# Structural and functional models for [NiFe] hydrogenase

Angamuthu, R.

## Citation

Angamuthu, R. (2009, October 14). *Structural and functional models for [NiFe] hydrogenase*. Retrieved from https://hdl.handle.net/1887/14052

# 8

# Light-Induced C–S Bond Cleavage in a Nickel Thiolate Complex: Relevance to the Function of Methyl Coenzyme M Reductase (MCR)†

**Abstract.** The dinuclear complex [Ni(ebsms)]$_2$ is found to be light-sensitive; it yielded another dinuclear complex [Ni(S$_2$S')]$_2$ and oligoisobutylene sulfide through a C–S bond cleavage reaction provoked by the light-induced formation of a Ni(I)-S$^{\bullet}$ radical species in solution. The presence of Ni(I)-S$^{\bullet}$ radical character of [Ni(ebsms)]$_2$ is indicated by the unusual disorder observed in the X-ray crystal structure of [Ni(ebsms)]$_2$, the broad signals observed in the $^1$H NMR spectra of [Ni(ebsms)]$_2$ and the products obtained from the light-induced C–S bond cleavage reaction. The results are discussed in the light of the function of methyl coenzyme M reductase.

---

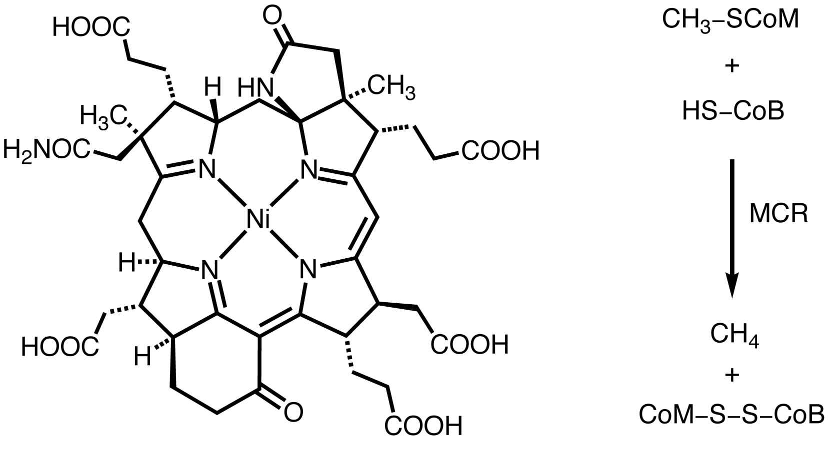
† R. Angamuthu, W. Roorda, M. A. Siegler, A. L. Spek and E. Bouwman, *manuscript in preparation*.

## 8.1. Introduction

Metal thiolate complexes, especially nickel thiolates, are enjoying much attention among bioinorganic chemists as they are important both as structural and as functional models for environmentally and industrially significant enzymes, such as hydrogenases,[1-3] superoxide dismutases,[4,5] carbon monoxide dehydrogenase/acetylcoenzyme A synthase[6-9] and methyl coenzyme M reductase (MCR).[10,11]

MCR is the key enzyme in biological methane formation by methanogenic archaea. The coenzyme F430 in MCR, a Ni-tetrahydrocorphinoid (Scheme 8.1), catalyzes the reaction of methyl-coenzyme M ($CH_3$–SCoM; methylthioethyl sulfonate) and coenzyme B (HS–CoB; 7-mercaptoheptanoylthreonine phosphate) to form methane and the disulfide Co–S–S–CoB.[10-12] Two widely accepted mechanistic pathways have been proposed for this reaction, based on the results of a number of experimental and theoretical studies on F430. Yet several other hypotheses are consistent with most of the findings. The key question to be resolved is whether **(1)** the catalysis involves a nucleophilic attack of a Ni(I) center of active F430 on the methyl group of $CH_3$–SCoM (in the presence of $H^+$) to form a Ni(III)–$CH_3$ intermediate and HS–CoM, or **(2)** the Ni(I) center attacks the thioether sulfur of $CH_3$–SCoM to form a Ni(II)–SCoM intermediate and a $CH_3^{\bullet}$ radical.[11-15] Due to the limited life time of the active form of the enzyme, experimental studies to detect short-lived intermediates in order to shed light on the mechanism have so far been unsuccessful.[10]

The focus of this chapter is the chemistry and reactivity of the nickel thiolate complex $[Ni(ebsms)]_2$ reported in Chapter **3** in relation with the function of the enzyme methyl coenzyme M reductase. This chapter reports on the light-induced reactivity of the complex $[Ni(ebsms)]_2$, forming the complex $[Ni(S_2S')]_2$ and oligoisobutylene sulfide (Scheme 8.2).

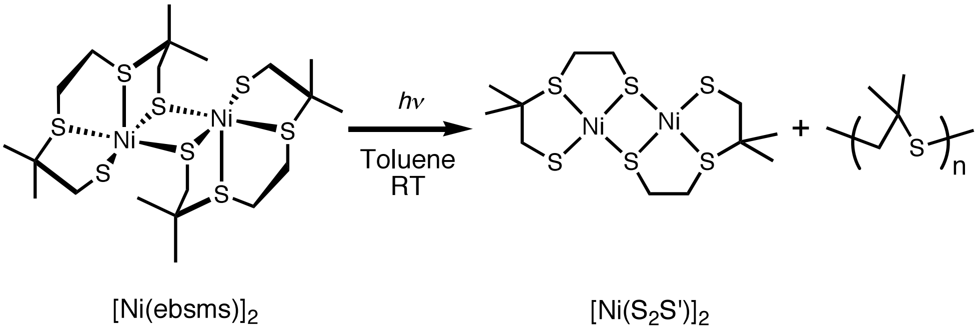


Scheme 8.1. Schematic structure of coenzyme F430 and the catalytic reaction leading to methane formation.

## 8.2. Results and Discussion

### 8.2.1. Synthesis of $[Ni(ebsms)]_2$ and the Formation of $[Ni(S_2S')]_2$

The reaction of $Ni(acac)_2$ with one equivalent of the dithiouronium dichloride salt of the ligand $H_2ebsms$ in toluene in the presence of two equivalents of tetramethylammonium hydroxide resulted in an immediate colour change to deep brown. The new low-spin nickel complex $[Ni(ebsms)]_2$ was isolated as a reddish-brown powder in high yield (see Chapter **3**). Single crystals of complex $[Ni(ebsms)]_2$ suitable for X-ray diffraction were obtained within hours from a dichloromethane solution. The yield of the reaction was found to be very low (15%) when the reaction was performed in the presence of day light; however, it could be dramatically improved using dark conditions (63%). Crystals of different dimensionality compared to the original complex $[Ni(ebsms)]_2$ were obtained from an acetonitrile solution of the complex $[Ni(ebsms)]_2$ after two weeks and revealed the structure of the new compound $[Ni(S_2S')]_2$ as determined by X-ray diffraction (Fig. 8.1).



Scheme 8.2. Schematic drawing of $[Ni(ebsms)]_2$ and the formation of $[Ni(S_2S')]_2$ and oligoisobutylene sulfide upon irradiation.

### 8.2.2. Molecular Structures of the Complexes $[Ni(ebsms)]_2$ and $[Ni(S_2S')]_2$

Although the molecular structure of the complex $[Ni(ebsms)]_2$ has been discussed in detail in Chapter **3**, some basic molecular details of the structure are discussed here as well. The asymmetric unit of $[Ni(ebsms)]_2$ contains one molecule of the dinuclear complex $[Ni(ebsms)]_2$ and one molecule of dichloromethane. The two Ni(II) centers are in slightly distorted square-pyramidal environments with three thiolate donors and two thioether sulfurs coordinated to each nickel center (Fig. 8.1). Two thiolate sulfurs from the same ligand coordinate to a nickel center in *trans* position of each $NiS_4$ square plane. One of these two thiolate sulfurs is bound in a terminal position and the other sulfur is bridging to the adjacent nickel center. One thioether sulfur of the same ligand and a thiolate bridging sulfur from the other ligand occupy the remaining two *trans* positions; the remaining thioether of the ligand binds axially to the Ni(II) center. The $Ni–S_{thiolate}$

distances (bridging, 2.2096(8)–2.2344(8) Å; terminal, 2.1928(8) and 2.1965(10) Å) are shorter than the Ni–S$_{\text{thioether}}$ distances (equatorial, 2.2360(8) and 2.246(3) Å; axial, 2.6011(8) and 2.7039(9) Å), as expected. However, a surprisingly short Ni–S distance (Ni1A–S19B, 2.139(3) Å) and unusual disorder is observed for the thioether site S19 (S19A and S19B; site occupancy = 0.6 : 0.4). One of the ligands in [Ni(ebsms)]$_2$ is disordered over two conformations: the major component is related by an approximate twofold axis to the first ligand, the other is related by an approximate inversion center.

Table 8.1. Selected distances (Å) and angles (°) for [Ni(S$_2$S')]$_2$.

| | | | | | |
|---|---|---|---|---|---|
| Ni1–Ni2 | 2.7041(3) | Ni1–S11 | 2.2107(6) | Ni1–S12 | 2.1783(5) |
| Ni1–S21 | 2.1387(5) | Ni1–S31 | 2.1604(6) | Ni2–S11 | 2.1818(6) |
| Ni2–S12 | 2.2057(5) | Ni2–S22 | 2.1347(5) | Ni2–S32 | 2.1559(5) |
| | | | | | |
| S11–Ni1–S12 | 81.53(2) | S11–Ni1–S21 | 89.18(2) | S11–Ni1–S31 | 173.30(2) |
| S12–Ni1–S21 | 170.35(2) | S12–Ni1–S31 | 97.55(2) | S21–Ni1–S31 | 91.37(2) |
| S11–Ni2–S12 | 81.57(2) | S11–Ni2–S22 | 169.37(2) | S11–Ni2–S32 | 97.51(2) |
| S12–Ni2–S22 | 89.25(2) | S12–Ni2–S32 | 175.06(2) | S22–Ni2–S32 | 91.19(2) |
| Ni1–S11–Ni2 | 75.99(2) | Ni1–S12–Ni2 | 76.17(2) | | |

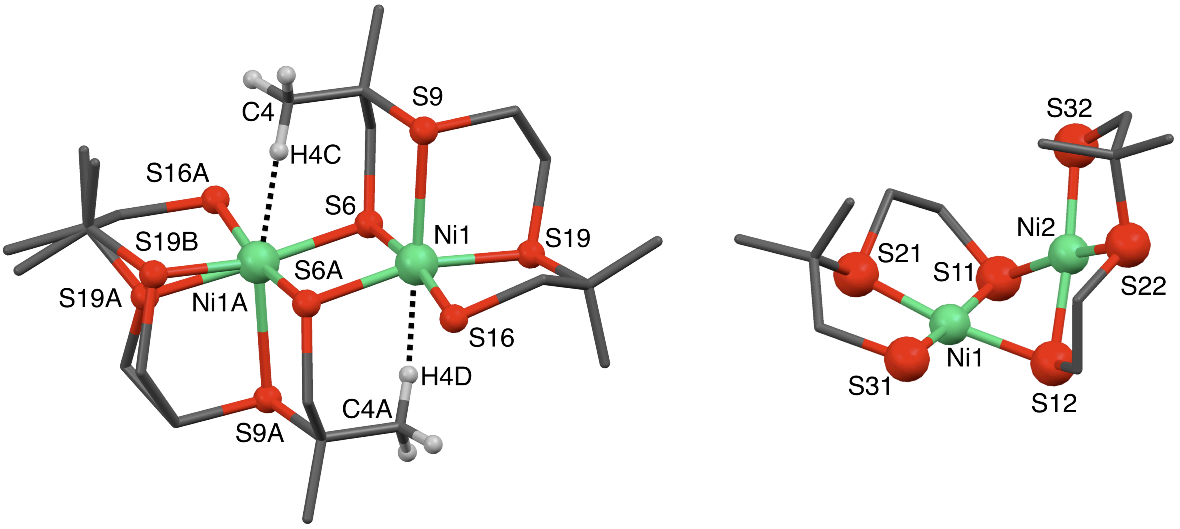


Fig. 8.1. Perspective views of [Ni(ebsms)]$_2$ (left) and [Ni(S$_2$S')]$_2$ (right). Ni, green; S, red; C, gray. Dichloromethane and hydrogen atoms are omitted for clarity. See Chapter 3 for further details regarding to the structure of [Ni(ebsms)]$_2$. Selected distances (Å) and angles (°) for [Ni(S$_2$S')]$_2$ are provided in Table 8.1.

The asymmetric unit of [Ni(S$_2$S')]$_2$ contains one dinuclear nickel complex of a new tridentate thioether-dithiolate (S$_2$S') ligand (Fig. 8.1 and Table 8.1). Two NiS$_2$S' units are bridged together by thiolate donors, resulting in two square-planar NiS$_4$ moieties. Interestingly, the Ni–S$_{\text{thiolate}}$ distances (bridging, 2.1784(5)–2.2056(6) Å; terminal, 2.1604(6) and 2.1560(6) Å) are longer than the Ni–S$_{\text{thioether}}$ distances (2.1386(5) and 2.1347(5)). This observation is in contrast to previous reports;[6,16-18] however, it is not unprecedented, as this behaviour has been reported in two previous cases in literature.[19,20] Usually, the Ni–$S_{thioether}$ distances are longer than (or similar to) the Ni–$S_{thiolate}$ distances.[21] The dihedral angle of the two $NiS_4$ planes in the complex $[Ni(S_2S')]_2$ (77.78°) is slightly larger than in related molecules (75.19° and 75.73°),[19,20] which might be due to the methyl groups of the ligand. Interestingly, the $S_2S'$ ligand of this complex formed from the $S_2S'_2$ ligand of the complex $[Ni(ebsms)]_2$ upon loss of one of the isobutylene sulfide arms. In contrast to $[Ni(S_2S')]_2$ and other oligonuclear nickel thiolate complexes[18,22] the molecular structure of the complex $[Ni(ebsms)]_2$ exhibits an unusual coplanar structure, instead of the butterfly or folded structures known for $[Ni(S_2S')]_2$ (see Chapter **3**). The dihedral angle between the two $NiS_4$ planes in the complex $[Ni(ebsms)]_2$ is approximately 7°. This coplanarity may be due to the dimethyl groups of the ligand, as reflected by the Ni-$H_{Me}$ anagostic interactions (2.66 and 2.74 Å), which may be strong enough to not allow the $NiS_4$ planes to fold (Fig. 8.1). The first example of this kind of Ni···H anagostic interaction in a nickel thiolate ($NiS_4$) system, which was observed to be stable both in the solid and in solution has been described in Chapter **7**.[6]

### 8.2.3. $^1$H NMR Spectra of the Complex $[Ni(ebsms)]_2$

To investigate whether the dinuclear structure and the Ni···H interactions are retained in solution, $^1$NMR spectra of the complex $[Ni(ebsms)]_2$ have been recorded in $CDCl_3$ solution at different temperatures ranging from 223 K to 303 K (Fig. 8.2). The NMR spectra in the whole temperature range show rather broad signals indicating some paramagnetism due to high-spin Ni(II) species, possibly due to the highly strained coordination geometry. The two Ni···H interactions observed in the X-ray structure of $[Ni(ebsms)]_2$ indeed are visible in the $^1$H NMR spectra in the presence of a broad peak at 4.15 ppm in the whole temperature range. This stability of the Ni···H interaction agrees with the observed coplanarity of the two $NiS_4$ planes of the complex $[Ni(ebsms)]_2$ in the crystal structure, and indicates that the dinuclear structure is largely retained in solution.

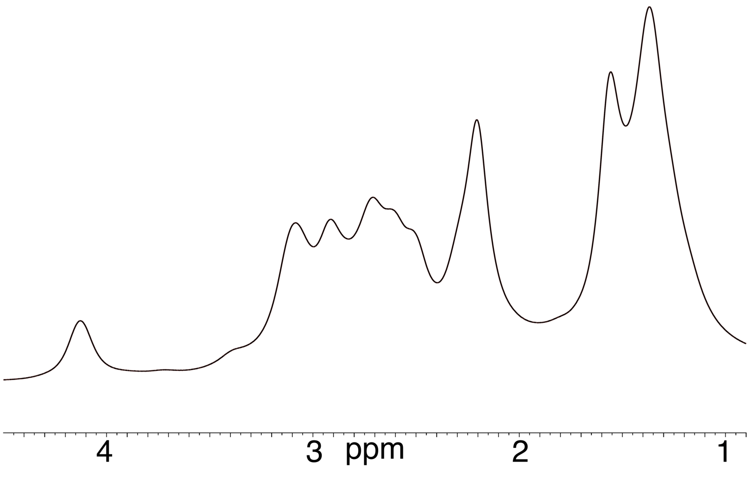


Fig. 8.2. $^1$H NMR spectra of $[Ni(ebsms)]_2$ in $CDCl_3$ recorded at 223 K.

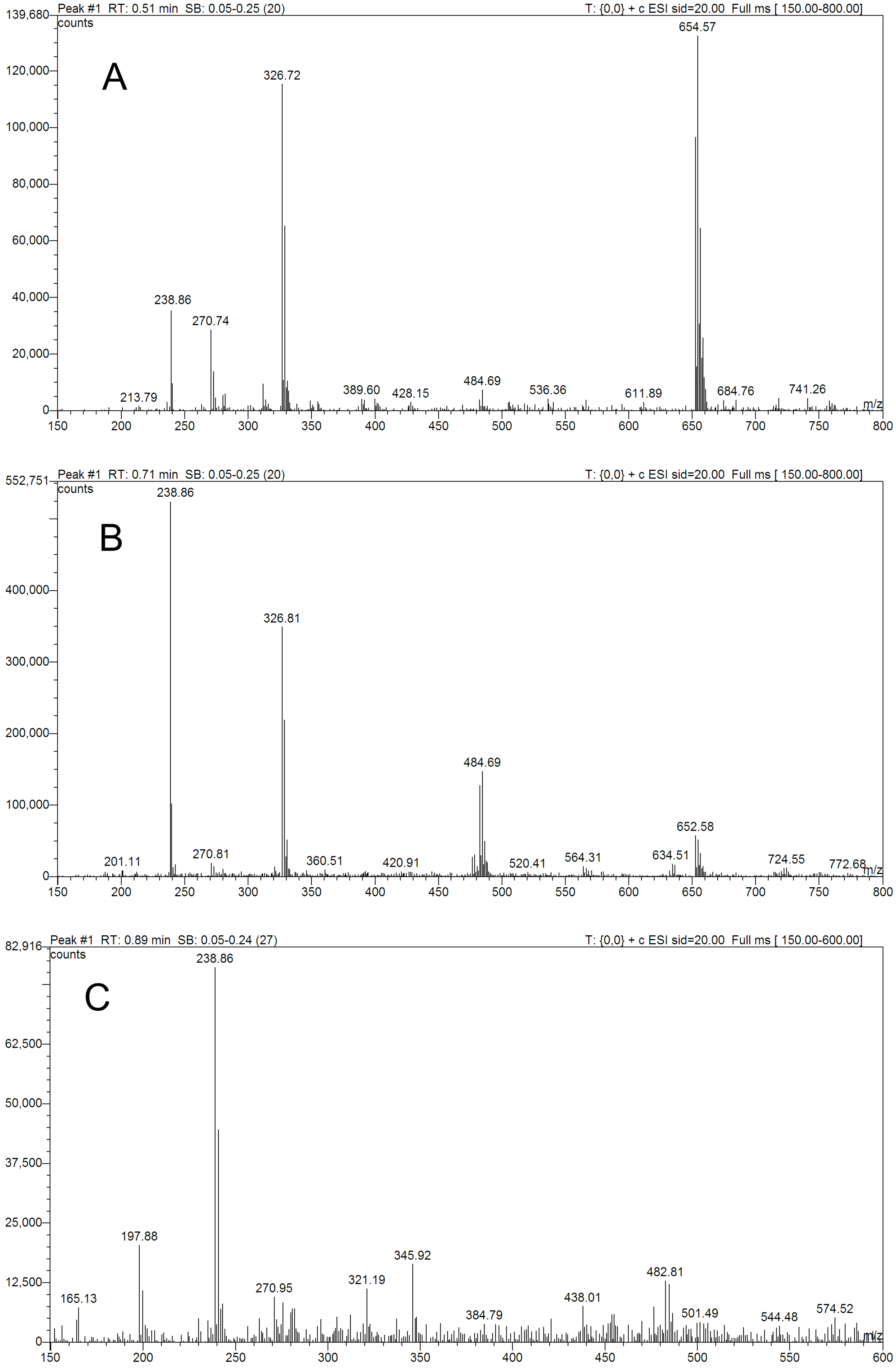


Fig. 8.3. Formation of $[Ni(S_2S')]_2$ from $[Ni(ebsms)]_2$, as followed by ESI-MS spectrometry upon irradiation on the toluene solution of $[Ni(ebsms)]_2$ at room temperature; (A) 0 hrs, (B) 6 hrs, (C) 12 hrs; $m/z = 326.72 = [Ni(ebsms)+H]^+$, $m/z = 652.57 = [Ni_2(ebsms)_2+H]^+$, $m/z = 238.86 = [Ni(S_2S')+H]^+$.

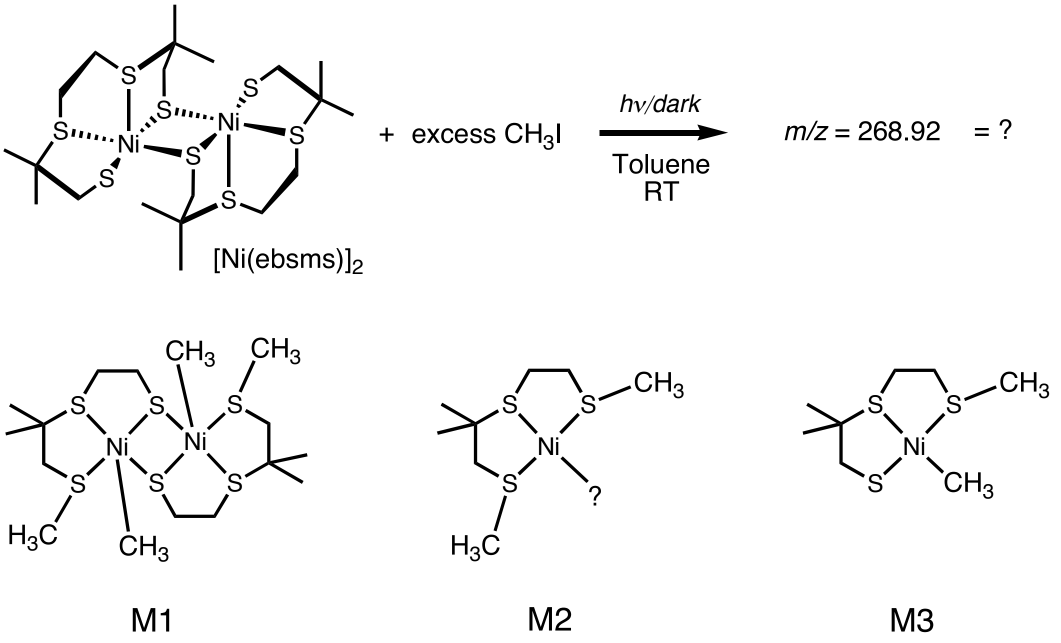
### 8.2.4. Light-Induced Disintegration of the Complex [Ni(ebsms)]$_2$ Monitored with ESI-MS Spectrometry

In order to understand the mechanism of formation of [Ni($S_2S'$)]$_2$ from [Ni(ebsms)]$_2$, a toluene solution of [Ni(ebsms)]$_2$ was irradiated using a mercury arc lamp; samples were collected at regular intervals and were analyzed using ESI-MS spectrometry. Interestingly, the formation of the new compound [Ni($S_2S'$)]$_2$ is clearly identified from the ESI-MS spectra, showing the gradual disappearance of the molecular ion peaks of [Ni(ebsms)]$_2$ with simultaneous growth of the peak corresponding to [Ni($S_2S'$)] (Fig. 8.3). When using the mercury lamp the decomposition reaction needs about 12 hrs for completion with the formation of [Ni($S_2S'$)]$_2$ and isobutylene sulfide. In an endeavour to detect the decomposition products and isolate pure [Ni($S_2S'$)]$_2$, the reaction mixture was distilled gently around 85 °C. A few drops of isobutylene sulfide were obtained; ESI-MS spectrometry and NMR spectra confirmed the identity of oligo-isobutylene sulfide. The remaining mixture was passed through a neutral alumina column and the pure [Ni($S_2S'$)]$_2$ was obtained in 87% yield.

### 8.2.5. Mechanistic Considerations

The unusual disorder of the nickel-thioether bond observed in the X-ray crystal structure of [Ni(ebsms)]$_2$ (Ni1A–S19A/S19B in Fig. 8.1) and the broadened signals observed in the variable temperature $^1$H NMR spectra of the complex [Ni(ebsms)]$_2$ indicate that the Ni(I)–S$^\bullet$ radical character may already present in the complex [Ni(ebsms)]$_2$. However, when kept in the dark the compound [Ni(ebsms)]$_2$ is found to be rather stable. Therefore, the light-induced formation of [Ni($S_2S'$)]$_2$ and oligoisobutylene sulfide from [Ni(ebsms)]$_2$ indicates that the Ni(I)–S$^\bullet$ radical and the concurrent reactivity is formed only after irradiation of the complex [Ni(ebsms)]$_2$.

In order to investigate the radical character of the complex [Ni(ebsms)]$_2$, it was reacted with iodomethane in the presence and absence of light and the products were analysed using ESI-MS spectrometry. Usually the reaction between methyl halides and metal thiolate compounds results in the methylation of the available thiolate sulfurs only.[23,24] If the thioether sulfur of the complex [Ni(ebsms)]$_2$ has radical character it would be more reactive than the thiolates. After the reaction of [Ni(ebsms)]$_2$ with methyl iodide, a molecular ion peak at $m/z$ = 268.92 was observed, matching with the calculated isotopic distribution for the fragment [[Ni($S_2S'$)+2$CH_3$] (269.00). This result was obtained both in the presence and absence of light. The three fragments 0.5×M1, M2 and M3, as shown in Scheme 8.3, are all matching the observed $m/z$ value of 268.92. All these fragments suggest that the Ni1–S19 bond is highly reactive; a possible explanation for this reactivity might be the presence of partial Ni(I)–S$^\bullet$ character. Furthermore, the fragment M3 might be the responsible species for the observed *m/z* value of 268.92 as the fragments M1 and M2 are not the most likely products due to the steric hindrance and the instability, respectively. Even though the present results support the presence of Ni(I)–$S^{\bullet}$ character, they are inadequate to confirm this hypothesis; therefore further studies are necessary.



Scheme 8.3. Reaction of $[Ni(ebsms)]_2$ with excess methyl iodide in toluene and the possible products.

### 8.2.6. Relevance to the Function of MCR

One of the two main intermediates proposed in the catalytic mechanism of MCR is an organometallic methyl–Ni(III) F430 species ($MCR_{Me}$).[11] The $MCR_{Me}$ is proposed to be formed from the reaction between the active MCR and methyl halides.[25,26] Yet the formation from the native substrate ($CH_3$–SCoM) has never been found. A recent paper from Siegbahn and coworkers reports the investigation of the reaction between MCR and the substrates $CH_3X$ (X = I, Br, Cl) and $CH_3$–SCoM using advanced theoretical methods;[27] the reaction between MCR and $CH_3X$ is exothermic and the $CH_3$–Ni(F430) species is proposed to be in a resonance state between $^{\downarrow\bullet}CH_3$–$^{\uparrow\uparrow}$Ni(II) F430 radical and $CH_3$–$^{\uparrow}$Ni(III) F430. The observed broad signals in the $^1H$ NMR spectra of $[Ni(ebsms)]_2$ are supposedly due to paramagnetic species, and the reactivity of the Ni–S bond in the presence of light and with methyl iodide correlates with the theoretically observed results. Further exploration of the reaction of $[Ni(ebsms)]_2$ with substrates such as $CH_3$–S–$CH_3$ are needed to shed light on the electronic structure of both $[Ni(ebsms)]_2$ and $[Ni(S_2S')]_2$.

## 8.3. Conclusions

A unique reactivity of [Ni(ebsms)]$_2$ is encountered in the formation of the low-spin nickel complex [Ni(S$_2$S')]$_2$, which is produced upon irradiation of the complex [Ni(ebsms)]$_2$. Formation of the complex [Ni(S$_2$S')]$_2$ from complex [Ni(ebsms)]$_2$ is demonstrated to proceed through a C–S bond-cleavage reaction provoked by the light-induced formation of Ni(I)-S$^\bullet$ radical species in solution. Further exploration of this light-induced reaction with a combination of techniques and the reaction of [Ni(ebsms)]$_2$ with other substrates, or with small molecules may shed light onto the reaction pathway.

## 8.4. Experimental Procedures

### 8.4.1. General

The synthesis of the thiouronium precursor salt TU-ebsms and the complex [Ni(ebsms)]$_2$ are discussed in Chapters **2** and **3**, respectively.

### 8.4.2. Formation of Complex [Ni(S$_2$S')]

The complex [Ni(ebsms)]$_2$ (0.98 g, 3 mmol) was dissolved in 50 ml toluene and the solution was irradiated using a Hanau TQ81 high-pressure mercury arc lamp. Completion of the reaction was monitored by recording ESI-MS spectra of the samples collected in regular intervals. The reaction needed 12 hrs for completion and the formed isobutylene sulfide was removed from the reaction mixture by distilling the reaction mixture gently. Isobutylene sulfide started to come out when the temperature was around 85 °C and the collection flask was kept at 0 °C using an ice bath. Elemental Analysis (%): Calculated for $C_{12}H_{24}S_6Ni_2$ (478.1): C 30.15, H 5.06, S 40.24. found C 30.27, H 5.18, S 40.29. MS (ESI): (*m/z*) calculated for $C_6H_{13}S_3Ni$ [M/2+H$^+$] requires (monoisotopic mass) 238.95, found 238.86.

### 8.4.3. X-ray Crystallographic Data for [Ni(S$_2$S')]

X-ray intensities were measured on a Nonius KappaCCD diffractometer with rotating anode (graphite monochromator, $\lambda$ = 0.71073 Å). Intensity integration was performed with EvalCCD[28] ([Ni(ebsms)]$_2$) or HKL2000[29] ([Ni(S$_2$S')]). Absorption correction was based on multiple measured reflections. The structures were solved with SHELXS-97[30] using Direct Methods and refined against $F^2$ of all reflections using SHELXL-97.[30] Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined with a riding model. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[31]

$C_{12}H_{24}Ni_2S_6$, Fw = 478.09, black block, 0.53 x 0.36 x 0.30 $mm^3$, orthorhombic, Pbca (no. 61), a = 12.9460(1), b = 22.3503(2), c = 12.9344(1) Å, V = 3742.53(5) $Å^3$, Z = 8, $D_x$ = 1.697 $g/cm^3$, $\mu$ = 2.67 $mm^{-1}$. 45877 Reflections were measured up to a resolution of $(\sin \theta/\lambda)_{max}$ = 0.65 $Å^{-1}$ at a temperature of 150(2) K. Absorption correction range 0.32-0.45. 4284 Reflections were unique ($R_{int}$ = 0.046), of which 3733 were observed [$I>2\sigma(I)$]. 185 Parameters were refined with no restraints. $R_1/wR_2$ [$I > 2\sigma(I)$]: 0.0250 / 0.0598. $R_1/wR_2$ [all refl.]: 0.0312 / 0.0630. S = 1.057. Residual electron density between -0.38 and 0.49 $e/Å^3$.

## 8.5. References

1. E. Bouwman and J. Reedijk, *Coord. Chem. Rev.*, 2005, **249**, 1555-1581.
2. V. Artero and M. Fontecave, *Coord. Chem. Rev.*, 2005, **249**, 1518-1535.
3. C. Tard and C. J. Pickett, *Chem. Rev.*, 2009, **109**, 2245-2274.
4. J. Wuerges, J. W. Lee, Y. I. Yim, H. S. Yim, S. O. Kang and K. D. Carugo, *Proc. Natl. Acad. Sci. U. S. A.*, 2004, **101**, 8569-8574.
5. J. Shearer, A. Dehestani and F. Abanda, *Inorg. Chem.*, 2008, **47**, 2649-2660.
6. R. Angamuthu, L. L. Gelauff, M. A. Siegler, A. L. Spek and E. Bouwman, *Chem. Commun.*, 2009, 2700-2702.
7. K. N. Green, S. M. Brothers, B. Lee, M. Y. Darensbourg and D. A. Rockcliffe, *Inorg. Chem.*, 2009, **48**, 2780-2792.
8. Y. Song, M. Ito, M. Kotera, T. Matsumoto and K. Tatsumi, *Chem. Lett.*, 2009, **38**, 184-185.
9. D. J. Evans, *Coord. Chem. Rev.*, 2005, **249**, 1582-1595.
10. U. Ermler, *Dalton Trans.*, 2005, 3451-3458.
11. U. Ermler, W. Grabarse, S. Shima, M. Goubeaud and R. K. Thauer, *Science*, 1997, **278**, 1457-1462.
12. R. K. Thauer, *Microbiology-(UK)*, 1998, **144**, 2377-2406.
13. V. Pelmenschikov and P. E. M. Siegbahn, *J. Biol. Inorg. Chem.*, 2003, **8**, 653-662.
14. V. Pelmenschikov, M. R. A. Blomberg, P. E. M. Siegbahn and R. H. Crabtree, *J. Am. Chem. Soc.*, 2002, **124**, 4039-4049.
15. E. C. Duin and M. L. McKee, *J. Phys. Chem. B*, 2008, **112**, 2466-2482.
16. J. A. W. Verhagen, M. Lutz, A. L. Spek and E. Bouwman, *Eur. J. Inorg. Chem.*, 2003, 3968-3974.
17. J. A. W. Verhagen, D. D. Ellis, M. Lutz, A. L. Spek and E. Bouwman, *J. Chem. Soc.-Dalton Trans.*, 2002, 1275-1280.
18. R. Angamuthu, H. Kooijman, M. Lutz, A. L. Spek and E. Bouwman, *Dalton Trans.*, 2007, 4641-4643.
19. D. Sellmann, D. Haussinger and F. W. Heinemann, *Eur. J. Inorg. Chem.*, 1999, 1715-1725.
20. R. Cao, M. C. Hong, F. L. Jiang, X. L. Xie and H. Q. Liu, *J. Chem. Soc.-Dalton Trans.*, 1994, 3459-3463.
21. M. A. Halcrow and G. Christou, *Chem. Rev.*, 1994, **94**, 2421-2481.
22. C. Zhang, S. Takada, M. Kölzer, T. Matsumoto and K. Tatsumi, *Angew. Chem.-Int. Edit. Engl.*, 2006, **45**, 3768-3772.
23. V. E. Kaasjager, E. Bouwman, S. Gorter, J. Reedijk, C. A. Grapperhaus, J. H. Reibenspies, J. J. Smee, M. Y. Darensbourg, A. Derecskei-Kovacs and L. M. Thomson, *Inorg. Chem.*, 2002, **41**, 1837-1844.
24. O. Yohan, PhD Thesis, *Structural and Functional Models for Hydrogenases*, Université Joseph Fourier-Grenoble I, 2007.
25. N. Yang, M. Reiher, M. Wang, J. Harmer and E. C. Duin, *J. Am. Chem. Soc.*, 2007, **129**, 11028-+.
26. M. Dey, J. Telser, R. C. Kunz, N. S. Lees, S. W. Ragsdale and B. M. Hoffman, *J. Am. Chem. Soc.*, 2007, **129**, 11030-+.

27. S.-l. Chen, V. Pelmenschikov, M. R. A. Blomberg and P. E. M. Siegbahn, *J. Am. Chem. Soc.*, 2009, 10.1021/ja904204g.
28. A. J. M. Duisenberg, L. M. J. Kroon-Batenburg and A. M. M. Schreurs, *J. Appl. Cryst.*, 2003, **36**, 220.
29. Z. Otwinowski and W. Minor, Processing of X-ray diffraction data collected in oscillation mode, in *Macromolecular Crystallography, Pt A*, 1997, pp. 307-326.
30. G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.
31. A. L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7.