# Theoretical Studies of the Reactions of the Sulfur–Sulfur Bond. 2. Binding and Reactions with Group 1A and 2A Metals

**Jan A. Pappas***

*Contribution from the Institute of Physics, University of Oslo, Blindern, Oslo 3, Norway.*
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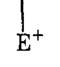
**Abstract:** Ab initio model studies of the binding and reactions of disulfides with alkali and alkaline earth metals are reported. The model systems considered are $H_2S_2M^{n+}$ and $H_2OM^{n+}$ with $M^{n+} = Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}$, and $Ca^{2+}$. The monovalent metals were found to bind to one of the sulfur atoms, while the alkaline earth metals additionally may form bridged bonds between both S atoms. The mechanisms of the reactions of the metals with RSSR are studied, and the traditional electrophilic scission is predicted to be of limited interest compared to the concomitant electrophilic and nucleophilic S–S scission. The mechanism is thus more like a metal-assisted nucleophilic substitution reaction leading to S–S bond fission rather than a purely electrophilic cleavage as is commonly assumed. The alkali metals will probably not react appreciably with RSSR, neither in the gas phase nor in solution. For alkaline earth metals, especially $Be^{2+}$, there are several reactions possible depending on the availability of nucleophiles, all leading to S–S bond fission in case of nucleophilic excess. Competition with $H^+$ may require high pH in the reactions while competition between the disulfide and $H_2O$ for the metal most likely will prevent $Ca^{2+}$ and to some extent $Mg^{2+}$ from reacting in solution. Thus among the metals considered, those which are predicted not to react with S–S bonds to any extent are also those metals naturally present in living systems. On the other hand, $Be^{2+}$ is the metal predicted to react most strongly with S–S bonds. This metal is also known to be very toxic. These results and suggestions have biological implications of interest.

## Introduction

The central role of disulfides in biochemistry, both as a structural stabilizer in proteins and in a variety of other reactions, has been recognized for a long time. The sulfur ligands are known to have high affinities for metal ions. Moreover, most reactions of disulfides involve S–S bond fission. In view of this, surprisingly little work has been done on the role of metal ions in cleavage of disulfides.

A series of theoretical investigations designed to gain further knowledge of the underlying electronic aspects governing the binding and reactions of metal ions with sulfur in biological systems has been started.[5-7] In the present paper we report studies of the binding and reactions of disulfides with cations of the alkali (group 1A) and alkaline earth (group 2A) metals. In subsequent papers we shall extend this study to a selection of the transition elements. We do believe that it is important in such a study to include both metals that form strong bonds and some that form weak bonds with sulfur ligands for a better understanding of why metals bind so differently to sulfur. From previous experience,[5,6] we know that the sulfur regions exhibit only minor changes even in quite different thiols like $H_2S$, $CH_3SH$, and cysteine, and disulfides like $H_2S_2$ and $(CH_3)_2S_2$. Although $H_2S$, $HS^-$, and $H_2S_2$ are very simple systems from the biochemical point of view, we still believe that they are relevant model systems for detailed investigations of the sulfur regions in molecules.

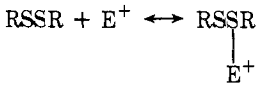
Experimentally, the reaction of metals with disulfides most frequently studied has been the hydrolysis in aqueous solvents. Based on earlier models for heterolytic cleavage of S–S bonds by electrophiles, the following scheme is usually assumed for these reactions:[2,8-10]

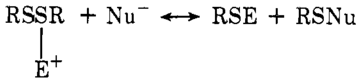

$$\mathrm{RSSR} + \mathrm{E}^+ \leftrightarrow \underset{\substack{|\\ \mathrm{E}^+}}{\mathrm{RSSR}} \leftrightarrow \mathrm{RS}^+ + \mathrm{RSE} \qquad (1)$$

$$\mathrm{RS}^+ + 2\mathrm{H_2O} \leftrightarrow \mathrm{RSOH} + \mathrm{H_3O}^+ \qquad (2)$$

$$2\mathrm{RSO} \leftrightarrow \mathrm{RSO_2H} + \mathrm{RSH} \qquad (3)$$

This postulated reaction scheme for the electrophilic cleavage has in the past few years seriously been questioned owing to accumulating evidence indicating that even trace amounts of nucleophiles ($10^{-4}$–$10^{-6}$ M in case of halogen anions) will increase the rate of the cleavage reactions drastically.[3,4] Accordingly, it has been proposed that the most likely mechanism for heterolytic fission of S–S bonds is the concomitant electrophilic and nucleophilic reaction scheme of eq 4 and 5. In fact, with $OH^-$ as nucleophile, eq 4 and 5 will yield


$$\mathrm{RSSR} + \mathrm{E}^+ \leftrightarrow \underset{\substack{|\\ \mathrm{E}^+}}{\mathrm{RSSR}} \qquad (4)$$


$$\underset{\substack{|\\ \mathrm{E}^+}}{\mathrm{RSSR}} + \mathrm{Nu}^- \leftrightarrow \mathrm{RSE} + \mathrm{RSNu} \qquad (5)$$

the same products RSE and RSOH as will eq 1 and 2, although the mechanisms are quite different.

The concomitant reaction mechanism has gained support from recent theoretical investigations on the general heterolytic cleavage reactions for disulfides, that is, on reactions 1–3, reactions 4 and 5, and the common scission by nucleophiles:[5,6]

$$\mathrm{RSSR} + \mathrm{Nu}^- \rightarrow \mathrm{RS}^- + \mathrm{RSNu} \qquad (6)$$

It was shown that the last step in eq 1, the S–S bond fission, is strongly endothermic even for such a strong electrophile as $H^+$, whereas the concomitant mechanism is quite exothermic for a variety of nucleophiles, even more than the pure nucleophilic fission (eq 6). The crucial part of the concomitant mechanism was found to be the way $H^+$ influences the behavior of the electron structure in the S–S region of $R_2S_2H^+$ when $Nu^-$ is approaching. The electrophile (in this case $H^+$) will greatly increase the accessibility of the LUMO (lowest unoccupied molecular orbital) into which the excess electron pair of $Nu^-$ will be transferred in eq 5. The S–S bond will then be cleaved if the LUMO of $R_2S_2E^+$ in addition is S–S antibonding.

In the present paper, we extend the study of the reactions 1–5 to the cases where the electrophiles are metals. First we investigate the binding of metals to disulfides, i.e., the formation of $R_2S_2M^{n+}$, which is common to both eq 1 and 4, and

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* Address correspondence to author at: Det Norske Veritas, Research Division, 1322 Høvik, Norway.

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**Table I.** Total Energies and Geometries

| molecule | $E$, au | geometry (bond distances, Å |
|---|---|---|
| $H_2S_2Li^+$ | −803.220 51 | SLi = 2.480,$^a$ SS = 2.108,$^a$ ∠LiSS = 99.1°,$^a$ ∠HSSH = 104.1°,$^a$ ∠HSSLi = 146.8°$^a$ |
| $H_2S_2Na^+$ | −957.577 70 | SNa = 2.750, rest as $H_2S_2Li^+$ |
| (I) $H_2S_2Be^{2+}$ | −809.780 24 | SBe = 2.037,$^a$ SS = 2.161,$^a$ ∠BeSS = 105.0°,$^a$ ∠HSSH = 114.0°,$^a$ ∠HSSBe = 140.2°$^a$ |
| (II) $H_2S_2Be^{2+}$ | −809.799 66 | SBe = 2.133,$^a$ SS = 2.187,$^a$ ∠HSSH = 155° |
| (I) $H_2S_2Mg^{2+}$ | −994.817 53 | SMg = 2.390, rest as $H_2S_2Be^{2+}$ |
| (I) $H_2S_2Ca^{2+}$ | −1471.0730 | SCa = 2.680, rest as $H_2S_2Be^{2+}$ |
| (IV) $H_2S_2BeH^+$ | −810.874 45 | BeH = 1.385, rest as $H_2S_2Be^{2+}$ (II) |
| (V) $H_2S_2BeH^+$ | −810.880 42 | SBe = 2.210,$^a$ rest as $H_3S_2$ |
| HSBeH | −413.192 08 | SH = 1.336,$^a$ SBe = 1.997,$^a$ BeH = 1.385,$^a$ ∠HSBe = 96.5°,$^a$ ∠SBeH = 180°$^a$ |
| $H_2O$ | −75.907 84 | OH = 0.957, ∠HOH = 104.5° |
| $H_3O^+$ | −76.184 32 | OH = 0.960, ∠HOH = 120° |

[a] Parameter optimized in the molecule.

discuss possible solvent effects on the stabilities. We then proceed to study the electrophilic and the concomitant mechanisms in more detail.

## Details of the Calculations

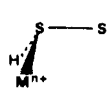
All calculations were performed within the closed-shell single determinant MO-LCAO-SCF framework, using the program system MOLECULE.[11] For first- and second-row atoms we used a medium-size Gaussian basis[12] being of the type (7s, 3p) and (10s, 6p), respectively; for third-row atoms we used a (12s, 6p) set,[13] and for H a (4s) basis[14] scaled by 1.25. This set was contracted to double $\zeta$ except for minimal basis in the K and L shells of K and Ca. 3d functions were added to O and S with exponents 1.33 and 0.54, respectively.[12] 2p and 3p functions were added to $Li^+$, $Be^{2+}$ and $Na^+$ and $Mg^{2+}$, respectively, after exponent optimisation in HSM or $HSM^+$. The basis for $K^+$ and $Ca^{2+}$ was augmented by a set of 3d, 4s, and 4p functions with exponents chosen to give maximum charge density in the bonding region. Further details of the basis for the metals are reported in ref 15.

To the author's knowledge, the geometries of most of the molecules included in the present investigation are not known. As we wish to compare calculated reaction energies, rather extensive geometry optimizations were necessary in order to ensure that errors due to nonoptimal geometries were considerably smaller than the differences in the reaction energies to be compared. The procedure has been to optimize the complexes with Li and Be in all important parameters and reoptimize the S-M distance for the other metals. In $H_2S_2Li^+$ and $H_2S_2Be^{2+}$ all parameters were optimized except for SH distances and HSS angles, which were fixed at the optimal values in $H_3S_2^+$.[5] The S-M distance in $H_2S_2M^{n+}$ for the other metals was estimated from the corresponding distances in the mercaptides[15] and the S-Li or S-Be distances in $H_2S_2M^{n+}$. The optimal geometries and calculated energies are summarized in Table I. The energies for some few molecules in the reactions to be studied were taken from ref 5 and 15.

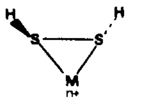
## Binding of Metals to Disulfides

In the following we will consider the three possible binding forms of mono- and bivalent metals to the disulfide group. We do not consider other chelates due to special complexing properties of the ligands R as our purpose is to study the local properties of the S-S region. Within these restrictions, the metal $M^{n+}$ may bind exclusively to one of the sulfurs as in I (later referred to as an open complex), it may bind to both sulfurs in a bridging way as in II (referred to as a bridged complex), or it may be inserted into the S–S bond forming a S–M–S bond as in III.

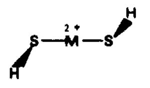
(A)



I



II



III

**Alkali Metals.** These metals are preferably monovalent, so it is reasonable to expect form I to be dominating. Previous experience shows in fact that form I is quite a stable conformation for monovalent ions, at least for $H^+$ bound to $R_2S_2$.[5] As to the stability of the corresponding bridged conformation II for monovalent ions $M^+$, we have studied the potential surface of $H_3S_2^+$ in the vicinity of the bridged form, revealing II to be a saddle point 50 kcal/mol higher in energy than the open form I. The potential surface of $H_3S_2^+$ shows a minimum for the variation preserving the $C_2$ symmetry, but a maximum when the symmetry is broken by moving $H^+$ away from the $C_2$ axis. Exactly the same behavior of the potential surface around II was found for $H_2S_2Li^+$, except that the saddle point was not that high in energy (∼6 kcal/mol). This instability of the bridged form of $R_2S_2M^+$ is in fact consistent with the electrostatic potential[1] of $H_2S_2$, which has a saddle point close to the position of $M^+$ in form II. As a consequence of the saddle point instability present in the bridged complexes of monovalent ions, great caution should be exercised when placing symmetry restrictions on geometry optimizations in similar complexes in order to prevent unstable complexes being found stable.

The stable form of alkali metals bound to disulfides is the open form I, the details of which are reported in Tables I and II. However, the stability of the complexes is in the range of ∼10-25 kcal/mol, which is much less than the binding energy of 175 kcal/mol for a proton bound to $H_2S_2$.[5] The calculated structure of form I shows a metal-sulfur bond of essentially the same geometry as the corresponding $S-H^+$ bond in $H_3S_2^+$ with the structure of the HSSH group intermediate between $H_2S_2$ and $H_3S_2^+$. On the other hand, there are several differences both in the electronic structure and geometry of the proton and alkali metal complexes, demonstrating the influence of an ionic structure in the alkali metal-sulfur bond. The distance of $Li^+$ from the trivalent S in $H_2S_2Li^+$ of 2.480 Å is as much as 0.28 Å longer than in LiSH,[15] whereas no corresponding distinction is observed between the S-H bonds to bi- or trivalent sulfur. Additionally, the small charge transfer of 0.15 e from $H_2S_2$ to $Li^+$ is negligible compared to the corresponding transfer of 0.69 e toward $H^+$ in $H_3S_2^+$. Another difference is that the alkali metals polarize the S-S bond somewhat in contrast to the covalently bound proton. This perturbation of the electron density in the disulfide region by hard cations confirms earlier predictions based on model systems simulating hard cations by point charges without allowing for charge transfer (by removing the basis functions on $H^+$). So the alkali metals seem to be mainly ionically bound to $R_2S_2$ without any appreciable charge transfer toward the metal.

**Alkaline Earth Metals.** The structure of the monovalent form I for these metals is quite similar to that of the alkali metals, except that the binding energies are considerably

**Table II.** Details of the Results for Binding of Metals to $H_2S_2$ and $H_2O$[g]

| | $H_2S_2$ | | | | | $H_2O$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| ion | $E$ to $H_2S_2$ | $q(S_M)$[a] | $q(S_H)$[b] | $q(M)$ | $p(SS)$ | $E$ to $H_2O$[c] this work | $E$ to $H_2O$ others | $E$ to $H_2O$ exptl | total hydration energy exptl |
| $Li^+$ | 24.1 | −0.214 | −0.102 | +0.851 | 0.411 | 46 | 34.1 (35.2)[d] | 34[19] | 132[19] |
| $Na^+$ | 14 | −0.242 | −0.120 | +0.877 | | | 23.3 (24.0)[d] | 24[19] | 106[19] |
| $K^+$ | | | | | | | 16.2 (16.6)[d] | 18[19] | 86[19] |
| $Be^{2+}$ | 141.5 (I),[f] 153.8 (II)[f] | −0.098 | +0.090 | +1.324 | 0.361 | 146 | 150[21] | | 602[29] |
| $Mg^{2+}$ | 76 | −0.233 | +0.031 | +1.556 | 0.365 | 92 | 80[21] | | 469[29] |
| $Ca^{2+}$ | 38 | −0.409 | −0.037 | +1.864 | 0.371 | 62 | 53[21] | | 386[29] |
| $H^+$ | 175.9[e] | +0.08[e] | +0.02[e] | 0.31[e] | 0.433[e] | 174 | 167.5[30] | 168[28] | 270[19] |

[a] S bound to M. [b] S bound to H. [c] Not corrected for zero-point energies (5.3 kcal/mol for $H^+$). [d] From ref 20; Hartree–Fock values in parentheses. [e] From ref 5. [f] Energy of structures I and II. [g] Binding energies $E$ in kcal/mol.

higher also for the larger ions like $Ca^{2+}$. In addition, there are several differences mirroring the stronger influence of the alkaline earth metals than the alkali metals on the disulfide group. Binding of group 2A metals to $H_2S_2$ lowers the S–S overlap populations by ~0.1 e compared to $H_2S_2$ (and $H_3S_2^+$) parallel to a lengthening of the S–S bond by 0.03 Å compared to $H_3S_2^+$. This is a longer S–S bond than expected from the opening of the HSSH dihedral angle alone (the S–S bond distances in disulfides increase as the dihedral angle opens from 90° [5,16]) suggesting that the alkaline earth metals weaken the S–S bond in type I complexes as opposed to $H^+$ and the alkali metals. Additionally, $Mg^{2+}$ and $Ca^{2+}$ polarize the S–S bond (but not so much $Be^{2+}$ owing to the larger charge transfer toward this metal).

The bridged binding form II of alkaline earth metals to disulfides is found to be electronically stable. The calculated binding energy of $Be^{2+}$ to $H_2S_2$ in form II was in fact predicted to be ~12 kcal/mol larger than in form I. The optimized structure of the bridged from of $H_2S_2Be^{2+}$ shows an almost equilateral S–S–Be triangle with the SH groups being approximately planar (dihedral angle 155°) and normal to the triangular plane. The S–Be distance of 2.130 Å is only 0.10 Å longer than in structure I. The S–S bond is also longer (2.187 Å) and the very low S–S overlap population of 0.22 e suggests that this bond is considerably weaker in the bridged form II than in the type I complex. The charge transfer of 0.75 e toward Be is about the same as in type I, except that the state of the metal resembles somewhat that of an excited state of $Be^+$ as 0.40 e is transferred into the 2p orbital of Be.

In the $M(SH)_2$ complexes (the neutral form of III) it has been shown from the correlation diagrams that all orbitals stabilize the linear structure in III.[15] It is natural then to expect $H_2S_2M^{2+}$ in form III also to be linear and stable, as this complex may be considered as the doubly ionized state of $M(SH)_2$. However, detailed calculations as displayed in Figure 1 revealed that $H_2S_2M^{2+}$ in form III ($M(SH)_2^{2+}$) is not even electronically stable, but transforms spontaneously to the bridged form II by pulling the metal out of the S–S bond. The reason why the stability of $ML_2^{2+}$ cannot be predicted from the correlation diagrams of $ML_2$ is to be found in the chemical changes following the ionization. In the ground state of $ML_2$ ($L^-$–$M^{2+}$–$L^-$) the ligands are electronically saturated and are not able to form L–L bonds. Ionization will take place from the long pairs of $ML_2$ as these are the highest orbitals,[15] yielding a $ML_2^{2+}$ complex of type $L^0$–$M^{2+}$–$L^0$. Electrons being removed from the ligands L, these are now able to form L–L bonds. The potential curve (Figure 1) of the singlet state of $ML_2$ with electron distribution $L^0$–$M^0$–$L^0$ (which then also is able to form L–L bonds) does in fact cross the potential curve of the ground state of $ML_2$ close to the minimum of $ML_2^{2+}$, indicating the true potential minimum of the excited state of $ML_2$ has the same geometry as $ML_2^{2+}$. So a proper treatment of $ML_2$ near the crossing will be necessary in order to have a correlation diagram of $ML_2$ that predicts the correct stability of $ML_2^{2+}$

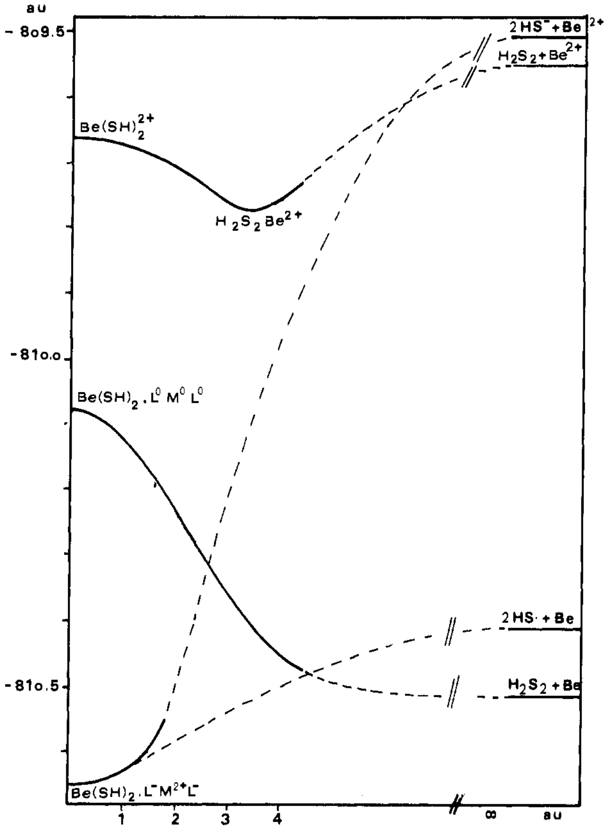


Figure 1. The energy of the different states of $Be(SH)_2$ and $Be(SH)_2^{2+}$ as function of Be's distance from the S–S bond. Solid curves are calculated; broken lines are drawn to combine the correct states. The energy of Be + 2HS is estimated as that of $H_2S_2$ + Be plus the experimental binding energy of $H_2S_2$ (63 kcal/mol).

## Binding of Metals to $H_2O$

The model reactions to be discussed in the next section apply primarily to the gas phase. In the HSAB terminology,[17,18] O is a harder base than S, so it is to be expected that competition between $R_2S_2$ and $H_2O$ for the hard cations of group 1A and 2A may change the reaction pattern of $R_2S_2$ with these metals in solution. In order to discuss which conclusions also may persist in solution, it is necessary to know the total hydration energies of the molecules involved, especially of the ions. To calculate this is an enormous task and is far beyond the scope of the present work. However, quite a few details on the competition between $R_2S_2$ and $H_2O$ for binding of the metals can be obtained by comparing the binding energies of the metals to one $H_2O$ molecule with the binding energy toward $R_2S_2$.

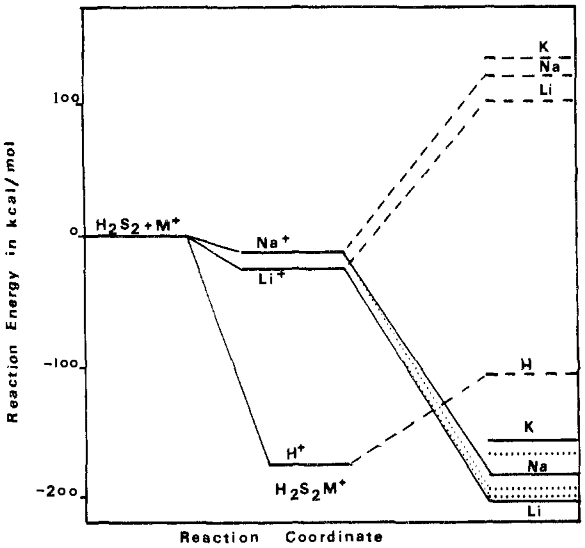


Figure 2. Calculated reaction energies for alkali metals with disulfides in electrophilic splitting (- - -), concomitant splitting with $F^-$ (—), and metal abstraction (• • •).

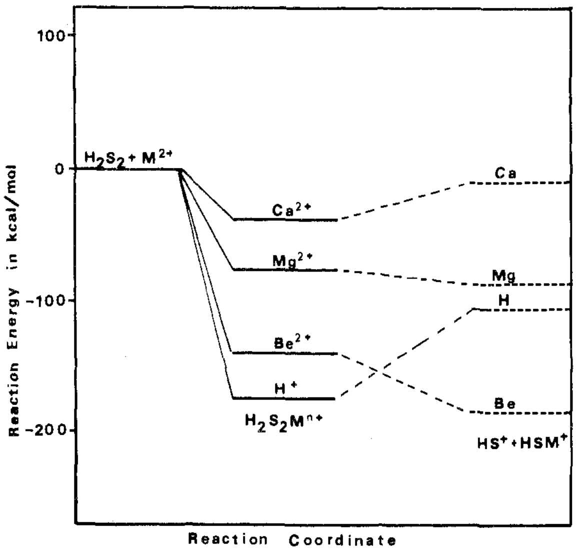


Figure 3. Calculated reaction energies for electrophilic cleavage of disulfides by alkaline earth metals.

The binding of the alkali cations to $H_2O$ has been extensively studied both experimentally[19] and theoretically, and large HF calculations (corrected for zero-point vibrations) are known to predict hydration energies in excellent agreement with experiment.[20] A summary of Clementi's first hydration energies[20] for $Li^+$, $Na^+$, and $K^+$ together with our values for $H^+$ and $Li^+$ is reported in Table II. Although our proton affinity is in close agreement with the experimental and best theoretical values, our calculated first hydration energy for $Li^+$ shows that we may expect Clementi's first hydration energies to be lower than ours. But even Clementi's values are considerably higher than the corresponding binding energies of the alkali metals to the disulfides, so the alkali metals are not likely to bind to SS bonds in aqueous solutions.

In contrast to the alkali metals, there are no experimental values available for the different $H_2O$ affinities of alkaline earth cations (except the total) and only a single theoretical study has previously been reported on the hydration energies of $Be^{2+}$, $Mg^{2+}$, and $Ca^{2+}$.[21] Our calculated first hydration energies for these ions are somewhat higher (which is to be expected in a smaller basis), but they nevertheless show a more delicate balance between $H_2O$ and $R_2S_2$ in their competition for the alkaline earth metals. Comparing the energy values displayed in Table II, we see that both the open form I and bridged form II of $H_2S_2Be^{2+}$ are likely to exist in aqueous solution. $H_2S_2Mg^{2+}$ (probably in either form) is less likely but may still be possible, whereas $H_2S_2Ca^{2+}$ seems to be quite unstable. As to which form of $H_2S_2Be^{2+}$ will be the more stable in solution, this is not possible to tell from our results.

Considering the large total hydration energy of $Be^{2+}$ of 602 kcal/mol compared to the difference in stability between structures I and II of 12 kcal/mol, it is evident that even small differences in the structure of the hydration shells of these complexes easily may interchange their relative stability in solution. One might, nevertheless, very tentatively suggest that the monodentate form (I) will be the more stable considering the less sterically crowded space in the vicinity of the metal in that structure, thereby allowing for more $H_2O$ molecules close to the metal.

## Reactions of Metal Cations with S–S Bonds

In this section we will try to elucidate the reaction of group 1A and 2A metal cations with disulfides by studying model reactions based on the results reported in the present work and on experience from the corresponding reactions with protons as electrophiles.[5] The reaction mechanisms to be considered will be those discussed in the Introduction, concomitant (eq 4 and 5) and electrophilic (eq 1 and 2), as these are believed to constitute the central mechanisms in these problems.

**Alkali Metals.** As these metals were found to bind stronger to $H_2O$ than to $H_2S_2$, it is not likely that sufficient amounts of $H_2S_2M^+$ will be formed so that neither the electrophilic nor the concomitant reaction will be of any importance in aqueous solution. As $H_2S_2M^+$ is stable in the gas phase, it may exist in nonaqueous solutions (often found locally in biological systems), but even then the S–S bond fission of $H_2S_2M^+$ in the last step of reaction 1 is very unlikely. As illustrated in Figure 2 this reaction (in the gas phase) will be even more endothermic than the corresponding fission of $H_3S_2^+$, i.e., with protons as electrophiles.

The concomitant reactions 4 and 5 are, on the contrary, exothermic for the alkali metals (if nucleophiles are present), but they are nevertheless very likely dominated by other reactions owing to special features in the electronic structure of $H_2S_2M^+$. The electronic requirement found for reaction 5 in the concomitant scheme was the existence of a LUMO being S–S antibonding and having a positive electron affinity. $H_2S_2M^+$ has in fact a positive electron affinity, but the LUMO is of metal 2s and 3s character, respectively, and not S–S antibonding. This in turn implies that the nucleophile will not break the S–S bond but rather bind to the metal instead. As the metal in addition is weakly bound to $H_2S_2$, this altogether suggests that metal abstraction from the disulfide will be dominating:

$$H_2S_2 + M^+ \rightarrow H_2S_2M^+ + Nu^- \rightarrow H_2S_2 + NuM \quad (7)$$

The abstraction of $Na^+$ and $K^+$ by the nucleophile is in fact more exothermic than the concomitant reaction (see Figure 2). Additionally, if a strong nucleophile is present in the solution, this alone is usually sufficient for scission of the S–S bond by the common nucleophilic cleavage reaction 6. This is most likely what happens when salts like PhLi and $Ph_3CNa$ cleave disulfides in ether.[22] Carbanions, like $Ph^-$ and $Ph_3C^-$, are among the strongest nucleophiles known toward sulfur centers,[25] so the metal has no active role in the reaction but being the counterion to the nucleophile.

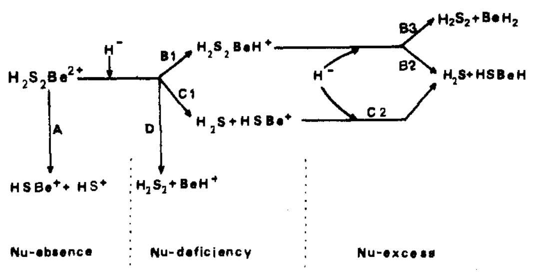
**Alkaline Earth Metals.** The reaction scheme with these metals is more complicated as the metal can bind to the disulfide in two different forms and because several reaction pathways are possible for each form. The necessary formation of $R_2S_2M^{2+}$ will in aqueous solution be restricted to M = $Be^{2+}$ and possibly some $Mg^{2+}$.

The electrophilic scission (eq 1) of $R_2S_2$ by $M^{2+}$ is, as displayed in Figure 3, endothermic in the gas phase for $Ca^{2+}$, but is in fact exothermic for $Mg^{2+}$ and $Be^{2+}$. This is the only case in our study as yet where the electrophilic scission (eq 1) is predicted to be exothermic in the gas phase, but we shall see that eq 1 and 2 still are the least favorable channels for $Be^{2+}$ and $Mg^{2+}$ when nucleophiles are present.

Both type I and II complexes of $R_2S_2M^{2+}$ have positive electron affinities as required in the concomitant scheme, but like the alkali-disulfide complexes $H_2S_2M^+$ the LUMO is of metal 2s, 3s, and 4s character, respectively. However, all $H_2S_2M^{2+}$ complexes have a second virtual orbital with negative eigenvalues indicating that the complex still will have a positive electron affinity when the LUMO is filled (i.e., in $H_2S_2M^+Nu$), and this orbital is strongly S-S antibonding. In $H_2S_2Ca^{2+}$ these two lowest virtual orbitals are very close ($\epsilon = -6.2, -5.1$ eV) so which of the metal 4s or the S-S antibonding orbital of $R_2S_2Ca^{2+}$ first will be filled will have to be determined by separate calculations on the complexes. In contrast to the alkali metal disulfide complexes, the group 2A metals are bound so strongly to $R_2S_2$ (see Table II) that $R_2S_2M^+Nu$ is likely to be stable against metal abstraction. This suggests that the S-S bond in $R_2S_2M^{2+}$ may be split by two nucleophiles, the first binding to the metal and the second to one of the sulfur atoms subsequently cleaving the S-S bond.

We do not, of course, know whether the conclusions based on these simple considerations of the electronic structure of $R_2S_2M^{2+}$ will be valid in a more complete model, and we have accordingly performed a closer study of the possible reaction pathways for the complex predicted to be most stable in solution, $H_2S_2Be^{2+}$, using $H^-$ as model nucleophile ($H^-$ is a strong nucleophile experimentally known to cleave S-S bonds in aprotic solvents[23]). The reaction scheme considered for $H_2S_2Be^{2+}$ is as shown in (B). The calculated reaction energies are summarised in Figure 4.

(B)



In the absence of nucleophiles the only reaction of $H_2S_2Be^{2+}$ will be scission of the S-S bond (A) corresponding to the electrophilic cleavage reaction 1. As previously discussed, we see from Figure 4 that this will now be exothermic, at least in the gas phase, as opposed to the case for $H^+$ and alkali metals, but will definitely be the least favorable channel even in the presence of small amounts of nucleophiles. In the presence of nucleophiles, reactions B1, C1, and D will all be energetically possible (exothermic) of which B1 (nucleophilic addition to the metal) will have the largest reaction energy and D (metal abstraction) will have the smallest. These are the same conclusions as those just suggested by simple reasoning based on the electron affinities of the complexes as represented by the orbital energies of the LUMO. Nucleophilic deficiency (i.e., stop at B1) will thus not cause splitting of S-S bonds (except possibly for $Ca^{2+}$ as routes B1 and C1 are likely to be almost degenerate in that case), but merely formation of the stable complex $[H_2S_2BeH]^+$.

The LUMO of $[H_2S_2BeH]^+$ has an electron affinity of 2.5 eV and is S-Be bonding and S-S antibonding as anticipated from the virtual orbitals of $H_2S_2Be^{2+}$. In case of excess of nucleophiles another nucleophile will thus add to S, split the S-S bond, but keep the S-Be bond intact (reaction B2) eventually yielding RSNu + RSMNu. These will be the same end products as those resulting from route C in case of nucleophilic excess.

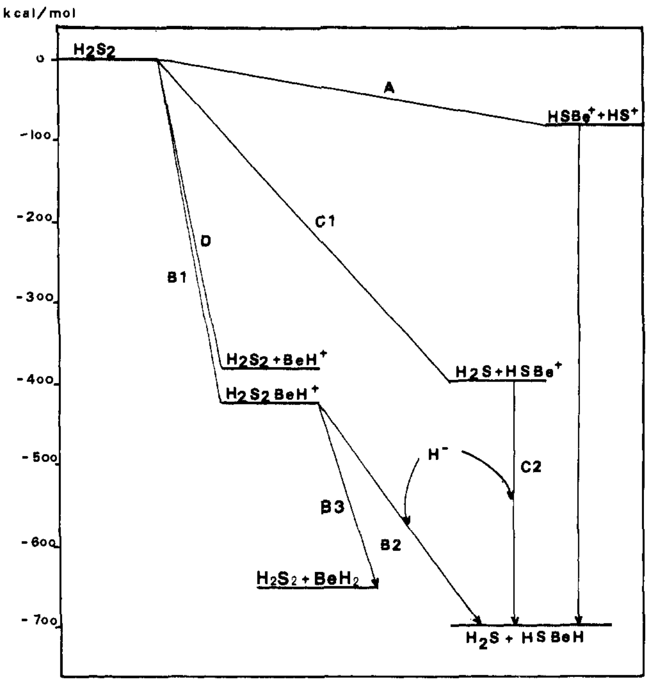
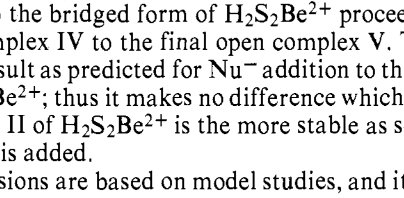


Figure 4. Calculated total energies of the different reactions of $H_2S_2$ with $Be^{2+}$ and $H^-$. The letters identifying the reactions refer to the scheme discussed in the text.

If the bridged rather than the open form of $R_2S_2M^{2+}$ is dominating, the conclusions concerning the model system of $Be^{2+}$ and $H^-$ will not be changed except for addition of an extra step. In general, two different complexes can result from adding a nucleophile to bridged $R_2S_2M^{2+}$; either the bridged complex IV is the more stable or the open complex V is so.

(C)

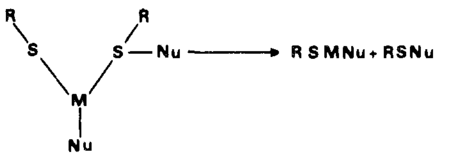


For the special case of $Be^{2+}$ and $H^-$ the calculations predict the open form V to be slightly more stable than the bridged form IV by ~3-4 kcal/mol. This suggests that the addition of a nucleophile to the bridged form of $H_2S_2Be^{2+}$ proceeds via the bridged complex IV to the final open complex V. This is the same end result as predicted for $Nu^-$ addition to the open form I of $H_2S_2Be^{2+}$; thus it makes no difference which of the two forms I and II of $H_2S_2Be^{2+}$ is the more stable as soon as the nucleophile is added.

These conclusions are based on model studies, and it is not unlikely that another combination of metal and nucleophiles will stabilize the bridged form IV over the open form V. However, even in form IV the LUMO of $[R_2S_2MNu]^+$ is S-S antibonding and has a negative eigenvalue ($\epsilon = -4.1$ eV for $[H_2S_2BeH]^+$), suggesting the addition of a second nucleophile to the bridged form IV also will cause fission of the S-S bond yielding VI which then most likely will decompose spontaneously (D).

The model reactions discussed in the present work are formally gas-phase reactions. In solution, the relative energies of the reactions may be changed considerably by the differences

(D)



VI

in hydration energies of the molecules involved, especially that of the ions. Direct participation of the solvent or its dissociation products in the reactions may also contribute to extend the relevant reaction schemes. However, previous experience has demonstrated that the solvent, in the form of adding $H_2O$ molecules to the complexes in consideration, has an almost negligible effect on those aspects of the electronic structure of the molecules that govern the different reaction mechanisms in our case.[5] Accordingly, we believe that the electronic aspects of the reaction mechanisms discussed in the present work are essentially valid also in aqueous solutions, although the relative reactivities of the different reaction channels may strongly be altered.

One of the solvent-dependent parameters that will be of interest in the present context is the relative strength of the metals in the reactions, especially with respect to $H^+$, in order to discuss pH dependency. To do this properly, it would be necessary among other things to calculate the total hydration energies of the molecules and ions involved, an enormous task far beyond the scope of the present work. We rather choose to get an indication of this parameter by looking at the effect of $H_2O$ on the rate-determining step in the reactions, i.e., formation of $R_2S_2M^{n+}$. In other words, how will $H_2O$ and $R_2S_2$ compete for the metal ions? The difference between the two corresponding binding energies of the metals will somewhat underestimate the stability of the hydrated $R_2S_2M^{n+}$, i.e., $[R_2S_2...M^{n+}...H_2O]$,[5] thus yielding a slightly conservative estimate of which metals will form sufficiently stable $R_2S_2M^{n+}$ complexes in solution. By performing this, one finds the excess binding energy of $H^+$ to $H_2S_2$ over that to $H_2O$ to be 2 kcal/mol, $Be^{2+}$ $-4$ (open form) and $+8$ kcal/mol (bridged), $Mg^{2+}$ $-16$ kcal/mol, and $Ca^{2+}$ $-24$ kcal/mol. $Be^{2+}$ and $H^+$ are rather close, $Be^{2+}$ may be stronger or weaker than $H^+$ depending on the binding form of $R_2S_2Be^{2+}$, while probably $Mg^{2+}$ and especially $Ca^{2+}$ will not bind to $R_2S_2$ in sufficient amounts in solution to participate in disulfide cleavage reactions.

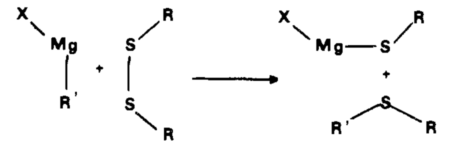
The detailed reactions discussed in the present work have not been studied experimentally, but some information may indirectly be obtained from existing experimental data. Arora and Karasch have recently proposed the importance of simultaneous coordination by metal and attack by nucleophilic species in biological S–S systems, based on studies of electrophilic cleavage of sulfenate esters.[31] The idea that protons are strong electrophiles compared to many metals is consistent with the observation that metal ions known to react with sulfur, like $Ag^+$ and $Hg^{2+}$, split S–S bonds in proteins either in high concentrations or at high pH[24] (presumably with the hydroxide ion acting as nucleophile). The possibility that Mg may react with disulfides under more favorable conditions derives indirect support from the fact that Grignard reagents are known to react with disulfides yielding thiols:[25]

$$\mathrm{RMgX + RSSR \leftrightarrow R'SR + RSMgX}$$

where X = halogen. A possible mechanism for this reaction is a kind of concomitant electrophilic mechanism as discussed below.

Studies of the charge distributions in methyl Grignard reagents, $CH_3MgX$,[26] have shown that the $CH_3$ group is polarized so as to have a partial carbanionic character and that Mg is quite positive ($q \sim +1$) owing to electron withdrawal by the halogen. Mg could then act as an electrophile and R′ as a nucleophile in the following overall way (i.e., not necessarily a four-center reaction) (E). As the binding sites of Mg already are occupied, an excess of free nucleophiles will be unnecessary. Whereas $Mg^{2+}$ was prevented from reacting with $R_2S_2$ by hydration effects on the metal ion, the corresponding Grignard reactions should be expected to be less solvent dependent as they are not ionic.

(E)



## Conclusions

The present study has shown that the alkali metals form weak complexes with disulfides by binding to one of the sulfur atoms. The disulfide complexes with the alkaline earth metals are more stable also for $Be^{2+}$ and to some extent $Mg^{2+}$ in aqueous solution. The complexes have two stable forms, the open I and the bridged II, whereas the form having the metal cation inserted in the middle of the disulfide bond, III, is electronically unstable and reverts spontaneously to the bridged conformation. The prediction that polyvalent metal ions can form stable complexes with disulfides is of great interest in several contexts, like the Cu-catalyzed oxidation of thiols to disulfides[27] by the reaction $2Cu^{2+} + 2RS^- \rightleftarrows RSSR + 2Cu^+$, where a similar complex of $Cu^+$ and $R_2S_2$ is postulated as a general intermediate.

The electrophilic scission of S–S bonds, traditionally considered as the main reaction mechanism for electrophiles and disulfides, was found to be of limited interest as the reaction $H_2S_2M^{n+} \rightarrow HS^+ + HSM^{(n-1)+}$ is exothermic only for $Be^{2+}$ and $Mg^{2+}$. The study showed that the mechanism of interest is the concomitant electrophilic, and nucleophilic reaction, which is more like a nucleophilic substitution reaction ($S_N2$) assisted by electrophiles, and confirmed that the main electronic factor governing the reaction is the availability and nature of empty orbitals (of positive electron affinity and with S–S antibonding character) in $H_2S_2M^{n+}$ into which electron pairs from nucleophiles may be transferred. However, the alkali metals will most likely not react with disulfides owing both to competition from $H_2O$ and because the LUMO is of metal *n*s character rather than S–S antibonding. The LUMO in $H_2S_2M^{2+}$ is also metal in character, but in the alkaline earth metal complexes there is a second vacant orbital, strongly S–S antibonding, which may cause S–S fission if there is excess of nucleophiles present. This is irrespective of whether the open or bridged form of $H_2S_2M^{2+}$ is the most stable.

In solution the formation of $H_2S_2M^{2+}$ in the rate-determining step will have to compete with hydration of the metal cations, thus preventing $Ca^{2+}$ and to some extent $Mg^{2+}$ from reacting. $Be^{2+}$ is also likely to be the only metal of those considered that may compete with $H^+$ in binding to $H_2S_2$, so generally high pH or high metal concentrations seem necessary to make these metals react with disulfides. Thus of the metals included in this study, those naturally present in living systems react only weakly with S–S bonds while Be, being very toxic, is the metal that reacts most strongly. Nevertheless, complexing of disulfides by metals in living systems seems worthy of special consideration for mechanistic purposes.

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# Light-Initiated Electron Transfer in Functional Surfactant Assemblies. 1. Micelles with Transition Metal Counterions

**Yoshikiyo Moroi, André M. Braun, and Michael Grätzel***

*Contribution from the Institute of Physical Chemistry, Federal Institute of Technology Lausanne, Switzerland.* *Received December 7, 1977*

**Abstract:** The photoinduced reduction of cupric ions by organic donors (D) was studied in functional surfactant assemblies in which the $Cu^{2+}$ ions constitute the counterion atmosphere of the micelle. The donors employed were *N*-methylphenothiazine (MPTH) and *N,N′*-dimethyl-5,11-dihydroindolo[3,2-*b*]carbazole (DI). Laser photolysis, steady-state illumination, and fluorescence techniques were used to investigate the photoredox processes. The transfer of an electron from the excited donor inside the micelle to the counterion occurs so rapidly that it cannot be resolved kinetically by nanosecond laser techniques. In the case of DI, the reactive excited state was found to be the first excited singlet state whose lifetime in the $Cu^{2+}$ micelles is $1.2 \times 10^{-9}$ s. The cuprous ion formed in the photoredox process escapes from the micelle into the bulk solution before back transfer of electrons to $D^+$ can occur. There it may be used for a second redox reaction with a negative ion or a zwitterion. In such a system, the back reaction between reduced acceptor ion and oxidized donor is prevented by the micellar surface potential allowing for storage of light energy. The dynamics of excited-state interaction with micellar counterions was investigated also in aggregates with $Co^{2+}$ and $Ni^{2+}$ counterion atmospheres, respectively.

## Introduction

In the photoredox reaction

$$A + D \underset{\Delta}{\overset{h\nu}{\rightleftarrows}} A^- + D^+ \qquad (1)$$

a large fraction of the incident light energy may be initially converted into chemical energy. The practical application of such a system is hampered by the fact that back reaction occurs rapidly. Thereby the chemical potential available in the radical ion pair $A^- \cdots D^+$ is degraded thermally. A promising approach to overcome this problem is to employ charged surfactant aggregates such as micelles or vesicles in aqueous solution as a reaction medium. Hitherto the role of these assemblies has been[1] (1) to solubilize hydrophobic photoactive species in their interior; (2) to provide an ultrathin electrostatic barrier, i.e., the electrical double layer surrounding the surfactant aggregate, through which kinetic control of the forward and backward reaction in eq 1 becomes feasible.[2]

Recently, light-induced charge separation has been investigated in our laboratory with systems where the micellar assembly itself serves as a functional unit, i.e., the electron donor and/or acceptor in the photoredox reaction are a part of the surfactant molecules constituting the micelle.

The simplest kind of such a "functionalized surfactant" is one where the counterion is a participant in the redox reaction. Cooperative effects obtained with such a system are reported in this paper.

## Experimental Section

*N*-Methylphenothiazine was synthesized by the method of Normant and Curigny.[3] The crude, pink-colored crystals were recrystallized several times from argon-saturated ethanol until no impurity could be detected by thin layer chromatography (solvent hexane-acetone (3:1); visualization, photooxidation and/or thermal oxidation by a mixture of 0.2% $H_2PtCl_6$ and 1% KI in $H_2O$). One obtains colorless needles, mp 99.5 °C (lit. 100 °C[4]). The chromophore *N,N′*-dimethyl-5,11-dihydroindolo[3,2-*b*]carbazole (DI) was a generous gift of Professor S. Hünig from the University of Würzburg, West Germany, and was used as supplied.

The transition metal ion lauryl sulfates, $Cu(LS)_2$, $Ni(LS)_2$, and $Co(LS)_2$, were synthesized according to a procedure described previously.[5a] The cmc value of these surfactants is $1.2 \times 10^{-3}$ M and the micellar aggregation number around 95.[5b] Deionized water was dis-

0002-7863/79/1501-0567$01.00/0