	0.604706968611	-2.441994468613	2.719551926482
H	2.779197606339	-1.566322799388	1.486863946958
N	3.082159424147	0.001023405379	0.201276491376
H	0.416949259801	0.232183655025	0.698320608415
O	1.057007074910	0.209001110552	2.688766802414
H	0.531969488262	-1.863012750082	3.493342997346
C	2.800961178031	1.157857063723	-0.490086826484
C	4.463181172162	-0.141553406069	0.152655769148
H	1.761786787477	0.869528218733	2.644526634966
H	1.777228683497	1.518434449623	-0.615576977063
N	3.877223388699	1.777721820373	-0.960961204946

C	4.908925341547	0.983384124889	-0.570483764507
N	5.197019628555	-1.099387427045	0.677308589604
C	6.320052727428	1.068105634784	-0.740527410339
C	6.525336281018	-0.895479826940	0.434272321190
N	6.904664823328	2.069209895450	-1.397466353455
N	7.106747366330	0.098182155672	-0.220451197176
H	7.193796626704	-1.658555097905	0.839274937000
H	7.916131773375	2.077275852459	-1.491191844329
H	6.355299563512	2.817084898969	-1.805406520989

[Fe(II)(Gly)(SMM)]⁺ transition state for heterolytic C_γ bond cleavage

C	6.096387044703	-0.347198490419	-1.041471605073
S	5.064120704992	0.866838425744	-0.192484865549
C	5.507381527161	0.527778609204	1.525902734622
C	2.992685889924	-0.382229652678	-0.308476624446
C	2.041504545406	0.575542490128	0.344829675689
C	0.641538771557	0.357087460269	-0.235021970839
C	0.453293403578	-1.150908944675	-0.368684903202
O	-0.727542920553	-1.617854975815	-0.355243129563
N	-0.492627823880	0.938252992863	0.486456153040
O	1.503159851520	-1.811601605471	-0.504237673649
H	-0.667561698071	1.909154971664	0.222093317284
H	0.607535724919	0.753135505369	-1.265399241534
H	2.352479066850	1.616792594072	0.184406078838
H	2.024744459373	0.401353091315	1.432261210149
H	3.094291584927	-0.400304428917	-1.392693435488
H	3.504485405306	-1.164147082829	0.244601695856
H	5.857487032061	-1.366015772842	-0.708830794198
H	5.902963658732	-0.250697077033	-2.115726086553
H	7.153089353164	-0.126492780317	-0.849502716626
H	5.322250057198	-0.524102532268	1.781472300964

H	6.565875309949	0.768212924995	1.683373554129
H	4.900339761259	1.181750333417	2.162454236509
Fe	-2.248119094252	-0.375992702101	-0.063118663171
H	-0.315514989230	0.948067065707	1.492701188497
N	-4.083671060340	-1.183912328013	0.762964705068
O	-3.388839466045	1.049981773272	-0.530360998126
C	-4.702925221895	0.966506795034	-0.363844110937
C	-5.179209382649	-0.406412977804	0.115974221584
O	-5.494008364214	1.848844504864	-0.589229455098
H	-4.259973757942	-2.185856358947	0.663364518535
H	-4.116088226418	-1.022505516862	1.771849795511
H	-5.519043271565	-0.962470297365	-0.769459345335
H	-6.051008927276	-0.292162373765	0.772518881454

[Fe(II)(OAc)(SMM)]⁺ (quintet state)

O	1.949542355053	0.033382175152	0.491403540207
C	2.981951830436	-0.643969570973	0.787778731172
Fe	1.079989809524	-1.948643647519	0.002247985742
N	-0.753704793467	-2.196255857915	1.177696417630
C	-1.613645511461	-1.158247382930	0.554526693524
C	-1.354660164851	-1.123237909091	-0.965687675940
O	-0.256719792766	-1.690811860077	-1.364223109354
H	-0.740006913738	-2.082724965429	2.194033460944
H	-1.175199518674	-3.116160842264	1.026450032565
H	-2.684624833656	-1.371801862678	0.699137973266
O	-2.140023374431	-0.497040278203	-1.668072630531
C	-1.272243158886	0.195042714063	1.204381807268
H	-1.826950614285	0.295884878757	2.149821834480
H	-0.202793111653	0.207825234604	1.475345908602
C	-1.593604197259	1.417372338212	0.365737731674
H	-2.554952992023	1.321272284366	-0.155221624136

H	-1.583056638203	2.341362159194	0.959376876965
S	-0.363836629373	1.653848349726	-0.992431380502
C	0.703168801828	2.928851320297	-0.303726752906
H	1.407594713793	3.221462610244	-1.090621985622
H	0.122337900461	3.791465471466	0.042585736048
H	1.260886593456	2.446071869423	0.507524200918
C	-1.352977464148	2.545564922258	-2.202230318696
H	-0.674916241099	2.892339794202	-2.989541256392
H	-2.048566222029	1.801172488439	-2.607428258946
H	-1.876332890034	3.387013134070	-1.734050296281
O	2.939713234994	-1.925285069809	0.650924888442
C	4.237273432896	-0.016550726012	1.276147792894
H	5.034614808757	-0.194005719160	0.542740509875
H	4.120510224302	1.058686073031	1.435187569077
H	4.561056366534	-0.503684075441	2.203678428012

[Fe(II)(Tm-Me)(SAM)]⁺ (quintet state)

Fe	-1.924100886991	-0.523942489388	0.485176055888
S	-2.670403715438	1.828260646572	0.904834224550
S	-3.651490270093	-1.673110622869	1.722083989130
S	-1.881914860775	-0.216504871262	-1.948168502561
N	-4.447886053798	1.543802973080	-1.212792124025
C	-3.455328794619	2.217459825268	-0.575380341170
C	-4.732760098293	2.204453769786	-2.393741778192
C	-3.922350723144	3.288435624433	-2.485059469587
N	-3.139253049834	3.292409147534	-1.346364698528
H	-3.836432596301	4.061025577873	-3.239458773103
H	-5.500566614541	1.839357959594	-3.065353359351
C	-2.075736093177	4.230546254993	-1.057012126636
H	-2.124694333052	5.048358584102	-1.782375831937
H	-2.196394995156	4.642384253310	-0.047303369625

H	-1.100683039063	3.727671043435	-1.135074170777
N	-5.596111134927	-0.162815518964	2.846342629377
C	-4.924787639473	-0.521020725065	1.715052730291
C	-6.571875583540	0.760891251746	2.530559889063
C	-6.497001969983	0.957340689839	1.189888518344
N	-5.484546742680	0.162209001822	0.682026562003
H	-7.084126511979	1.595027056420	0.539166069083
H	-7.230331779103	1.178725669939	3.282560592180
N	-3.131699515419	-2.660956383695	-2.039493136485
C	-3.195669953144	-1.323145528036	-1.775503273156
C	-4.354228424159	-3.238460169440	-1.774978299926
C	-5.179549399876	-2.243064746423	-1.364466693866
N	-4.470777713086	-1.057171160607	-1.364292330043
H	-6.220038518466	-2.271983910948	-1.062265334503
H	-4.522843811602	-4.300236624958	-1.908030436396
C	-5.300882035250	-0.676570118927	4.166721001920
H	-5.929093001034	-0.154415863120	4.894264406884
H	-5.501125740553	-1.754032133097	4.217694848974
H	-4.243059408703	-0.511807402897	4.404960881003
C	-1.954938692407	-3.388594001742	-2.469478180057
H	-1.540388403066	-3.967254627744	-1.634659026883
H	-2.220413131815	-4.051469835682	-3.301543261798
H	-1.203861054485	-2.664817736368	-2.801070812706
B	-5.178650575455	0.228630229881	-0.850315823026
H	-6.256918181052	0.279257075866	-1.403371649555
N	0.186666692820	-0.284066297346	1.130201905461
H	0.297541443035	-0.651862102896	2.077893247944
H	0.539955785514	0.672323571452	1.152385693653
C	0.932148775694	-1.118999856915	0.178910632721
C	0.219459849775	-2.495002515129	0.093019443947
H	0.802988209760	-0.637641060089	-0.808260414845

O	0.893615140367	-3.490603995247	-0.227908452957
O	-1.025308273982	-2.465673269784	0.343154704677
C	2.427806578338	-1.264771180796	0.468248853764
C	3.138275180322	-1.768591094192	-0.776920257586
H	2.861534940353	-0.299120697178	0.778909919093
H	2.548576431429	-1.965429627812	1.311921848122
H	2.486071788332	-2.451095804624	-1.341789785254
H	3.506792726395	-0.964120490958	-1.427949001504
S	4.581967274571	-2.842148608375	-0.472490257821
C	7.131307439501	0.090248513562	1.054959371494
C	7.221189400614	1.351061215065	0.185430731927
C	5.908085395122	1.304311086190	-0.588123883383
O	5.620092733679	-0.081122179641	-0.769171334276
C	6.450122162107	-0.878992152783	0.072367758692
O	8.344299059778	-0.359858916221	1.559443285680
H	6.463583677515	0.277431247669	1.912920155958
H	8.999151726856	-0.188892439873	0.861650495997
O	8.319857731765	1.105431381298	-0.668313583786
H	8.576991631990	1.926555700372	-1.106439414266
H	7.350056646932	2.275000237711	0.771435560447
H	7.227500182120	-1.368361613433	-0.542330430834
H	5.976033090883	1.751598318244	-1.589379737897
C	3.845232034294	-4.137040329605	0.560278512786
H	3.917107510374	-3.855573747168	1.616729899393
H	2.785968375700	-4.210696210158	0.258202580439
C	4.695599104820	2.430507134580	1.401401925476
N	3.490588350486	2.831459050261	1.722360512280
C	2.749388696638	2.587773563597	0.583378056847
C	1.372605355502	2.720929886151	0.300633720862
N	0.921957200582	2.312582941697	-0.905804434233
C	1.805127189736	1.802946994298	-1.776048284142

N	3.123649311684	1.603975148011	-1.632059039600
C	3.528970896605	2.027601803354	-0.428496321185
N	4.801402017200	1.940587344405	0.105526287603
N	0.484791302552	3.203530556397	1.193007059252
H	5.559560460498	2.493879977965	2.060034773048
H	1.380164588949	1.490829488476	-2.735692342065
H	0.807908654114	3.420101907060	2.126215765165
H	-0.513132012678	3.032426393196	1.038646733838
C	5.592449547061	-1.922495892763	0.747988458662
H	4.395482412717	-5.064503007772	0.371883207119
H	4.894215554442	-1.486678588252	1.479935692189
H	6.212337207898	-2.678001906990	1.251837710950

[Fe(III)(Tm-Me)(SAM)]²⁺ (sextet state)

Fe	-1.966317408656	-0.758513824444	-0.030274518642
S	-2.555264802056	1.548992029825	0.619507048373
S	-3.590972286937	-1.858937984496	1.287113881175
S	-2.482498676845	-0.588934618690	-2.311575338100
N	-4.649487399882	1.511084164342	-1.219684826723
C	-3.504209771095	2.049224678481	-0.730542815351
C	-5.023591084749	2.241077420797	-2.332454529539
C	-4.112215499316	3.230954581468	-2.522797642597
N	-3.174228327721	3.104264099105	-1.519931743268
H	-4.054437435460	4.018207243858	-3.265000063132
H	-5.921817478065	1.997230418661	-2.887698204848
C	-2.011723007686	3.954279396812	-1.334846878489
H	-1.929261397449	4.621207232491	-2.197410105853
H	-2.124658265340	4.562105571472	-0.427582755932
H	-1.102153323540	3.342420052239	-1.256064599566
N	-5.242207876593	-0.437610312855	2.889808250042
C	-4.806154572444	-0.679206409816	1.625150069599

C	-6.211665706043	0.539560700455	2.854902180329
C	-6.369024890939	0.886893319646	1.549633246669
N	-5.502465951908	0.127893292595	0.786327732984
H	-7.039733976412	1.604016303751	1.090576264230
H	-6.709726731354	0.885195947378	3.752999351061
N	-4.112411560977	-2.770585444535	-2.390625001464
C	-3.951840597533	-1.467210347369	-2.045986139757
C	-5.371167444005	-3.179585553493	-2.018054479254
C	-5.981080190086	-2.102958783117	-1.448972380883
N	-5.101459947798	-1.040870904390	-1.468661021535
H	-6.979937015695	-1.997977856527	-1.040653405130
H	-5.725854600857	-4.186253965900	-2.205253715221
C	-4.765293599426	-1.120548567113	4.080497005890
H	-5.232366605665	-0.660917183836	4.955244896938
H	-5.028812568165	-2.184105021895	4.044529100715
H	-3.675909824334	-1.028273376535	4.154496021547
C	-3.083477346691	-3.603122913702	-2.993445171931
H	-2.233880776704	-3.697944249102	-2.305798277040
H	-3.508844994051	-4.590493802236	-3.189779895704
H	-2.742802346009	-3.159958660511	-3.935569020072
B	-5.496348092742	0.294025702007	-0.764652096054
H	-6.635597281486	0.528826266235	-1.085741469059
N	0.089637043981	-0.152409572979	0.445388307512
H	0.244046502294	-0.112502247589	1.456659012368
H	0.270332597045	0.796501320234	0.089137064361
C	0.993429202646	-1.127316680635	-0.184612464453
C	0.335391842553	-2.519985471592	-0.094325675985
H	1.012216640002	-0.863977179393	-1.259107443233
O	1.027939641121	-3.529411086310	-0.091840644774
O	-0.958959995719	-2.477340433294	-0.048255784011
C	2.429571085282	-1.139979813002	0.348131846566

C	3.351843384921	-1.797208199251	-0.670435390297
H	2.775762775952	-0.114038064157	0.551791172105
H	2.432093382239	-1.682822001294	1.307308896132
H	2.820108145083	-2.552291425532	-1.266682713372
H	3.828939661911	-1.070744313345	-1.343939310713
S	4.741099028248	-2.787614040787	-0.021734269003
C	7.337250712350	0.222170347122	1.273147666173
C	7.522444645555	1.403752377082	0.310031467668
C	6.208031021419	1.392296776081	-0.463543409003
O	5.832304485009	0.019914334074	-0.564381960213
C	6.588702063892	-0.765541653546	0.357692683132
O	8.505724443242	-0.282839943999	1.819062943150
H	6.683753980830	0.519667875342	2.110709077185
H	9.180761900865	-0.215426535296	1.121980770201
O	8.592455353151	1.011143263096	-0.519219088017
H	8.957800580741	1.782599910272	-0.971647545251
H	7.717690561123	2.357698773539	0.824981563337
H	7.330978129340	-1.364990208215	-0.199161513765
H	6.293602401104	1.783090383568	-1.485837253431
C	3.931624293353	-3.916451611434	1.133197891653
H	3.688475611612	-3.397985530779	2.067419025282
H	3.014054358276	-4.269566926834	0.644733706785
C	5.060494970354	2.653971925657	1.488492484696
N	3.858608128348	3.043239884527	1.835923007329
C	3.089227143006	2.742706231629	0.733344194879
C	1.703479982164	2.821271133582	0.499634135030
N	1.224655857792	2.388887527857	-0.689748283195
C	2.100888684643	1.898819725821	-1.590768772091
N	3.418155407349	1.727522706034	-1.476513381932
C	3.851618269898	2.174122854748	-0.288893916025
N	5.136172844873	2.121396092637	0.207589070308

N	0.822598176843	3.206617926750	1.451131419709
H	5.943444625168	2.760357482293	2.115431418690
H	1.657766367825	1.585248088681	-2.541992403230
H	1.182478796362	3.710113940301	2.252811609331
H	-0.128927770568	3.407137609527	1.164822043253
C	5.649900659633	-1.673915902928	1.113239310515
H	4.629107004260	-4.740345723862	1.319133334776
H	4.905350207286	-1.117444237249	1.704957373916
H	6.211597963281	-2.344926288936	1.780546896194

[Fe(II)(Tp*)(SAM)]⁺ (quintet state)

C	-2.086957822510	3.331159525441	0.553778435289
N	-2.707737144772	2.148881218066	0.696207307627
N	-4.005445212098	2.413091774481	1.044523958156
C	-4.202004705719	3.755624176344	1.119890170935
C	-2.996438454278	4.368256986512	0.810523112448
Fe	-2.261991477669	0.072465024793	0.530154549688
N	-4.050849275864	-0.183936752416	-0.544029018133
N	-5.148147841404	0.401319173640	0.016762003091
C	-6.240174156990	0.170612699241	-0.753422394911
C	-5.829662914242	-0.583774511052	-1.847533319989
C	-4.453926734985	-0.780121273091	-1.678534581301
C	-7.590346095874	0.682186898286	-0.411931954048
C	-5.508126968552	4.363425640206	1.476595077002
N	-1.614750014699	-2.191698518577	0.299483802109
C	-0.176422950810	-2.245688043982	0.001712068295
C	0.380198225163	-0.841723171432	-0.315352451625
O	-0.401736690114	0.155689261774	-0.173947316048
C	0.155020791510	-3.303074346430	-1.065140654550
C	1.523357940324	-3.242979816321	-1.726218659975
S	2.890154388572	-3.100422933890	-0.503288674372

C	3.644271605952	-4.741606208331	-0.622636810964
C	4.089991993350	-2.082170596891	-1.434555173500
C	5.441119685305	-2.060541969034	-0.743769219741
C	5.367949789143	-1.639572775242	0.728202221388
C	6.715309429679	-0.944063411423	0.903700096512
C	6.977542858555	-0.326074773711	-0.480348501929
O	6.229593906435	-1.089907981747	-1.418272969953
N	6.637067536669	1.072494584203	-0.604475427099
C	5.380206797046	1.652723671065	-0.586091588457
C	5.618808680039	3.016780386456	-0.753111326281
N	6.965936279068	3.294290229974	-0.878086407092
C	7.529801747313	2.118261386848	-0.792382313134
N	4.189952392892	1.054342153473	-0.447977103124
C	3.193066569213	1.956212404061	-0.477555877071
N	3.261377458265	3.285075557305	-0.619498009273
C	4.477731864102	3.845218821799	-0.769039799694
N	4.560347680887	5.177812816990	-0.958996761980
O	7.633210899351	-1.998335960176	1.161663744752
O	5.162750566830	-2.731852339903	1.590120781983
O	1.574746294203	-0.773360870239	-0.639166864460
N	-3.256919860179	-0.257548815436	2.340365253516
C	-3.024551992349	-0.904404093919	3.495252773054
C	-4.100195238057	-0.701057597134	4.367195395865
C	-4.996974584720	0.110569953047	3.679201690653
N	-4.465587458979	0.365346859467	2.458893799203
C	-6.305134265893	0.655551906277	4.118401455194
B	-5.001774047517	1.261335272876	1.304877376645
H	-6.453843467364	-0.932900691529	-2.665001962359
H	-7.617752110518	1.780638439063	-0.384376496689
H	-8.321144283424	0.346995900120	-1.156440253547
H	-7.925904062065	0.330047925346	0.573590050773

H	-2.802080898453	5.436261921235	0.774769995852
H	-6.075317170232	1.704973142022	1.611517511907
H	-5.429071000021	5.456439603508	1.465903856161
H	-6.304243475609	4.079025471784	0.773597435056
H	-5.844845866516	4.062844053159	2.479142827536
H	-7.123010549607	0.352784432611	3.449791026744
H	-6.543940634434	0.298908785027	5.126637524214
H	-6.302339445695	1.754323335161	4.142605486326
H	-1.857518996165	-2.804814060064	1.076900135011
H	-2.159804680189	-2.535373286674	-0.492539129195
H	-0.010552757343	-4.303517305321	-0.633014691256
H	-0.572891908388	-3.219494768157	-1.890804873004
H	1.718946137710	-4.140459510583	-2.330507946438
H	1.636259416486	-2.353660247915	-2.354786594321
H	4.465003191446	-4.754098537996	0.102372339081
H	2.886595676385	-5.476207447235	-0.325614090310
H	4.003527570441	-4.946053316010	-1.638600586547
H	4.548142249542	-0.917898982252	0.862685132782
H	6.717868135980	-0.186693322049	1.702562304158
H	8.049783034851	-0.404605585717	-0.722515564669
H	5.940276899635	-3.048278637509	-0.807834128877
H	6.055981587668	-3.075397194195	1.770865950939
H	8.435879095769	-1.631424699842	1.551926755368
H	8.599124927600	1.924933394958	-0.859064917611
H	2.188536652600	1.534759004331	-0.380020764789
H	5.464020919832	5.627066672337	-0.916845764096
H	3.729168200508	5.734770897712	-0.817577570748
H	-4.215834049937	-1.082318358923	5.377578632127
H	4.137925678254	-2.483039772451	-2.457040590863
H	3.649942004612	-1.072968241295	-1.418115537182
H	0.343615670652	-2.525605511773	0.934951942965

C	-1.768457038458	-1.672504247276	3.699424268286
H	-1.338213297001	-1.478027882329	4.690483687970
H	-1.931444749720	-2.760496912803	3.639650925194
H	-1.011935744056	-1.392495193006	2.951794514729
C	-3.483909918650	-1.493695011024	-2.551485387066
H	-2.456369427778	-1.148924834755	-2.359893808587
H	-3.522154282754	-2.587576528910	-2.415445835773
H	-3.694070004206	-1.310038969154	-3.613107656249
C	-0.648013751783	3.420860727831	0.191735913199
H	-0.003196772135	3.040668001269	0.997497929773
H	-0.410052076371	2.830547753824	-0.702642831587
H	-0.359315583701	4.461005431199	0.002009326922

[Fe(III)(Tp*)(SAM)]²⁺ (sextet state)

C	-2.505231590697	2.903368890829	0.029095318882
N	-3.087581289856	1.677139625641	0.060073054265
N	-4.434371418934	1.861651962462	0.253277044238
C	-4.702954815466	3.185016837683	0.341535557405
C	-3.493660231248	3.869639356688	0.202167149972
Fe	-2.543288567049	-0.284275408875	-0.100878299937
N	-4.051113360001	-0.640920255244	-1.402229743065
N	-5.268122075705	-0.167310952439	-0.987137748640
C	-6.193531916732	-0.404968558335	-1.945157332152
C	-5.551941421120	-1.050021756782	-3.005503093524
C	-4.215554508362	-1.173763240885	-2.635016357972
C	-7.613400436366	-0.005805040993	-1.810135527669
C	-6.068950153808	3.717254560272	0.549906596818
N	-1.684277518186	-2.452755996162	-0.245304607897
C	-0.212901926538	-2.387811284921	-0.334595896696
C	0.224518315139	-0.951236521295	-0.655470536779
O	-0.701986196103	-0.042557230839	-0.580011432339

C	0.374823922703	-3.457885890312	-1.268440668618
C	1.829079485345	-3.309450849291	-1.697906502479
S	2.965625914788	-2.968316180120	-0.289862637965
C	3.843232238605	-4.538683473801	-0.123451463326
C	4.210932693255	-1.899757617352	-1.098586181307
C	5.423749267263	-1.707520338797	-0.205280248520
C	5.075632487416	-1.246239918668	1.213747421700
C	6.323493048387	-0.442412342278	1.568755378746
C	6.733099376324	0.168968919409	0.217183269888
O	6.199700955033	-0.675540392503	-0.794602853771
N	6.285118025791	1.529483409418	-0.000650755376
C	4.994441968161	1.994282250678	-0.189916807154
C	5.138050014048	3.377149368292	-0.338690588570
N	6.451670212357	3.772412195615	-0.258601083390
C	7.098397810682	2.649561922253	-0.064931997826
N	3.850078694326	1.301729576754	-0.237846155696
C	2.799859931577	2.120274725225	-0.443450735438
N	2.771674386595	3.446335285745	-0.591960931572
C	3.948063717968	4.108975117266	-0.546969309818
N	3.950520146827	5.442269100606	-0.693187980510
O	7.263230513352	-1.418900768545	1.984354246029
O	4.804892427866	-2.321459027923	2.077329160226
O	1.399706295615	-0.720471805096	-0.902907780101
N	-3.624554590573	-0.739065169432	1.556573673806
C	-3.453764028465	-1.372162038929	2.739586678618
C	-4.641391398351	-1.305724327116	3.464000173056
C	-5.543083705897	-0.591820176583	2.671725117784
N	-4.908220555837	-0.258726866283	1.524104000426
C	-6.946764009401	-0.212641442803	2.954377341694
B	-5.378374996349	0.636432172830	0.341875512439
H	-6.010686222976	-1.375760870903	-3.933789563187

H	-7.721442004959	1.084318418857	-1.725970492646
H	-8.184201603901	-0.333689868819	-2.684703268360
H	-8.076787628205	-0.445681078776	-0.916854482222
H	-3.355929958603	4.946110570488	0.225744274180
H	-6.510327553309	0.986270767863	0.516325299462
H	-6.047516908949	4.810695802189	0.595849938840
H	-6.747443056446	3.426460758406	-0.264029018753
H	-6.511675824937	3.347379419724	1.485058063689
H	-7.634007495656	-0.593593077941	2.187016943685
H	-7.261199747333	-0.617074062146	3.921739252740
H	-7.072830422732	0.878312002373	2.987350649666
H	-1.985676258138	-3.098393949759	0.485405256812
H	-2.073429803485	-2.837995891010	-1.109284421701
H	0.217767904572	-4.444505447462	-0.804552955896
H	-0.208848559039	-3.479837128539	-2.204835890847
H	2.187325390958	-4.221143196047	-2.195876977486
H	1.973449789444	-2.459520909580	-2.372955276942
H	4.521467021792	-4.413636428555	0.728132127451
H	3.100430604063	-5.310147752022	0.110102516288
H	4.386831984342	-4.785617932171	-1.043009084910
H	4.195985816526	-0.586367132246	1.179890553749
H	6.149161301143	0.327424234677	2.336133739597
H	7.831094088455	0.189439951604	0.132359617964
H	6.024285505830	-2.636345183514	-0.143199254398
H	5.675435234060	-2.587002217670	2.426830276347
H	7.972625327395	-0.996030528792	2.485068600848
H	8.178090689296	2.556473658481	0.038326721427
H	1.831995174155	1.615136781134	-0.507498004056
H	4.825037816554	5.948812603344	-0.713375673029
H	3.085633121615	5.924547828153	-0.894197462241
H	-4.833666129430	-1.712833513778	4.451705746469

H	4.455886276306	-2.353029367161	-2.069657587635
H	3.694359862683	-0.935680623851	-1.225920074984
H	0.180396077946	-2.559859000136	0.683169567499
C	-3.070182030750	-1.762219779292	-3.375357480229
H	-3.058457143038	-2.862031755684	-3.310156360233
H	-3.127393933767	-1.520631837003	-4.443740517487
H	-2.109934543865	-1.371953192570	-3.006023834208
C	-2.153030829918	-1.990917567560	3.100408187208
H	-1.328313697449	-1.566961716257	2.509438760849
H	-1.917185861073	-1.818561714294	4.157696154251
H	-2.161353030989	-3.083377704691	2.961787311909
C	-1.045596925251	3.083693672978	-0.162136542310
H	-0.709572820948	2.694632243609	-1.132575944521
H	-0.780682022029	4.144710389431	-0.114153323006
H	-0.465918823290	2.556261342869	0.607237296896

[Fe(II)(Tp-Me,Ph)(SAM)]⁺ (quintet state)

C	0.226296799375	-3.826282319093	1.472116645856
C	-1.042410816337	-3.292819027229	1.724371776773
C	-1.248374882200	-2.558087763123	2.902998342013
C	-0.207325199794	-2.346208300728	3.800365918647
C	1.057911966084	-2.870635469068	3.533457186080
C	1.268915619033	-3.613231446095	2.372397087621
C	-2.164719025145	-3.432584287808	0.788899184020
N	-2.872793055887	-2.334636042513	0.477705990846
N	-3.918987514312	-2.732194666306	-0.295316266344
C	-3.866480790865	-4.076960925195	-0.495776457879
C	-2.748374294945	-4.555291163938	0.176308289975
Fe	-2.343527864669	-0.257451059964	0.334477969070
N	-4.339466236443	0.011363797227	0.969407714059
N	-5.301001190975	-0.715868025787	0.341571390087

C	-6.506597659089	-0.494497009918	0.927474830861
C	-6.311036492400	0.409600281205	1.965813800661
C	-4.935151675551	0.685076391908	1.970610748771
C	-7.753285405034	-1.163988655081	0.481364151965
C	-4.126394404751	1.487273458048	2.888539532505
C	-4.613383465831	2.683957153392	3.436112536188
C	-3.822903387570	3.445751778495	4.293077357859
C	-2.532823011785	3.026394097340	4.622923395904
C	-2.041393721997	1.829422392864	4.097287492869
C	-2.831403819247	1.065300507732	3.241458333420
C	-4.886726722590	-4.803517059619	-1.291013718488
N	-1.847186034816	2.020020515157	0.276533568214
C	-0.386869571172	2.172087202195	0.380814681870
C	0.296105784824	0.833347683731	0.719248900888
O	-0.437602885675	-0.203553665080	0.856517431616
C	0.023115529043	3.313382214307	1.322336796402
C	1.494118650755	3.383460255801	1.698259850703
S	2.574686967323	3.285230636747	0.206149623134
C	3.201784187821	4.983221616145	0.142247073142
C	4.033389863405	2.378274891366	0.829122126167
C	5.200861848133	2.488356385164	-0.137545922198
C	4.852929457222	2.129297557779	-1.588072315187
C	6.174382250245	1.545354268563	-2.080525734706
C	6.763158714971	0.893222859244	-0.819781885753
O	6.176521327391	1.547988082761	0.295697093572
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H	-4.647736400167	-5.871988845650	-1.330839308036
H	-5.893596898994	-4.700387747987	-0.861230247399
H	-4.940816959119	-4.433064109154	-2.325234897133
H	-6.778619064546	-0.522637530742	-3.110706104829
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H	-6.054810462206	-2.002320076229	-3.746861301163
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H	1.978301351596	0.273722448297	-1.983277807042
H	2.319778353345	2.460053246173	-3.152413253479
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H	-2.200126756219	2.501519155100	-0.550746493455
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H	-0.296781825787	4.269928901662	0.877130080818
H	-0.532734363772	3.226483623425	2.272362557404
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H	1.806304218869	2.533681074095	2.314626517778
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H	6.053338017917	0.822571422626	-2.901985097743
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[Fe(III)(Tp-Me,Ph)(SAM)]₂⁺ (sextet state)

C	0.246808430769	-3.818363164237	1.383862301128
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C	-1.240153490407	-2.618792952472	2.873171385444
C	-0.199942404267	-2.438433725042	3.777776684155
C	1.069710794020	-2.935711059167	3.481276688156
C	1.288719298709	-3.624278574211	2.287567879425
C	-2.152712045663	-3.436447897708	0.743322676713
N	-2.891938777276	-2.330781404171	0.462948259107
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C	-2.747190797733	-4.540115870023	0.128868515803
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C	-4.843699735565	0.758433096855	1.967957909324
C	-7.770574423209	-0.944555035829	0.511685028794
C	-3.986909024410	1.524724507748	2.873040112252
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C	-1.925070930906	1.708598730348	4.152291766226
C	-2.749637756969	0.994972924717	3.285511977268
C	-4.931924168523	-4.795203618870	-1.266665738815
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C	-0.092706519303	3.264221378272	1.262860354974
C	1.372229928757	3.372619627729	1.658523412224
S	2.486304375623	3.278620759772	0.190200069971
C	3.052603398481	4.992684614663	0.081017078772
C	3.954586555593	2.414229292677	0.851012075099
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O	1.412376551806	0.730564580932	0.903491660906

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C	1.171047860541	0.667448684383	-2.424337780490
C	-0.109548602867	0.121069377958	-2.345178819114
C	-5.939831740935	-0.899603485297	-3.724741861344
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