Electrophilic Attack on Sulfur–Sulfur Bonds: Coordination of Lithium Cations to Sulfur-Rich Molecules Studied by Ab Initio MO Methods

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Abstract: Complex formation between gaseous Li^+ ions and sulfur-containing neutral ligands, such as H_2S, Me_2S_n (n = 1–5; Me = CH_3) and various isomers of hexasulfur (S_6), has been studied by ab initio MO calculations at the G3X(MP2) level of theory. Generally, the formation of LiS_n heterocycles and clusters is preferred in these reactions. The binding energies of the cation in the 29 complexes investigated range from $-88\,kJ\,mol^{-1}$ for $[H_2SLi]^+$ to $-189\,kJ\,mol^{-1}$ for the most stable isomer of $[Me_2S_5Li]^+$ which contains three-coordinate Li^+. Of the various S_6 ligands (chair, boat, prism, branched ring, and triplet chain structures), two isomeric complexes containing the $S_5{=}S$ ligand have the highest binding energies ($-163 \pm 1\,kJ\,mol^{-1}$). However, the global minimum structure of $[LiS_6]^+$ is of C_{3v} symmetry with the six-membered S_6 homocycle in the well-known chair conformation and three Li–S bonds with a length of 256 pm (binding energy: $-134\,kJ\,mol^{-1}$). Relatively unstable isomers of S_6 are stabilized by complex formation with Li^+. The interaction between the cation and the S_6 ligands is mainly attributed to ion–dipole attraction with a little charge transfer, except in cations containing the six sulfur atoms in the form of separated neutral S_2, S_3, or S_4 units, as in $[Li(S_3)_2]^+$ and $[Li(S_2)(S_4)]^+$. In the two most stable isomers of the $[LiS_6]^+$ complexes, the number of S–S bonds is at maximum and the coordination number of Li^+ is either 3 or 4. A topological analysis of all investigated complexes revealed that the Li–S bonds of lengths below 280 pm are characterized by a maximum electron-density path and closed-shell interaction.

Keywords: ab initio calculations · cluster compounds · ion–molecule reactions · lithium · sulfur ligands

Introduction

Sulfur-containing ligands are of fundamental importance in chemistry, particularly in biological chemistry.[1] The most familiar ligands of this type contain only a single sulfur atom (sulfido and thiolato ligands, S^{2-} and RS^-). However, in recent years, the chemistry of polysulfido ligands S_x^{2-} (x = 2–10) has been developed systematically.[2] Owing to the negative charge on the mentioned ligands, the interaction with metal cations is very strong and covalent bonds are formed. Less stable complexes are obtained if the ligands as a whole are uncharged and if the sulfur atoms bear only a small charge, as in Me_2S or Me_2S_2, or no charge at all, as in highly symmetrical sulfur homocycles such as *cyclo*-S_8.

The highest occupied molecular orbital (HOMO) in compounds containing S–S bonds between two-coordinate atoms, with torsion angles (τ) close to 90°, is the antibonding π* MO resulting from the overlap of the nonbonding 3p atomic orbitals, which are approximately orthogonal to the neigboring σ bonds that are fully occupied.[3,4] Removal of electron density from such a –S–S- bond should therefore increase the bond strength and change the torsion angle at this bond from about 90° towards a more planar structure. For instance, the radical cation $Me_2S_2^{\cdot+}$ contains a *trans*-planar structural unit C-S-S-C (C_{2h} symmetry) with an S–S bond length of 200.3 pm at the MP2/6-311G(d) level of theory.[6] This internuclear distance is about 5 pm shorter than that calculated for Me_2S_2 (τ_{calcd} = 87.6°) as a result of the three-electron π bond, which is not present in the neutral molecule. The adiabatic ionization energy of Me_2S_2 (τ_{exp} = 85°[5]) is 8.18 ± 0.03 eV.[6]

The gas-phase ionization energies of the homocycles S_6 and S_8 are approximately 9 eV. However, if one torsion

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angle of a sulfur ring is much smaller or larger than 90° (e.g., on account of the smaller or larger ring size compared to S_8), the ionization energy will be smaller owing to the larger overlap of the mentioned 3p orbitals and the larger energetic splitting between the resulting π and π^* MOs. For example, the ionization energy of *cyclo*-S_6 of 9.00 eV[7] (τ = 73.8°[8]) is slightly smaller than that of *cyclo*-S_8 (9.04 eV;[7] τ = 98.5°[9]). In *cyclo*-S_7 one torsion angle has the value 0°[10] resulting in a considerably lower ionization energy of 8.67 eV.[7] The structure of S_6^+ calculated with the B3PW91 method and the 6-31+G* basis set has been predicted to be a chair conformation with D_{3d} symmetry (d = 208.1 pm, α = 108.5°, τ = 62.4°).[11]

The interaction of metal cations with neutral sulfur molecules S_n is very weak and only a few solid coordination compounds are known in which sulfur molecules function as neutral ligands. Examples are several silver salts with the cations $[AgS_8]^+$ and $[Ag(S_8)_2]^+$, respectively, and weakly coordinating anions,[12,13] the rhenium complexes $[Re_2X_2(CO)_6(S_8)]$ (X = Br, I),[14] and the rhodium compounds $[Rh_2(O_2CCF_3)_4]_n(S_8)_m$ with n:m = 1:1 and 3:2.[15] The X-ray structure determinations of these compounds revealed that the S_8 ligands exhibit basically the same crown-shaped ring conformation as the molecules in orthorhombic *cyclo*-octasulfur, and S_8 functions as either a bidentate, tridentate or tetradentate ligand or as a bridging ligand between two metal centers. The mean S–S bond lengths in these complexes are practically identical to the value determined for orthorhomic S_8 (205 pm[9]). The binding energy of gaseous $[Ag(S_8)]^+$ (C_{4v} symmetry) with respect to the free components has been calculated by various density functional and ab initio MO methods to be between −208 and −247 kJ mol^{-1}.[13]

A considerable number of complexes of univalent metal cations with sulfur molecules, $[MS_n]^+$ with n = 1–21, has been generated in the gas phase and detected by ion cyclotron resonance (ICR) mass spectrometry. These metals include Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Cu, and many rare-earth metals.[16,17] The structures and relative energies of these complexes are only partially known from preliminary reports on density functional calculations of polysulfur cations containing calcium, scandium, vanadium, or copper.[17] These calculations (of which no details have been released yet) show that Ca^+ forms complexes with the S_3 ligand in a planar geometry and with the crown-shaped *cyclo*-S_8 ligand in a bidentate, tridentate, and tetradentate manner. Complexes of composition $[Ca(S_3)]^+$, $[Ca(S_8)]^+$, $[Ca(S_3)(S_8)]^+$, and $[Ca(S_3)_3]^+$ have been found to be local energy minima on the potential energy surfaces (PES). The most stable cationic complexes of Sc, V, and Mn with between four and eight sulfur atoms contain the sulfur exclusively in the form of S_2 ligands, whereas in the case of copper the ion of composition $[Cu(S_{12})]^+$ is the most stable as a twelve-membered sulfur ring with the metal cation in the center.

From the above, it follows that there is no systematic structural study of the coordination of univalent metal ions to neutral sulfur-rich molecules. Therefore, in this work we have studied the interaction of H_2S, Me_2S_n (n = 2–5) and the sulfur homocycle S_6 and various isomers of S_6 with a gaseous metal cation using Li^+ as a model ion. In a subsequent publication, we will report on the cationic lithium adducts of the homocycles S_7 and S_8 and their various isomers. The coordination of gaseous Li^+ to H_2S,[18,19,20] H_2S_2,[21] Me_2S,[22] and S_3[23] has been investigated previously by quantum-chemical calculations; however, to the best of our knowledge, the larger sulfur-rich complexes, such as $[Me_2S_nLi]^+$ ($n>1$) and $[LiS_n]^+$ ($n>3$) have neither been calculated nor observed before. We define here the binding energy as the energy difference between the complex and the sum of the energies of the two separated components *in the same conformation as found in the complex*.

Computational Methods

Standard ab initio and density functional calculations were carried out with the GAUSSIAN 98 and GAUSSIAN 03 series of programs[24] at the G3X(MP2) level of theory.[25] This theory corresponds effectively to the QCISD(T)/G3XL//B3LYP/6-311G(2df,p) energy together with zero-point vibrational and isogyric corrections. The G3X(MP2) theory represents a modification of the G3(MP2) theory[26] with three important changes: 1) B3LYP/6-311G(2df,p) geometry, 2) B3LYP/6-311G(2df,p) zero-point energy, and 3) addition of a g polarization function to the G3 large basis set for the second-row atoms at the Hartree–Fock level. These features are particularly important for the proper description of the sulfur-containing compounds examined in this work.[27,28,29] For instance, the geometries and stabilities of several cluster species are poorly predicted by the MP2 theory.[28] For the prism form of S_6, we have previously shown that the MP2 theory grossly overestimates its stability owing to the low-lying unoccupied molecular orbitals.[29] As a consequence, the additivity approximation at the MP2 level is rather unsatisfactory. We recommended a direct QCISD(T)/GTMP2 large calculation to obtain the G3X(MP2) energy in that case.[29] Here, we have adopted a similar procedure for the calculation of G3X(MP2) energies of the two lithiated forms of the S_6 prism (**6d** and **6e**).

Harmonic frequencies were calculated at the B3LYP/6-311G(2df,p) level to characterize stationary points as equilibrium structures, with all wavenumbers real, or transition states, with one imaginary wavenumber. The binding energy (ΔE) of the lithium ion complex was computed as the difference between the energy of the lithiated species and the total energy of the two free monomers, namely, the sulfur-containing compound and lithium ion. The free energy differences (ΔG) were computed by means of Equation (1), where ΔS is the entropy change and $\Delta H_T = \Delta H_0 + (H_T - H_0)$.

$$\Delta G_T = \Delta H_T - T\Delta S \qquad (1)$$

The thermal correction ($H_{298} - H_0$ = 6.197 kJ mol^{-1}) and entropy value (S_{298} = 133.017 J mol^{-1} K^{-1}) of the lithium cation were taken from the JANAF compilation.[30]

For all investigated molecules, a charge density analysis was performed by using the natural bond orbital (NBO) approach based on the B3LYP/6-311G(2df,p) wavefunction.[31] NBO atomic charges of small molecules have recently been demonstrated to agree well with experimental values obtained from X-ray diffraction data.[32] The topological analysis was carried out on the basis of Bader's theory of atoms in molecules (AIM)[33] based on the B3LYP/6-311G(2df,p) wavefunction. Unless otherwise stated, all relative energies reported herein are given as ΔE_0 and correspond to the G3X(MP2) level, while all reported structural parameters correspond to the B3LYP/6-311G(2df,p) level. All structures were optimized initially without any symmetry constraints and were re-optimized with a higher symmetry after a local energy minimum had been obtained. The Cartesian coordinates of all calculated cations are given in the Supporting Information.

Results and Discussion

The adducts $[H_2SLi]^+$ and $[Me_2SLi]^+$: The ions $[H_2SLi]^+$ and $[Me_2SLi]^+$ were calculated for comparison with the Li^+ adducts of the dimethyl polysulfanes and the sulfur homocycles. Both ions have been calculated previously, but not at the same level of theory used in the present work. Therefore, we have re-calculated these ions to obtain data which can be compared to our other results. According to the literature, the $[H_2SLi]^+$ ion is of C_s symmetry with an Li–S bond length of 241 pm and a binding energy of −97.1 kJ mol^{-1} at the CCSD(T)/6-311+G(d,p) level[18] and of −103.5 kJ mol^{-1} at the QCISD(T)/6-311+G** level.[20] The binding enthalpy at 298 K was calculated as −94.6 kJ mol^{-1} by the G2 method, as −91.6 kJ mol^{-1} by the CBS-Q method, and as −100.8 kJ mol^{-1} at the B3LYP/6-311+G(d,p) level.[19]

The geometry optimization of $[H_2SLi]^+$ resulted in the bond lengths $d_{\mathrm{LiS}} = 242.3$ pm and $d_{\mathrm{SH}} = 135.0$ pm (H_2S: 134.5 pm). The H-S-H bond angle of 93.6° is slightly larger than in H_2S (92.4°) and the H-S-Li angle is 99.7°. In other words, the coordination sphere at the sulfur atom is approximately trigonal-pyramidal, and thus, similar to that in the related cation H_3S^+.[34] The atomic charges of $[H_2SLi]^+$ are as follows: S −0.40, H +0.22, Li +0.96. Evidently, the charge transfer from H_2S to Li^+ is only 0.04 electrons. A comparison of the charge distribution with that of the free H_2S molecule (NBO charges: S −0.32, H +0.16) demonstrates that the lithium cation strongly polarizes the H_2S molecule, thus increasing its dipole moment considerably. The calculated [B3LYP/6-311G(2df,p)] dipole moments of H_2S and its lithiated form are 1.20 and 7.55 D, respectively (Table 1). The interaction between Li^+ and the sulfur atom in this adduct can therefore be described as a superposition of Coulombic attraction (ion–dipole interaction) and a weak covalent bond. This view is supported by the sum of the valence angles at the sulfur atom, which is 293°. It is conceivable that this value is strongly influenced by the direction of the rotational axis of the 3p lone pair orbital (HOMO) on the sulfur atom. Our calculated G3X(MP2) binding energy is −88.2 kJ mol^{-1} (Table 1), slightly less than the earlier theoretical estimates. The absolute energies of all species calculated in this work are given in Table 5 of the Supporting Information.

The $[Me_2SLi]^+$ ion is confirmed to have C_s symmetry with an Li–S bond length of 235.5 pm and a C-S-Li angle of 109.4°. The binding energy (−124.5 kJ mol^{-1}) is significantly larger than that of $[H_2SLi]^+$, probably because of the larger dipole moment (1.68 D) and polarizibility of Me_2S compared to H_2S (see above). The charge transfer to Li^+ is only 0.04 units; however, the NBO charge on the sulfur atom changes from +0.22 in Me_2S to +0.08 in the $[Me_2SLi]^+$ ion. Despite the relatively weak interaction, the Li–S bonds in $[H_2SLi]^+$ and $[Me_2SLi]^+$ are shorter than in some monomeric thiolate complexes of the type $[(thf)_3LiSR]$ (R = supermesityl, *o*-tolyl, 2,4,6-triphenylphenyl) for which bond lengths of 241–245 pm have been determined by X-ray crystallography.[35] The sum of the three valence angles at the sulfur center of the $[Me_2SLi]^+$ ion is 321°.

Table 1. Calculated binding energies[a] and dipole moments[b] of the various Li^+ complexes studied in this work. The $[LiS_6]^+$ ions contain the S_6 ligand in the chair (**6a**), boat (**6b**,**c**), prism (**6d**,**e**), branched ring (**6f**–**k**) or triplet-chain form (**6o**).

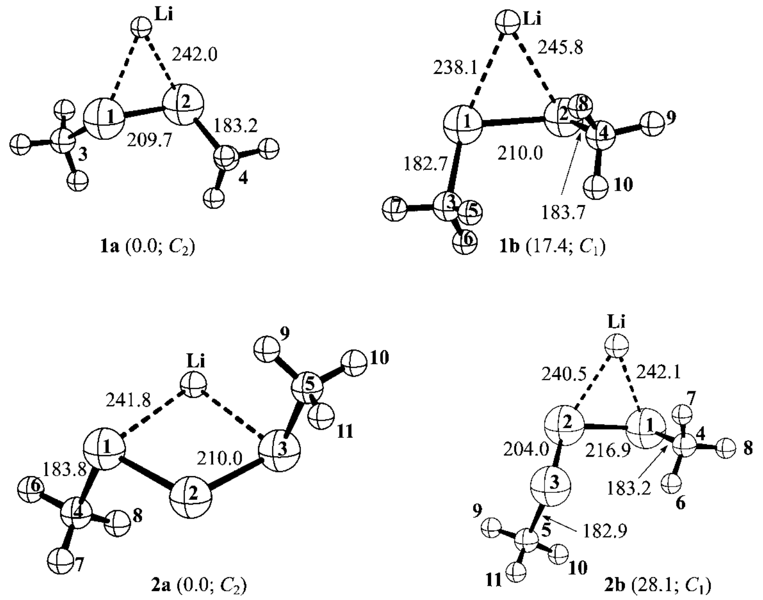
Species	Symmetry	CN[c]	Binding energy [kJ mol^{-1}]	Dipole moment [Debye]
$[H_2SLi]^+$	C_s	1	−88.2	7.55
$[Me_2SLi]^+$	C_s	1	−124.5	7.84
$[Me_2S_2Li]^+$ (**1a**)	C_2	1+1	−139.2	5.59
$[Me_2S_2Li]^+$ (**1b**)	C_1	2	−121.7	5.86
$[Me_2S_3Li]^+$ (**2a**)	C_2	2	−147.3	5.95
$[Me_2S_3Li]^+$ (**2b**)	C_1	2	−119.3	6.27
$[Me_2S_4Li]^+$ (**3a**)	C_2	2	−173.6	5.07
$[Me_2S_4Li]^+$ (**3b**)	C_1	1+1+1	−157.9	4.69
$[Me_2S_4Li]^+$ (**3c**)	C_1	1+1	−119.1	8.81
$[Me_2S_4Li]^+$ (**3d**)	C_2	2	−112.7	8.47
$[Me_2S_5Li]^+$ (**4a**)	C_s	2+1	−188.6	5.48
$[Me_2S_5Li]^+$ (**4b**)	C_1	2+1	−152.1	6.15
$[Me_2S_5Li]^+$ (**4c**)	C_1	1+1	−123.0	8.65
$[Me_2S_5Li]^+$ (**4d**)	C_1	2	−120.1	10.92
$[LiS_6]^+$ (**6a**)	C_{3v}	3	−133.9	5.28
$[LiS_6]^+$ (**6b**)	C_{2v}	3	−146.4	4.40
$[LiS_6]^+$ (**6c**)	C_s	2	−113.2	8.89
$[LiS_6]^+$ (**6d**)	C_{2v}	4	−131.2	5.09
$[LiS_6]^+$ (**6e**)	C_{2v}	2	−112.0	9.94
$[LiS_6]^+$ (**6f**)	C_1	2+1	−164.1	4.46
$[LiS_6]^+$ (**6g**)	C_s	1+2	−162.3	4.48
$[LiS_6]^+$ (**6h**)	C_1	1	−137.5	11.57
$[LiS_6]^+$ (**6i**)	C_s	1+2	−144.5	4.48
$[LiS_6]^+$ (**6j**)	C_1	1	−128.7	12.16
$[LiS_6]^+$ (**6k**)	D_{2d}	1+1	−115.3	7.21
$[LiS_6]^+$ (**6o**)	C_1	2	−124.4	6.34

[a] G3X(MP2) level. [b] B3LYP/6-311G(2df,p) level. [c] Coordination number of the Li^+ ion.

In most of the species discussed below, the lithium cation is coordinated to several sulfur atoms. In this context we will consider Li···S distances larger than 280 pm as nonbonding. The use of this criterion is supported by the charge-density analysis based on the AIM approach. Each Li···S interaction is characterized by a bond path and its associated bond critical point (see below).

The adducts $[Me_2S_2Li]^+$ (1a,b): Dimethyldisulfane (**1**) is predicted to react with gaseous Li^+ to give an adduct of either C_2 or C_1 symmetry in which the metal atom is coordinated to both sulfur atoms (Figure 1). In other words, the lithium cation induces a cyclization with formation of an LiS_2 heterocycle. This behavior is typical for most of the lithium cation adducts with sulfur-rich molecules studied in this work.

The C_2-symmetric adduct **1a** represents the global energy minimum. The S–S bond length of 209.7 pm is slightly larger



1a (0.0; C_2) **1b** (17.4; C_1) **2a** (0.0; C_2) **2b** (28.1; C_1)

Figure 1. Structures of the complex cations $[Me_2S_2Li]^+$ (**1a**,**b**) and $[Me_2S_3Li]^+$ (**2a**,**b**); bond lengths in pm. Relative energies (kJ mol^{-1}) and molecular symmetries are given in parentheses.

than that in Me_2S_2 (206.2 pm). The C-S-S-C torsion angle changed from the 85° observed[5] or the 87.5° calculated for gaseous Me_2S_2 to 113.7° in the $[Me_2S_2Li]^+$ ion **1a**. Thus, the expected increase of the value of the torsion angle (see the Introduction) is clearly observed; however, as a consequence of a small charge transfer of only 0.05 electrons (NBO charge of Li^+ in **1a**: +0.95), there is no shortening of the S–S bond in the lithiated form. The Li–S bonds of 242.0 pm and the C–S bonds of 183.2 pm are of normal length. All Li···H distances are larger than 350 pm. The bond angles are: $\alpha_{SLiS} = 51.3°$, $\alpha_{CSS} = 104.6°$, and $\alpha_{CSLi} = 125.9°$.

In the C_1-symmetric adduct of the $[Me_2S_2Li]^+$ ion **1b**, there is a relatively close contact (274 pm) of the Li^+ ion to one of the hydrogen atoms (H8) and the two interatomic Li–S distances are 238.1 and 245.8 pm. As a consequence, the two C–S bonds now have slightly differing lengths (182.7 and 183.8 pm).[36] The Li-S2-C4-H8 torsion angle is 10.1°. The methyl groups are staggered with respect to the sulfur atom that is not linked directly to the corresponding methyl group. The Li···C distances of 310 and 398 pm exclude any bonding interaction between these atoms. Since the Li^+ ion is neither located on the approximate C_2 symmetry axis of the ligand nor on the C–S axes (which represent local dipole moment vectors) the interaction between Li^+ and Me_2S_2 can best be understood in terms of the maximum polarization axis of the ligand. Adduct **1b** is 17.4 kJ mol^{-1} less stable than the isomeric form **1a**.

The positive charge of the sulfur atoms in free Me_2S_2 (+0.10) decreases to +0.01 in **1a** and to +0.003 for S1 and to +0.07 for S7 in **1b**. Hence, there is only a negligible polarization of the S–S bond in **1b**. The negative charge rests solely on the carbon atoms (–0.83 in **1a**; the same value for C3 of **1b** and –0.86 for C4, compared to –0.85 in Me_2S_2).

The charge on the hydrogen atoms is +0.28±0.01 in **1a** and in the range from +0.24 to +0.30 in **1b**. Hence, the coordination of Li^+ to Me_2S_2 increases the positive charge on the hydrogen atoms and unexpectedly decreases the positive charge on the sulfur atoms, whereas the carbon atoms are almost unaffected. The polarity of the C–S and C–H bonds is therefore enhanced. The calculated binding energies of the two isomeric $[Me_2S_2Li]^+$ ions with respect to the components Li^+ and Me_2S_2 (C_2) are –139.2 (**1a**) and –121.7 kJ mol^{-1} (**1b**), respectively, and agree well with the value of –124.5 kJ mol^{-1} obtained for the $[Me_2SLi]^+$ ion (Table 1).

The adducts $[Me_2S_3Li]^+$ (2a,b): The geometrical structure of Me_2S_3 has been studied by electron diffraction in the vapor phase at 383 K, and the results were interpreted in terms of a mixture of mainly *trans*-Me_2S_3 (**2**; symmetry C_2) and a little *cis*-Me_2S_3 (symmetry C_s).[37] The C-S-S-S torsion angle of **2** was determined to be 79(5)°. For the calculation of the binding energy of the Li^+ adduct, we used the helical *trans*-conformer with the calculated torsional angle $\tau_{CSSS} = 91.3°$.

In the adduct $[Me_2S_3Li]^+$ (**2a**), the Li^+ ion binds to the two terminal sulfur atoms in such a way as to retain the C_2 symmetry of the ligand. The lithium ion is not only located on the C_2 axis but approximately also on the rotation axes of the 3p lone pair orbitals of the terminal sulfur atoms (Figure 1). The lithium atom is coplanar with the three sulfur atoms in **2a**. The bond lengths $d_{SS} = 210.0$ pm and $d_{CS} = 183.8$ pm as well as the torsion angle $\tau_{CSSS} = 100.8$ have normal values; the binding energy is –147.3 kJ mol^{-1} (Table 1). The NBO atomic charges reveal that 0.10 electrons are transferred to the metal ion and that the sulfur atoms of **2a** are less charged than those of Me_2S_3 (+0.02/+0.11 for the terminal and +0.03/-0.05 for the central S atoms of **2a**/**2**). The strongest charge change occurs at the carbon atoms (from –0.85 in **2** to –0.62 in **2a**).

In the isomeric structure **2b** of the $[Me_2S_3Li]^+$ ion (Figure 1), the Li^+ ion is coordinated only along one S–S bond, similar to species **1b**. It is 28.1 kJ mol^{-1} less stable than the symmetrical structure **2a**, and the binding energy is only –119.3 kJ mol^{-1}. There are two remarkable structural features: the very long S–S bond of 216.9 pm as a result of the coordination of the two atoms to the Li^+ ion, and the relatively short distance of 269.1 pm of the Li^+ ion to one of the hydrogen atoms of the neighboring methyl group. The related H-C-S-Li torsion angle is –0.3°. The two C-S-S-S torsion angles are quite different in **2b**. The unusually small value of −41.1° was obtained for the S1−S2 bond, whereas a normal value of −90.2° was calculated for the S2−S3 bond. In this way, the lithium ion can interact favorably with the 3p lone pairs of both sulfur atoms (S1 and S2). Nevertheless, the charge transfer to the metal atom is only 0.05 electrostatic units.

Adducts of composition $[Me_2S_4Li]^+$ (3a–d): There is no experimental structure determination for either H_2S_4 or Me_2S_4; however, according to ab initio MO calculations, a mixture of several conformers with the motifs +++, +−+ and ++− is to be expected for these molecules (a motif is defined as the order of signs of the torsion angles at the S−S bonds along the chain; the values of these angles will be 80±10°).[38,39] The helical Me_2S_4 conformer (**3**, C_2 symmetry) with the calculated torsion angles τ_{CSSS} = 80.5° and τ_{SSSS} = 81.0° was used to calculate the binding energies.

The most stable isomer of the adduct $[Me_2S_4Li]^+$ (**3a**) consists of an LiS_4 heterocycle with an approximately envelope conformation and two methyl groups which are staggered with respect to the neigboring sulfur atoms (Figure 2). The lithium ion is only coordinated to the two terminal sulfur atoms of the tetrasulfane chain (S5 and S8). The helical Me_2S_4 fragment has approximately C_2 symmetry and the cation is positioned on this C_2 axis so that the symmetry axes of the 3p orbitals of the coordinating sulfur atoms are pointing towards the Li atom. Thus, the torsion angles S-S-S-S (−74.5°), C1-S-S-S (−70.5°), and C9-S-S-S (−70.4°) are not only very similar, but all have the same sign. The two Li-S-S-S torsion angles are 46.2°. The two Li−S bonds (243.5 and 243.4 pm) are comparable to those of the $[Me_2S_2Li]^+$ ion (238.1 and 245.8 pm), whereas the other two Li···S distances (307.8 pm) are clearly nonbonding. The NBO atomic charges of free helical Me_2S_4 (C: −0.85, S_{term}: +0.13, S_{center}: −0.05) change to the following values upon coordination to Li^+: C −0.84, S_{term} +0.03, S_{center} +0.02, Li + 0.90. The Li^+ ion is located on the axis of the dipole moment of the ligand, but not on the two C–S axes.

A slightly less stable isomer $[Me_2S_4Li]^+$ (**3b**) has C_1 symmetry and contains the Li^+ ion coordinated to three sulfur atoms with Li−S bond lengths of 243.4, 248.1, and 254.7 pm (Figure 2). The remaining Li−S distance is 304.6 pm. The relative energy of this isomer with respect to the global minimum is 15.7 kJ mol^{-1}.

The asymmetric isomer **3c** consists of a helical Me_2S_4 ligand to which the Li^+ ion is coordinated in a similar manner as in **1b** and **2b**. Only two sulfur atoms participate in this interaction. Again, there is a relatively short Li···H distance of 273.8 pm with a related H-C-S-Li torsion angle

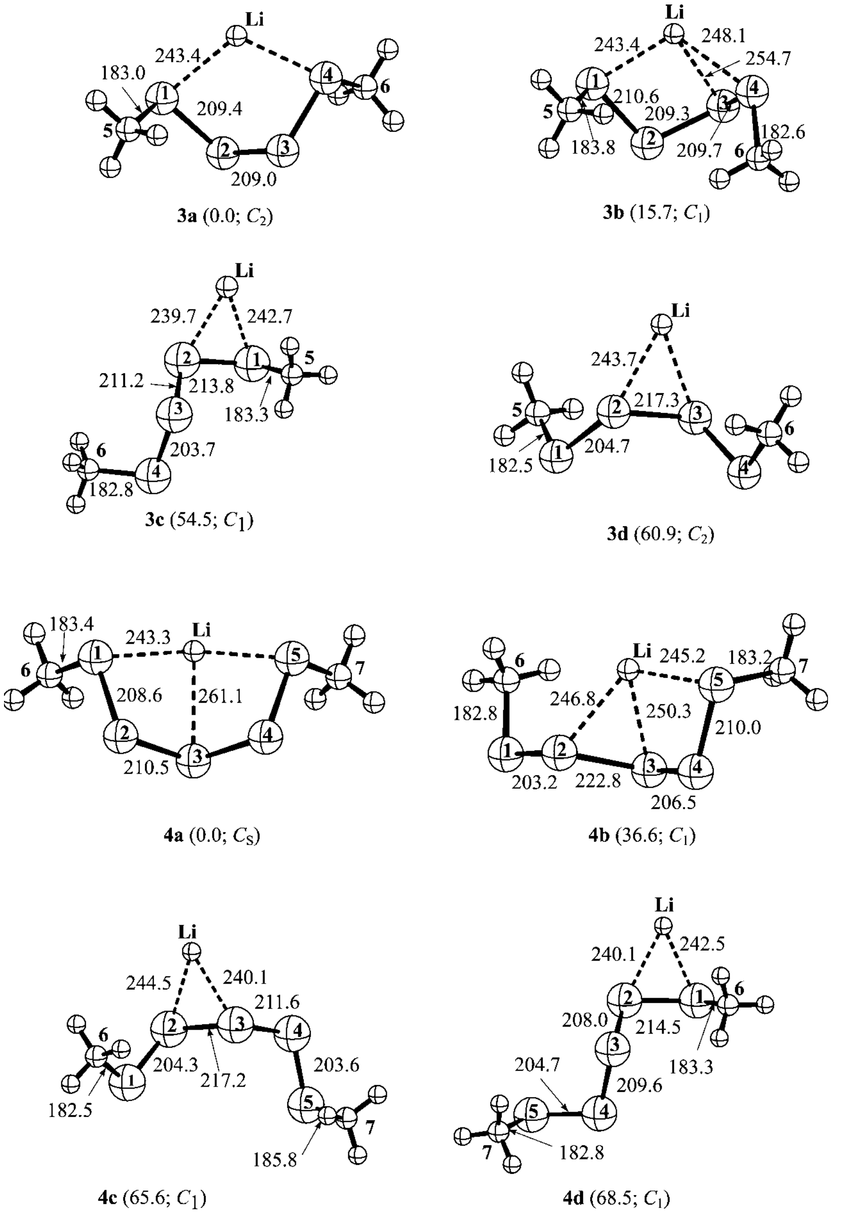

3a (0.0; C_2) **3b** (15.7; C_1) **3c** (54.5; C_1) **3d** (60.9; C_2) **4a** (0.0; C_S) **4b** (36.6; C_1) **4c** (65.6; C_1) **4d** (68.5; C_1)

Figure 2. Structures of the complex cations $[Me_2S_4Li]^+$ (**3a–d**) and $[Me_2S_5Li]^+$ (**4a–d**); bond lengths in pm. Relative energies (kJ mol^{-1})and symmetries are given in parentheses.

of −3.3°. Whereas the C5-S1-S2-S3 torsion angle is smaller than expected (−42.7°), the dihedral angles at the S2−S3 (−85.4°) and S3−S4 (−83.6°) bonds show normal values. This cation is less stable than **3a** by 54.5 kJ mol^{-1}.

An even less stable isomer of the $[Me_2S_4Li]^+$ ion (**3d**), in which the lithium ion is coordinated symmetrically to the two central sulfur atoms and the Li−S distances are 243.7 pm, is 60.9 kJ mol^{-1} less stable than **3a** (see Figure 2). This coordination changes the central S−S bond length to 217.3 pm, whereas the two terminal S−S bonds shrink to 204.7 pm (torsion angle of S-S-S-S: −102.3°).

Adducts of composition $[Me_2S_5Li]^+$ (4a–d): The structure of Me_2S_5 (**4**) has not been experimentally determined. The binding energies were calculated with the conformer having the (calculated) torsion angles $\tau_{CSSS} = \pm 82.7°$ and $\tau_{SSSS} = \pm 92.2°$ (motif: $-+-+$; C_s symmetry) because its conformation is closest to that of the most stable Li^+ adduct of Me_2S_5 (**4a**). It should, however, be mentioned that the isomer with the motif $-++-$ (C_2 symmetry) is lower in energy by 2 kJ mol^{-1}.

The cation of composition $[Me_2S_5Li]^+$ can exist as four isomers that differ considerably in their geometry (Figure 2). The global energy minimum (**4a**) has the lithium ion coordinated to three sulfur atoms (S1, S3, and S4) to form a six-membered LiS_5 heterocycle (or bicycle) of boat (or cradle) conformation. This cation has the highest binding energy (−188.6 kJ mol^{-1}) of all complexes studied in this work. In contrast, the less stable isomer **4b** has no symmetry at all and contains a five-membered LiS_4 heterocycle with one additional exocyclic sulfur atom to which one of the two methyl groups is attached. In this structure, the metal ion is also coordinated to three sulfur atoms (S5, S7, and S8). The energy difference between **4a** and **4b** is 36.6 kJ mol^{-1}. In both isomers, the 3p rotation axes of the lone pair orbitals of the coordinating sulfur atoms are pointing towards the Li atom.

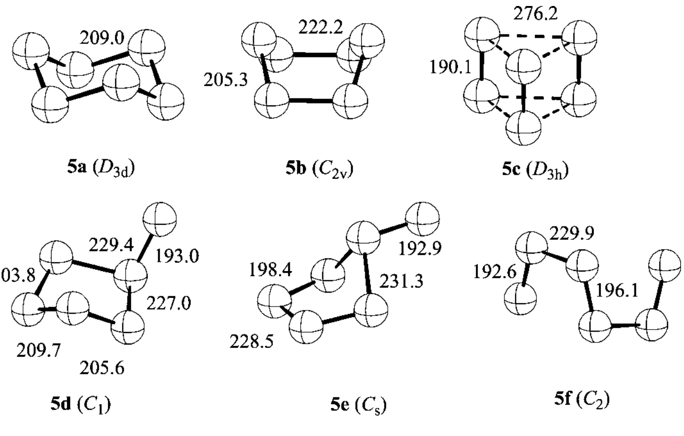
The C_s-symmetric structure of **4a** is characterized by Li−S bonds of length 243.3 (to S3 and S4) and 261.1 pm (to S1) and torsion angles S-S-S-S of +96.1° and −96.1°. The lengths of the four S−S bonds are 208.7 pm (terminal bonds) and 210.4 pm (central bonds). The two torsion angles Li-S3-S2-S1 and Li-S4-S5-S1 are ±22.5°. All these values are quite normal. The NBO atomic charges are as follows (data for Me_2S_5 in parentheses): Li +0.85, S1 −0.06 (+0.13), S2 +0.05 (−0.03), S3 +0.06 (−0.05), C −0.84 (−0.85), H + 0.26–0.29 (0.25–0.26). Evidently, the sulfur atoms coordinated to Li^+ gain electron density and, as a consequence, the polarities of the C−S and S−S bonds decrease upon coordination.

The geometry of the asymmetric ion **4b** is considerably different from that of the isomeric **4a** with one very long S−S bond of 222.8 pm, probably caused by the related S6-S7-S8-S9 torsion angle of 176.7° (Figure 2). The other three S−S bonds have "normal" bond lengths of between 203 and 210 pm, related to the normal values of the dihedral angles of −83.1° for C1-S5-S6-S7, −84.9° for S5-S6-S7-S8, and −86.2° for S7-S8-S9-C10. The Li-S5-S-S7 torsion angle is 25.9°. Owing to the low symmetry, the five possible Li···S distances are all different, ranging from 245.1 to 380.3 pm, but only three of these contacts can be considered to be chemical bonds.

The **4c** ion is even less stable, by 65.6 kJ mol^{-1} with respect to **4a**; it contains a lithium ion coordinated to the second and third atom of the sulfur chain of the Me_2S_5 ligand (Figure 2); however, details of its structure will not be discussed here. In a similar fashion, the **4d** isomer contains the Li^+ ion coordinated to the two terminal sulfur atoms of a helical Me_2S_5 ligand (Figure 2). The relative energy (68.5 kJ mol^{-1}) and the binding energy (−120.1 kJ mol^{-1}) of **4d** are similar to those of **4c**: the binding energies with respect to Me_2S_5 (**4**) decrease in the order **4a** > **4b** > **4c** > **4d** (Table 1).

Adducts of composition $[LiS_6]^+$: The coordination of a cation to *cyclo*-hexasulfur may change its structure or its conformation, as was observed in the protonation of S_6.[40] For this reason, the S_6 molecule had to be calculated in the various symmetries observed in the cationic lithium adducts reported below; these calculations have been published separately.[29]

Isomers of cyclo-S_6: Beside the experimentally observed chair conformation of D_{3d} symmetry (**5a**),[8] the S_6 ring can also exist as a boat-shaped molecule of C_{2v} symmetry (**5b**).[41,42] In addition, a prism-like structure of D_{3h} symmetry (**5c**) was recently found to be a novel isomer of fairly low relative energy on the S_6 potential energy hypersurface (PES).[29,43] Furthermore, S_6 can exist as two branched isomers with $S_5{=}S$ connectivity (**5d,e**).[29] The optimized structures and their bond lengths are shown in Figure 3.



5a (D_{3d}) **5b** (C_{2v}) **5c** (D_{3h})
5d (C_1) **5e** (C_s) **5f** (C_2)

Figure 3. Structures of six isomeric S_6 molecules (**5a–f**) corresponding to minima on the potential energy hypersurface (bond lengths in pm).[29]

Of the four mentioned S_6 isomers, the boat (**5b**) is less stable than the chair by 52.4 kJ mol^{-1}, the prism (**3**) by 50.8 kJ mol^{-1}, and the twisted branched ring structure (**5d**) by 89.4 kJ mol^{-1} (ΔE_o data). The second branched ring structure (**5e**) is less stable than **5a** by 104.0 kJ mol^{-1}.[29] For comparison, the activation energy for the homolytic ring opening of *cyclo*-S_6 (**5a**) is considerably higher, 148.8 kJ mol^{-1},[29] and the dissociation of *cyclo*-S_6 (**5a**) into two S_3 molecules of C_{2v} symmetry requires 185 kJ mol^{-1}[44] (all relative energies and reaction energies were calculated at the G3X(MP2) level of theory).

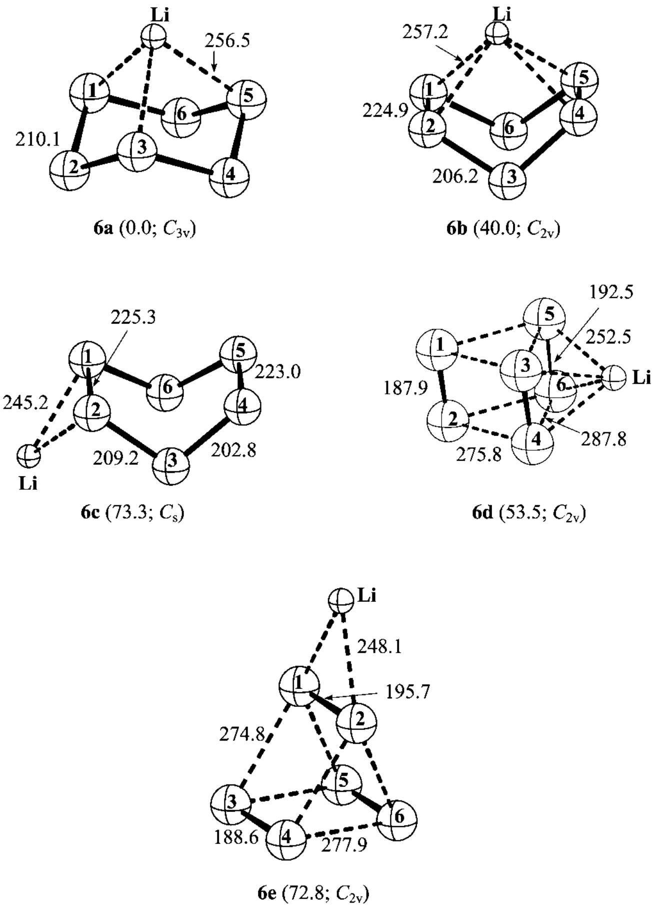
Whereas the bond lengths in the ground state of *cyclo*-S_6 are all the same (calculated 209 pm; experimental 206.8 pm[8]), the **5b** boat structure has two torsion angles of 0° and, as a consequence, two bonds are much longer (222.2 pm) than the other four (205.3 pm). The four nonzero torsion angles are ±73.4°. The prism structure is most interesting because it is practically a cluster of three parallel-oriented singlet S_2 molecules with S–S bond lengths of 190 pm (three times) and 276 pm (six times). For comparison, the triplet ground state of $S_2(^3\Sigma_g)$ is characterized by a bond of length of 188.9 pm, and 189.8 pm was determined spectroscopically for singlet $S_2(^1\Delta_g)$.[45] This prismatic S_6 structure of **5c** indicates that *cyclo*-hexasulfur may react as an S_2 donor at elevated temperatures. The activation energy for the transformation of **5a** into **5b** has been calculated to be 130.3 kJ mol^{-1}.[29] For the isomerizations **5a**→**5c** and **5a**→**5d**, the activation energies are slightly higher; however, **5c** and **5d** can be obtained from the boat structure **5b** in reactions with barriers smaller than 130 kJ mol^{-1}.[29]

Isomers of composition [LiS$_6$]$^+$: Fourteen isomeric structures have been located on the singlet PES of $[LiS_6]^+$ and one on the triplet PES. These ions contain the S_6 unit either in the normal chair-like conformation (**6a**), in the boat-like conformation (**6b**,**c**), in the prism-shaped conformation (**6d**,**e**), in the branched ring form (S_5=S, **6f–k**), or in the triplet-chain form (**6o**). These species and their relative energies are shown in Figures 4–6; their absolute energies are listed in Table 5 of the Supporting Information.

In addition, two $[LiS_6]^+$ isomers with two separate S_3 units as well as one isomer with an S_2 and an S_4 ligand attached to the lithium cation were located on the PES. These species (**6l–n**) will be discussed below.

The global minimum structure of $[LiS_6]^+$ (**6a**) contains a tridentate S_6 ring of chair conformation attached to the cation. The three Li–S bonds (255.6 pm) are slightly longer than in $[H_2SLi]^+$ (242 pm); however, the total binding energy of −134 kJ mol^{-1} (Table 1) with respect to the components Li^+ and S_6 (**5a**) is much larger than in the case of H_2S (−88 kJ mol^{-1}). Interestingly, the S–S bonds of **6a** are slightly longer (210.1 pm) than those calculated for S_6 (209 pm), whereas the torsion angles within the coordinated homocycle (72.9°) have hardly changed from those calculated for the free S_6 molecule **5a** (73.2°[29]). The bond angles at Li are 79.1°, and the SSS angles are either 101.7° or 104.7°, with the larger value at the three-coordinate atoms. The lithium cation induces a small negative charge (−0.05) on the three atoms it is coordinated to and a small positive charge (+0.09) on the other three sulfur atoms. Whereas no solid complexes with the S_6 ligand are known, the compounds $[Ag_2Se_6][AsF_6]_2$ and $[AgSe_6][Ag_2(SbF_6)_3]$, which contain the related Se_6 molecule coordinated to Ag^+ ions, have recently been prepared. The coordination geometry between the chair-like Se_6 ring and the metal ions is similar to that in **6a** (threefold symmetry axis), but the Se_6 ligand bridges two Ag^+ ions to form three Ag–Se bonds each to the metal atoms.[46]

The basket-shaped $[LiS_6]^+$ complex **6b** (Figure 4), derived from the boat conformation of S_6, is less stable than **6a** by 40.0 kJ mol^{-1}. The four identical Li–S bonds are 258 pm long and result in a binding energy of −146 kJ mol^{-1} with respect to the S_6 boat (**5b**); the reaction energy with regard to the chair-form of S_6 (**5a**) and Li^+ is −94 kJ mol^{-1}. The S–S bonds of **6b** (206.2 and 224.9 pm) are all slightly longer than in the related S_6 isomer, **5b**, but the S-S-S-S torsion angles have hardly changed on coordination to the lithium ion (0° and ±74.1°). For bond angles and further torsion angles, see Table 2. Whereas the four equivalent sulfur atoms attached to Li^+ are slightly negatively charged (−0.05), the other two are positively charged (+0.15). Thus, 0.11 electrons have been transferred from the S_6 ligand to the metal cation.



6a (0.0; C_{3v}) **6b** (40.0; C_{2v})

6c (73.3; C_s) **6d** (53.5; C_{2v})

6e (72.8; C_{2v})

Figure 4. Structures of five complex cations of composition $[LiS_6]^+$ (**6a–e**) derived from the unbranched ring and prism structures of S_6; bond lengths in pm (for bond angles and torsion angles, see Table 2). Relative energies (kJ mol^{-1}) and symmetries are given in parentheses.

Table 2. Calculated bond angles and torsion angles of the $[LiS_6]^+$ isomers **6b–d** and **6f–o** (B3LYP/6-311G(2df)-optimized geometries). For the numbering of sulfur atoms, see Figures 4–6.

Species	Bond angles (α) and torsion angles (τ) [°]
6b	$\alpha_{123} = 102.0$, $\alpha_{234} = 104.7$, $\alpha_{1\mathrm{Li}2} = 51.7$, $\alpha_{1\mathrm{Li}5} = 78.6$, $\alpha_{12\mathrm{Li}} = 64.2$, $\tau_{1234} = 74.1$
6c	$\alpha_{123} = 101.8$, $\alpha_{234} = 105.3$, $\alpha_{345} = 102.5$, $\alpha_{1\mathrm{Li}2} = 54.7$, $\tau_{1234} = 73.4$, $\tau_{4561} = 73.9$, $\tau_{3456} = 0.0$, $\tau_{561\mathrm{Li}} = -137.1$
6d	$\alpha_{3\mathrm{Li}4} = 44.8$, $\alpha_{3\mathrm{Li}5} = 69.5$, $\alpha_{3\mathrm{Li}6} = 86.6$, $\alpha_{213} = 89.5$, $\alpha_{153} = 58.5$
6f	$\alpha_{123} = 94.5$, $\alpha_{234} = 101.4$, $\alpha_{345} = 95.8$, $\alpha_{451} = 103.6$, $\alpha_{215} = 96.4$, $\alpha_{46\mathrm{Li}} = 86.8$, $\alpha_{3\mathrm{Li}5} = 63.1$, $\tau_{1234} = 62.3$, $\tau_{1546} = -123.2$, $\tau_{2345} = 70.1$, $\tau_{346\mathrm{Li}} = -66.6$, $\tau_{4512} = 45.1$
6g	$\alpha_{123} = 100.2$, $\alpha_{234} = 101.6$, $\alpha_{345} = 84.1$, $\alpha_{452} = 101.6$, $\alpha_{512} = 100.2$, $\alpha_{46\mathrm{Li}} = 102.0$, $\tau_{1234} = 43.0$, $\tau_{2345} = -64.7$, $\tau_{5123} = 0.0$, $\tau_{2346} = 46.2$, $\tau_{546\mathrm{Li}} = 45.9$
6h	$\alpha_{123} = 102.5$, $\alpha_{234} = 93.4$, $\alpha_{345} = 96.0$, $\alpha_{516} = 98.8$, $\alpha_{215} = 97.9$, $\alpha_{451} = 102.1$, $\alpha_{216} = 114.1$, $\alpha_{16\mathrm{Li}} = 100.8$, $\tau_{1234} = 55.8$, $\tau_{2345} = -67.3$, $\tau_{3451} = 52.2$, $\tau_{4516} = -133.8$, $\tau_{3216} = 79.6$, $\tau_{216\mathrm{Li}} = 121.6$
6i	$\alpha_{312} = 105.4$, $\alpha_{245} = 102.6$, $\alpha_{354} = 84.1$, $\alpha_{356} = 100.1$, $\alpha_{56\mathrm{Li}} = 80.4$, $\tau_{3124} = 0$, $\tau_{2456} = -155.5$, $\tau_{1245} = 39.3$, $\tau_{456\mathrm{Li}} = 42.9$
6j	$\alpha_{312} = 101.3$, $\alpha_{245} = 100.3$, $\alpha_{354} = 84.8$, $\alpha_{356} = 102.5$, $\alpha_{56\mathrm{Li}} = 101.4$, $\tau_{3124} = 0$, $\tau_{2456} = -165.8$, $\tau_{1245} = 42.7$, $\tau_{356\mathrm{Li}} = 136.3$
6k	$\alpha_{123} = 102.0$, $\alpha_{234} = 92.9$, $\tau_{1234} = -7.3$, $\tau_{1236} = 102.4$, $\tau_{632\mathrm{Li}} = 177.9$
6l	$\alpha_{123} = 114.9$, $\alpha_{1\mathrm{Li}3} = 78.6$, $\alpha_{34\mathrm{Li}} = 126.8$, $\tau_{123\mathrm{Li}} = 0$, $\tau_{23\mathrm{Li}4} = -128.1$
6m	$\alpha_{123} = 115.5$, $\alpha_{23\mathrm{Li}} = 102.2$, $\alpha_{3\mathrm{Li}4} = 179.4$, $\tau_{123\mathrm{Li}} = 180$, $\tau_{23\mathrm{Li}4} = 107.3$
6n	$\alpha_{1\mathrm{Li}2} = 45.0$, $\alpha_{12\mathrm{Li}} = 67.6$, $\alpha_{3\mathrm{Li}6} = 92.8$, $\alpha_{345} = 113.1$, $\tau_{3456} = 0$, $\tau_{\mathrm{Li}345} = 0$
6o	$\alpha_{1\mathrm{Li}4} = 99.3$, $\alpha_{34\mathrm{Li}} = 102.8$, $\alpha_{456} = 105.5$, $\tau_{1234} = 21.1$, $\tau_{3456} = 1.6$, $\tau_{\mathrm{Li}456} = 111.1$

In the $[LiS_6]^+$ isomer **6c** (Figure 4), the boat-like sulfur ring functions as a bidentate ligand to result in shorter Li–S bonds (245.2 pm), although the binding energy with respect to **5b** and Li^+ is only $-113\,kJ\,mol^{-1}$; the reaction energy starting from **5a** and Li^+ is $-23\,kJ\,mol^{-1}$. The two S_4 units of the ligand are essentially planar. The lithium ion occupies a position where the electron density of the HOMO of the two neigboring sulfur atoms is probably at its maximum. For bond and torsion angles, see Table 2. The NBO atomic charges are summarized in Table 3.

Table 3. Atomic charges of $S_5{=}S$ and of 14 adducts of composition $[LiS_6]^+$, calculated by the NBO method based on the B3LYP/6-311G(2df,p) wavefunction.

Species	Li	S1	S2	S3	S4	S5	S6
5d ($S_5{=}S$)	–	+0.04	+0.05	−0.06	+0.30	−0.07	−0.25
6a $[LiS_6]^+$ (C_{3v})	+0.88	−0.05	+0.09	−0.05	+0.09	−0.05	+0.09
6b $[LiS_6]^+$ (C_{2v})	+0.89	+0.15	−0.05	−0.05	−0.05	−0.05	+0.15
6c $[LiS_6]^+$ (C_s)	+0.95	+0.09	+0.06	−0.12	+0.06	−0.12	+0.09
6d $[LiS_6]^+$ (C_{2v})	+0.92	+0.14	+0.14	−0.06	−0.06	−0.06	−0.06
6e $[LiS_6]^+$ (C_{2v})	+0.95	−0.25	−0.25	+0.14	+0.14	+0.14	+0.14
6f $[S_5\text{-}SLi]^+$ (C_1)	+0.88	−0.00	+0.16	−0.09	+0.35	+0.07	−0.37
6g $[S_5\text{-}SLi]^+$ (C_s)	+0.89	+0.34	+0.12	−0.06	−0.06	−0.36	+0.12
6h $[S_5\text{-}SLi]^+$ (C_1)	+0.95	+0.10	+0.13	+0.04	+0.29	+0.04	−0.55
6i $[S_5\text{-}SLi]^+$ (C_s)	+0.89	+0.11	+0.11	−0.06	−0.06	+0.35	−0.33
6j $[S_5\text{-}SLi]^+$ (C_s)	+0.95	+0.07	+0.07	+0.09	+0.09	+0.27	−0.55
6k $[LiS_5{=}S]^+$ (C_1)	+0.92	+0.04	−0.04	+0.08	+0.44	−0.34	−0.10
6l $[Li(\eta^2\text{-}S_3)_2]^+$ (D_{2d})	+0.73	+0.42	−0.14	−0.14	+0.42	−0.14	−0.14
6m $[Li(\eta^1\text{-}S_3)_2]^+$ (C_2)	+0.85	−0.33	+0.05	+0.05	+0.36	−0.33	+0.36
6n $[Li(S_2)(S_4)]^+$ (C_{2v})	+0.79	−0.24	−0.24	+0.31	+0.04	+0.31	+0.04

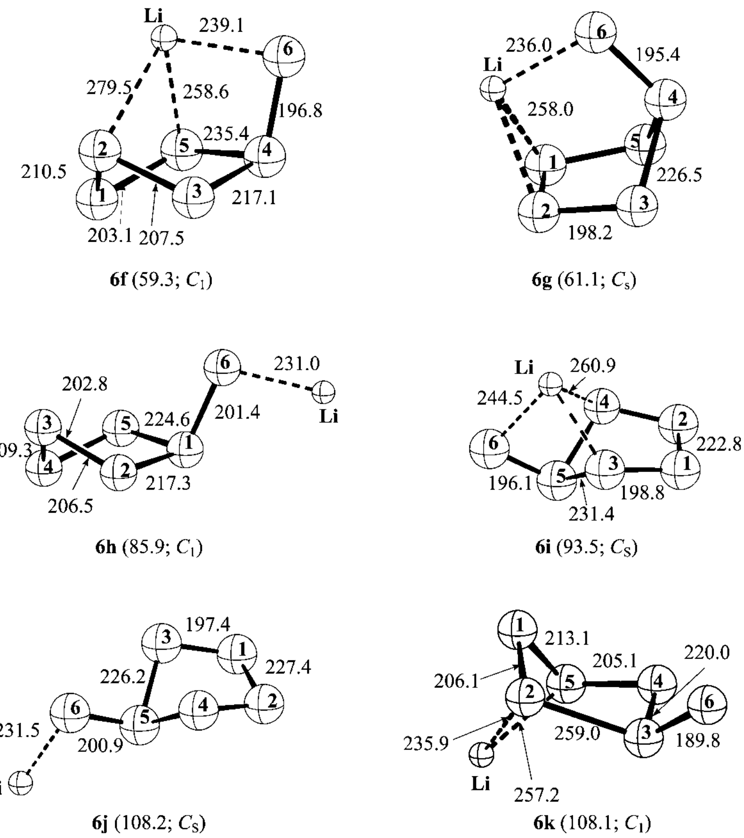
In the case of the prismatic S_6 isomer **5c** (Figure 3), we found two adducts with Li^+ (**6d** and **6e**). Whereas **6d** is a tetradentate coordinated complex, **6e** has a bidentate structure (Figure 4). In **6d**, the Li^+ ion causes the neighboring S–S bonds to increase in length. The shortest bond in this ion (187.9 pm) is therefore the prism edge on the opposite side from the Li^+ ion. The bond angles of **6d** are given in Table 2. The charge transfer to the Li^+ ion of 0.08 electrostatic units causes a positive charge of 0.14 units on atoms S1 and S2, whereas all other sulfur atoms are slightly negative.

As expected, **6d** is more stable than **6e** by $19.3\,kJ\,mol^{-1}$. The computed binding energy, with respect to **5c**, is $-131.2\,kJ\,mol^{-1}$ for **6d** and $-112.0\,kJ\,mol^{-1}$ for **6e**. Evidently, the structure with the maximum number of Li···S interactions is preferred.

The **6e** isomer also has C_{2v} symmetry (Figure 4) with two Li–S bonds of length 248.1 pm. The S_6 unit is very close to a perfect prism with all S-S-S angles within ±0.8° of either 60° or 90°, and S-S-S-S torsion angles inside the rectangles of 0°. The S-Li-S angle is 46.5°. The two sulfur atoms attached to the Li^+ ion bear a negative charge of −0.25, whereas the other four atoms are positively charged (+0.14). Thus, the Li^+ ion induces a dipole moment within the S_6 units of **6d** and **6e** that is directed towards the metal ion.

The addition of a Li^+ ion to the branched rings $S_5{=}S$ (**5d** and **5e** in Figure 3) gave six isomeric complexes. They differ in the position and the coordination number of the metal ion as well as in the equatorial or axial position of the exocyclic sulfur atom (Figure 5). In the first three cases (**6f–h**), the lithium atom is mainly bonded to the exocyclic atom, which is always in an axial position and which bears the highest negative atomic charge in the free ligand (Table 3). In the most stable *endo* isomer, **6f**, the Li^+ ion is also attached to one or maybe even two of the ring atoms (Li–S5 258.6, Li–S2 279.5 pm), and it may be these additional bonds that stabilize this isomer with respect to the *exo* structure **6h** (Li^+ coordination number = 1). The same holds for the structure of intermediate energy, **6g**, which is of C_s symmetry with one S-S-S-S torsion angle of 0°. The charge distribution in these $[S_5{-}SLi]^+$ isomers is quite different (Table 3); for further geometrical details, see Table 2.

There are also two $[S_5{-}SLi]^+$ isomers in which the exocyclic sulfur atom is in an equatorial position (**6i,j**) (Figure 5). These isomers have C_s symmetry with coordination numbers for the lithium atom of 3 (*endo* isomer) and 1 (*exo* isomer), respectively. The related but completely asymmetrical isomer of connectivity $[LiS_5{=}S]^+$ (**6k**) contains the metal ion exclusively attached to two ring atoms of the $S_5{=}S$ ligand (Figure 5). The Li–S1 distance is 268.7 pm; however, our topological analysis (see below) shows that there is no bonding interaction between these two atoms. The S_5 ring has an envelope conformation with four atoms almost in one plane (torsion angle −7.3°). Both the exocyclic sulfur atom and the lithium atom are in axial positions with regard to the average plane through the ring atoms, but *trans* to each other with a Li-S-S=S torsional angle of 177.9°. As expected, the three three-coordinate atoms of **6k** possess an approximately pyramidal coordination sphere. Interestingly, the charge transfer to the metal ion is 0.08 electrons and thus higher than in the case of **6h** (0.05) but smaller than in the related species **6f** (0.12) and **6g** (0.11) (Table 3). The exocyclic S–S bond of **6k** is about as short as that in the $^3S_2$ molecule. We denote this species as $[LiS_5{=}S]^+$; it is less stable than **6a** by 108.1 kJ mol^{-1}.



6f (59.3; C_1) **6g** (61.1; C_s)

6h (85.9; C_1) **6i** (93.5; C_S)

6j (108.2; C_S) **6k** (108.1; C_1)

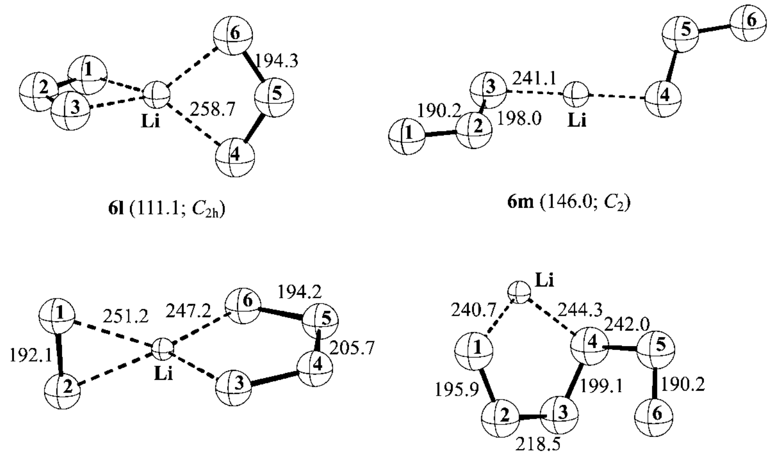
Figure 5. Structures of six complex cations of composition $[LiS_6]^+$ (**6f–k**) derived from the branched ring structures $S_5{=}S$; bond lengths in pm (for bond angles and torsion angles, see Table 2). Relative energies (kJ mol^{-1}) and symmetries are given in parentheses.

During the search for other isomers of composition $[LiS_6]^+$, we discovered several novel structures of connectivity $[Li(\eta^2\text{-}S_3)_2]^+$ (**6l**), $[Li(\eta^1\text{-}S_3)_2]^+$ (**6m**) and $[Li(\eta^2\text{-}S_2)(\eta^2\text{-}S_4)]^+$ (**6n**) as minima on the PES (Figure 6). However, these three ions are less stable than any of the previously discussed isomers, with relative energies of 111–169 kJ mol^{-1}, respectively, compared to the global minimum **6a**. The highly symmetric ion $[Li(\eta^2\text{-}S_3)_2]^+$ (**6l**) contains a four-coordinate lithium ion and two planar LiS_3 units perpendicular to each other. The Li–S bonds are considerably longer (258.7 pm) than in the more stable adducts of the same composition, whereas the S–S bonds are almost as short (194.3 pm) as in the free S_3 molecule (experimental: 193.3 pm[47]). The structure of **6l** is similar to the calculated structure of the planar ion $[CaS_3]^+$, which has been detected by mass spectrometry.[17]

The nonplanar cation $[Li(\eta^1\text{-}S_3)_2]^+$ is of C_2 symmetry with two co-linear Li–S bonds of 241.1 pm and S–S bonds of 198.0 and 190.2 pm, respectively. Each Li-S-S-S unit is of *trans*-planar geometry, similar to the related [H-S-S-S]$^+$ ion,[48] but the torsion angle between the two Li-S-S-S units is 148°. The Li$^+$ ion strongly polarizes the S_3 ligands resulting in NBO charges of −0.33 on the ligating atoms and +0.36 on the central sulfur atoms, whereas the terminal atoms are only slightly positively charged (+0.05). The remaining charge on the lithium atom is +0.85. The formation of **6m** from **5a** and Li$^+$ is exothermic by only −18 kJ mol^{-1}, but the binding energy is −203 kJ mol^{-1} with respect to 2 S_3 and Li$^+$!

The C_{2v}-symmetric ion $[Li(\eta^2\text{-}S_2)(\eta^2\text{-}S_4)]^+$ (**6n**) contains a four-coordinate lithium atom with an approximately tetrahedral coordination sphere. The two structural units, LiS_2 and LiS_4, are both planar and perpendicular to each other. This type of coordination is well-known from transition-metal polysulfido complexes, although planar five-membered rings are unusual.[1,2] The binding energy with respect to $^3S_2$ + S_4 is −141 kJ mol^{-1}.

Because S_6 can also exist as a triplet chain (**5f** in Figure 3),[29] we have investigated the possibility that this chain adds a chain-teminating Li$^+$ ion. This structure (**6o**) is in fact a local minimum on the PES. However, the geometry is cluster-like with a five-membered LiS_4 ring and an unusual exocyclic S_2 group (Figure 6). The conformation of the S_6 chain in **6o** is quite similar to the structure of the free ligand **5f** with a strong bond length alternation along the chain. The binding energy of **6o** with respect to Li$^+$ and **5f**



6l (111.1; C_{2h})

6m (146.0; C_2)

6n (168.5; C_{2v})

6o (126.4; C_1)

Figure 6. Structures of the complex cations $[Li(\eta^1\text{-}S_3)_2]^+$ (**6l**), $[Li(\eta^2\text{-}S_3)_2]^+$ (**6m**) and $[Li(S_2)(S_4)]^+$(**6n**) and of the triplet cluster $[LiS_6]^+$ (**6o**); bond lengths in pm (for bond angles and torsion angles, see Table 2). Relative energies ($kJ\,mol^{-1}$) and symmetries are given in parentheses.

is $-124\ kJ\,mol^{-1}$. The relative energy of this triplet cation of $126.4\ kJ\,mol^{-1}$ with respect to isomer **6a** is slightly larger than the relative energy of **5f** with respect to **5a** ($116.8\ kJ\,mol^{-1}$).[29] In other words, the ring opening reaction energy of S_6 does not change much after coordination of an Li^+ ion. As with the neutral diradical **5f**, the spin densities of **6o** are highest on the two terminal S_2 units (i.e., on S1, S2, S5 and S6).

General properties of the novel complexes

Geometries: In all the stable complexes (labelled with "**a**") studied in this work, the ligands exhibit practically the same conformation as in the free molecules. The S–S bonds of the Me_2S_n ligands vary in length between 203.2 and 222.8 pm, whereas the Li–S bond lengths are calculated to be in the range 238.1–250.3 pm. In all cases, the coordination of a Li^+ ion causes the neighboring S–S bonds to increase in length. This is in accordance with the observation that the increase in coordination number at the sulfur atoms from 2 to 3 results in somewhat longer bonds.[3] For instance, the S–S bond in the $[Me_2S\text{-}SMe]^+$ ion is longer than in Me_2S_2 by 8 pm.[49]

Surprisingly, the Li^+ ion is not usually located on the vector of the dipole moment of the particular molecule but prefers to be in one plane with the 3p lone pairs of the sulfur atoms it is coordinated to. It seems that the Li^+ ion is attracted by the local electron density maxima of the 3p lone pairs of the sulfur atoms,[22] in addition to the ion–dipole attraction (which would favor a *planar* $[H_2SLi]^+$ ion).

We did not investigate the coordination of a Li^+ ion to the thiosulfoxide isomers of the dimethyl polysulfanes, which are known to be local minima on the PES.[28,50]

In the case of S_6, the coordination to a Li^+ ion results in a more or less strong bond length alternation, and S–S bond lengths of between 189.8 and 259.0 pm have been obtained. The Li–S bond lengths lie in the range 231–280 pm (longer distances are considered to be nonbonding). The lower coordination number of the Li^+ ion is usually associated with a shorter Li–S bond.

Atomic charges: In the 29 complexes studied in this work, the transfer of electron density from the ligands to the lithium ion varies between 0.04 and 0.27 electrons (Table 3). For comparable cations, the higher the coordination number, the larger the charge transfer. The calculated order of charge transfer is: $[H_2SLi]^+$ < $[Me_2S_2Li]^+$ (**1a**,**b**) $\cong$ $[LiS_6]^+$ (**6c**, C_s) $\cong$ $[LiS_6]^+$ (**6e**, C_{2v}) $\cong$ $[S_5\text{–}SLi]^+$ (**6h**,**j**) < $[Me_2S_nLi]^+$ (**2b**, **3c**, **4c**, **4d**) < $[S_5\text{=}SLi]^+$ (**6i**) < $[Me_2S_3Li]^+$ (**2a**) < $[Me_2S_4Li]^+$ (**3a**,**b**) < $[LiS_6]^+$ (**6b**, C_{2v}) $\cong$ $[S_5\text{–}SLi]^+$ (**6g**,**k**) < $[Me_2S_5Li]^+$ (**4b**) $\cong$ $[S_5\text{–}SLi]^+$ (**6f**) $\cong$ $[LiS_6]^+$ (**6a**) < $[Me_2S_5Li]^+$ (**4a**) $\cong$ $[Li(\eta^1\text{-}S_3)_2]^+$ (**6m**) $\leqslant$ $[Li(S_2)(S_4)]^+$ (**6n**) < $[Li(\eta^2\text{-}S_3)_2]^+$ (**6l**). Evidently, the global minimum structures experience the largest charge transfer if one excludes the high-energy hexasulfur adducts **6l**–**n**. The main effect of the lithium cation on the ligands is to induce a (higher) dipole moment by polarizing the electron clouds in the neighboring bonds. The attraction is then mainly caused by the well-known ion–dipole interaction. Our argument is supported by a point-charge calculation that readily reproduces the D_{2d} geometry of $[Li(\eta^2\text{-}S_3)_2]^+$ (**6l**).

Topological analysis: To further characterize the $Li^+\cdots S$ interaction in these cationic complexes, we examined the topological properties of the electron density, based on Bader's theory of atoms in molecules (AIM).[33] Except for **6k**, all Li–S bonds less than 280 pm are characterized by a maximum electron density path and its associated bond critical point (bcp). In **6k**, the Li^+ ion is mainly coordinated to S2 and S5. Although S1 is in close contact with the Li^+ ion (268.7 pm), our calculation reveals that there is no significant bonding interaction between the two atoms.

The calculated electron density (ρ_b), Laplacian ($\nabla^2\rho_b$) and ellipticity (ε) values at the bcp, based on the B3LYP/6-31G(2df,p) wavefunction, are summarized in Table 6 in the Supporting Information. In all cases, the calculated Laplacian of the electron density ($\nabla^2\rho_b$) is positive, indicating the closed-shell nature of the interaction. The electron density values, ρ_b, are relatively small, ranging from 0.013–0.028. However, there is a strong correlation between the ρ_b values and the Li–S bond lengths. In other words, the ρ_b value may be used as a measure of the bond strength of the $Li^+\cdots S$ interaction. Our finding is consistent with the topological study of the complexes between ethers and Li^+ ions.[51] Significant ellipticity values (ε) were calculated for most of the

Li–S bonds examined here. These values reflect the orientation of the 3p lone pair orbital of sulfur towards the Li^+ ion. A large value indicates that the Li^+ ion and the axis of the sulfur lone pair orbital are essentially in the same plane.

Thermodynamics: The absolute and relative energies of the 29 cations and their components are given in Table 5 in the Supporting Information. The binding energies (Table 1) range from $-88\,kJ\,mol^{-1}$ for the $[H_2SLi]^+$ ion to $-189\,kJ\,mol^{-1}$ for the most stable isomer of the $[Me_2S_5Li]^+$ ion (**4a**). Of the various possible S_6 ligands, the two S_5=S complexes **6f** and **6g** have the highest binding energies, namely −164 and $-162\,kJ\,mol^{-1}$, respectively, whereas the global minimum structure **6a** is predicted to have a binding energy of only $-134\,kJ\,mol^{-1}$. Compared with the high binding energies of protons to the various S_6 isomers (735–836 $kJ\,mol^{-1}$[40]), the corresponding interaction of the Li^+ ion is much weaker.

Since the calculated binding energies between a Li^+ ion and S_6 are always larger than or close to the homolytic dissociation enthalpy of *cyclo*-S_6 (116.8 $kJ\,mol^{-1}$[29]), it can be expected that the structure of any $[LiS_6]^+$ complex formed in a real gas-phase experiment from *cyclo*-S_6 will correspond to that of the global minimum. The fact that **6a**, which contains the *cyclo*-S_6 ligand, is much more stable than the **6m–o** complexes, which contain S_2, S_3 and S_4 ligands, indicates that any alkali metal cation will react with the homocycle S_6 (and probably also with S_8) to complexes of the type **6a**.

The various isomers of the $[LiS_6]^+$ ion show that the isomers which contain the highest number of S–S bonds are most stable. The second factor influencing the stability is the coordination number (CN) of the lithium cation: a higher CN is associated with a greater stability. This is in sharp contrast to the interaction of protons with related sulfur-rich molecules in which case covalent bonds with mono-coordinate hydrogen are always formed with a transfer of ≈ 0.8 electrons to the proton.[34,40]

The coordination to the Li^+ ion stabilizes certain unstable S_6 isomers (see Table 5 in the Supporting Information). For example, the boat form of S_6 (**5b**) has a relative energy of 52.4 $kJ\,mol^{-1}$ compared to the chair form **5a**. The lithiated boat form (**6b**) is only 40.0 $kJ\,mol^{-1}$ less stable than **6a**. The same reduced relative energies have been calculated for the lithiated branched rings (**6f,g**) which are less stable than **6a** by 59.3–85.9 $kJ\,mol^{-1}$, whereas the axially branched ring S_5=S (**5d**) has a relative energy of 89.4 $kJ\,mol^{-1}$. Thus, the coordination of Li^+ (and other cations) may enhance the reactivity of S_6 (and other sulfur rings) because of the liberated binding energy, but also owing to favourable changes in the potential energy hypersurface.

Lithium cation basicities: The gas-phase lithium cation basicity (LCB) of a base (B) is defined as the negative Gibbs energy associated with the equilibrium reaction (2).[52]

$$Li^+ + B = [Li{-}B]^+ \qquad (2)$$

This definition is comparable to the definition of the gas-phase (proton) basicity of a molecule. LCB values for more than 200 small bases have been calculated and determined; however, there are only a few data of sulfur compounds in the literature.[51] Alkyl thiols and dialkyl sulfides have LCB values in the range 84–130 $kJ\,mol^{-1}$; the LCB of a thiol, RSH, is always lower than that of the related sulfide, R_2S. The only disulfide investigated seems to be $(CF_3)_2S_2$ with LCB = 80 $kJ\,mol^{-1}$,[51] and data on more sulfur-rich molecules, as investigated in this work, are missing.

To check the reliability of our calculation method, we have first examined the well-known lithium cation affinities of H_2O and Me_2O at the G3X(MP2) level. Our computed values of 137 and 157 $kJ\,mol^{-1}$ are in very good agreement with the experimental estimates[53] (137 ± 14 and 167 ± 10 $kJ\,mol^{-1}$, respectively). This lends strong confidence to our predicted lithium ion affinities and basicities of the various sulfur-rich compounds examined in this paper. The corresponding data for the most stable isomers **1a–4a** and **6a** are listed in Table 4. They range from 103.6 $kJ\,mol^{-1}$ for $[S_6Li]^+$ via 112.6 $kJ\,mol^{-1}$ for $[Me_2S_2Li]^+$ to 155.7 $kJ\,mol^{-1}$ for $[Me_2S_5Li]^+$. In other words, the dimethyl polysulfane molecules are increasingly stronger ligands as the sulfur content increases, whereas chair-like S_6 with its zero dipole moment is a considerably weaker base and ligand.

Table 4. Reaction enthalpies and Gibbs energies for the addition of Li^+ ions to the gaseous ligands Me_2S_n (n = 2–5) and hexasulfur, S_6, to generate the complex cations **1a–4a** and **6a** [G3X(MP2) level]. The lithium cation basicities (LCB) of the ligands are defined as the negative Gibbs energies of Reaction (2).

Species	ΔH°_{298} [kJ mol^{-1}]	ΔG°_{298} [kJ mol^{-1}]
$[Me_2S_2Li]^+$ (**1a**)	−140.9	−112.6
$[Me_2S_3Li]^+$ (**2a**)	−149.4	−117.8
$[Me_2S_4Li]^+$ (**3a**)	−176.0	−144.2
$[Me_2S_5Li]^+$ (**4a**)	−189.1	−155.7
$[LiS_6]^+$ (**6a**)	−135.9	−103.6

Harmonic vibrations: To facilitate the experimental discovery of the complexes studied in this work, the vibrational wavenumbers below 600 cm^{-1} (unscaled) and the corresponding IR intensities of the most stable species **1a**, **2a**, **3a**, **4a**, and **6a** are given in Table 7 in the Supporting Information. In the case of S_6, the irreducible representation (Γ) changes from $2A_{1g} + A_{1u} + A_{2u} + 2E_g + 2E_u$ for D_{3h} symmetry to $3A_1 + A_2 + 4E$ for C_{3v} symmetry. The three additional vibrational degrees of freedom introduced by the Li atom of **6a** result in two vibrations at 291 cm^{-1} (E) and 240 cm^{-1} (A_1).

Conclusion

Neutral molecules containing two-coordinate sulfur atoms, such as dimethyl sulfanes Me_2S_n (n = 1–5) and the homocycle S_6, form stable complexes with lithium cations with binding energies ranging from −125 to −189 kJ mol^{-1}. In cases where several equivalent or nearly equivalent sulfur atoms are available the cation prefers to coordinate to more than one atom forming LiS_n heterocycles or clusters with Li–S bond lengths in the range 231–280 pm. In these cases, the stability generally increases with the coordination number of the Li^+ ion, which reaches a maximum value of 4. Relatively unstable isomers of the usually chair-like S_6 molecule (boat, prism, branched ring conformation) are stabilized by coordination to Li^+. Branched rings with an exocyclic negatively charged atom (S_5=S) preferentially form complexes of the type $[S_5\text{-}S\text{-}Li]^+$; however, in most of these species there are additional Li–S interactions. The charge transfer from the ligand to the cation increases with the coordination number of the latter, but remains as small as 0.05–0.12 electrons. However, $[LiS_6]^+$ complexes with the neutral ligands S_2, S_3 and S_4 and tetrahedrally coordinated lithium atoms exhibit a much stronger charge transfer (0.21–0.27 e) and much higher absolute binding energies. The ligand–cation interaction is explained in terms of ion–dipole attraction with the dipole moments generated or increased by the polarizing force of the cation. Lithium cation basicities for the global minimum structures have also been calculated (range 103.6–155.7 kJ mol^{-1}).

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