Coordination of Li^+, Ca^+, V^+, and Cu^+ to the Molecules S_8 and S_4 – A Computational Study

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The complex formation between the Li^+ cation and the sulfur homocycle S_8 has been studied by ab initio MO calculations at the G3X(MP2) level of theory. Starting with various isomers of S_8, the formation of LiS_8 heterocycles and clusters is preferred over complexes with a monodentate ligand. The binding energies of the cation in the 23 complexes investigated range from –95 to –217 kJ·mol^{-1}. The global minimum structure of $[LiS_8]^+$ is of C_{4v} symmetry with the S_8 homocycle in the well-known crown conformation and four Li–S bonds of length 254.2 pm (binding energy: –156.5 kJ·mol^{-1}). The S–S bonds of the various ligands are slightly weakened by the complex formation and a more or less strong bond length alternation is induced. Relatively unstable isomers of S_8 (chair, tub, *exo–endo* ring, branched rings, triplet chain) are partly stabilized and partly destabilized by complex formation with Li^+. The interaction between the cation and the S_8 ligands is mainly due to ion–dipole attraction with little to moderate charge transfer (0.04–0.27 electrostatic units). In the four most stable isomers of $[LiS_8]^+$, the number of sulfur–sulfur bonds is at a maximum and the coordination number of Li^+ is either 4 or 3. Complexes of the type $[Li(S_4)_2]^+$ are much less stable than isomers with an eight-atomic ligand. The Li–S bond lengths in all of these complex cations (230–273 pm) depend on the coordination number of Li and on the atomic charge of the donating sulfur atom(s). In contrast to $[LiS_8]^+$, the complexes of composition $[MS_8]^+$ with M = Ca, V, and Cu are more stable as $[M(S_4)_2]^+$ than with an eight-atomic crown-shaped ligand.

Introduction

There are numerous metal complexes with *anionic* sulfur-containing ligands such as sulfide (S^{2-}), thiolate (RS^-), or polysulfide anions (S_n^{2-}).[1] These species are of tremendous importance in inorganic and biological chemistry, in geology and mineralogy as well as in industrial chemistry. However, the interaction of metal cations with *neutral* sulfur molecules S_n has not been studied systematically. This unsatisfactory situation is probably due to the fact that the interaction of neutral molecules with metal cations is comparably weak. Consequently, only a few solid coordination compounds are known in which sulfur molecules S_n function as neutral ligands. Examples include several silver salts with the cations $[AgS_8]^+$ and $[Ag(S_8)_2]^+$, respectively, and weakly coordinating anions,[2,3] the rhenium complexes $[Re_2X_2(CO)_6(S_8)]$ (X = Br, I)[4] and the rhodium compounds $[Rh_2(O_2CCF_3)_4]_n(S_8)_m$ with n/m = 1:1 and 3:2.[5] 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 bi-, tri-, or tetradentate ligands 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 orthorhombic S_8 (205 pm[6]). 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 as between –208 and –247 kJ·mol^{-1}.[3] Related solid complexes with other sulfur ring sizes have not been reported.

However, a large number of complexes of univalent metal cations with various sulfur ligands, $[MS_n]^+$ with n = 1–21, have been generated in the gas phase and detected by ion cyclotron resonance (ICR) mass spectrometry. The metals include Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Cu and many rare-earth elements.[7–10] The structures and relative energies of these complexes are only partially known from preliminary reports on density functional calculations of calcium-, scandium-, vanadium-, and copper-containing polysulfur cations.[9,10] 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 bi-, tri-, and tetradentate manner. Complexes of compositions $[Ca(S_3)]^+$, $[Ca(S_8)]^+$, $[Ca(S_3)(S_8)]^+$, and $[Ca(S_3)_3]^+$ have been found to be local energy minima on the potential energy surfaces (PES). The

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most stable cationic complexes of Sc, V, and Mn with between four and eight sulfur atoms have been predicted to contain the sulfur exclusively in the form of S_2 ligands; for the vanadium complexes a singlet ground state has been assumed. In the case of copper, the ion of composition $[Cu(S_{12})]^+$ was predicted to be most stable as a 12-membered sulfur ring with the metal ion at the center.

To elucidate the possible structures of complexes between a univalent cation and a sulfur homocycle, we have previously studied the various isomers of composition $[LiS_6]^+$.[11] In this work we have investigated theoretically the interaction of the sulfur homocycle S_8 with gaseous Li^+ which serves as a simple model ion to allow calculations at a high level of theory. Besides S_6,[11] only the coordination of gaseous S_3 to Li^+ has been investigated previously by quantum-chemical calculations: $[LiS_3]^+$ is of C_{2v} symmetry.[12] In the case of $[LiS_6]^+$, 15 isomeric structures have been identified on the potential energy hypersurface (PES). The most stable structure is of C_{3v} symmetry and contains a chair-like S_6 ligand of similar geometry as that of solid S_6. The metal ion is linked to three equivalent sulfur atoms resulting in a binding energy of –134 kJ·mol^{-1}.[11] We define here the (adiabatic) binding energy as the energy difference between the complex and the sum of the energies of the two separated components in the same (or closest) conformation as found in the complex.

In the present work, we investigate the interaction of Li^+ with various isomers of S_8 to find out whether an activation of these molecules takes place. We did not intend to scan the total PES of this system. Instead, using existing knowledge of the various isomers of $[LiS_6]^{+[11]}$ we investigated mainly the coordination of Li^+ to the previously studied isomeric cyclic forms of S_8 and to only one of the eight-atomic chains. In agreement with our earlier results (topological analysis),[11] all Li–S distances above 280 pm will be treated as nonbonding. In addition to the Li^+ complexes, we report on preliminary calculations of univalent cations of composition $[MS_8]^+$ with M = Ca, V, and Cu.

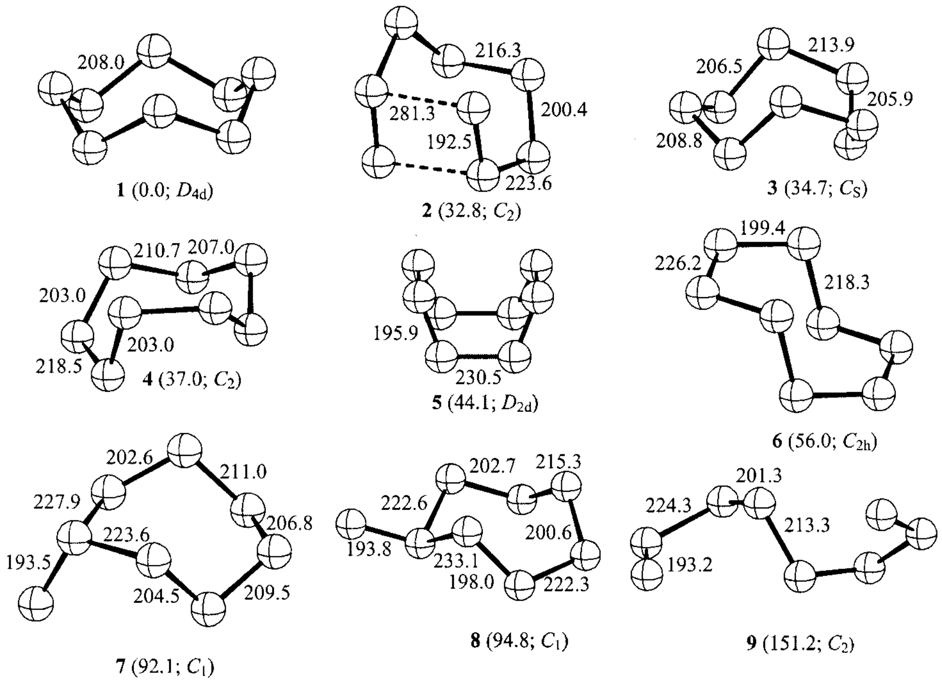
Results and Discussion

Structures and Energies

There are at least nine isomeric structures on the PES of the S_8 molecule.[13] The five stable eight-membered rings are of D_{4d} (**1**), C_s (**3**), C_2 (**4**), D_{2d} (**5**), and C_{2h} (**6**) symmetry (Figure 1). The crown-shaped structure (**1**) is the global energy minimum, while a spiral cluster with C_2 symmetry (**2**) is the next most stable structure. The two branched rings of the type S_7=S (**7** and **8**) are of C_1 symmetry and are much less stable. The least stable is the triplet open chain of C_2 symmetry (**9**). These isomers and their relative energies are shown in Figure 1.

Using the various S_8 isomers as ligands, we have located 20 isomeric structures on the PES of $[LiS_8]^+$ with coordination numbers (CN) of the metal atom of between 1 and 4. In addition, three cations with two S_4 ligands each were found to be minima on this PES. The absolute energies are given in Table S1 in the Supporting Information. The symmetries, relative energies, binding energies and dipole moments of all investigated Li^+ complexes are listed in Table 1. In the following discussion these various isomers will be discussed approximately in the order of increasing relative energy.

The global minimum structure of $[LiS_8]^+$ (**8a**) is of C_{4v} symmetry with a crown-shaped S_8 ligand and four Li–S



1 (0.0; D_{4d})
2 (32.8; C_2)
3 (34.7; C_S)
4 (37.0; C_2)
5 (44.1; D_{2d})
6 (56.0; C_{2h})
7 (92.1; C_1)
8 (94.8; C_1)
9 (151.2; C_2)

Figure 1. Various cyclic and chain-like isomers of the S_8 molecule with relative energies (kJ·mol^{-1}) and symmetries (according to ref.[13]).

Table 1. Symmetries, relative energies (ΔE_o) and binding energies ($kJ\cdot mol^{-1}$) as well as dipole moments (Debye) of 22 isomers of composition $[LiS_8]^+$, calculated by the G3X(MP2) method (CN is the coordination number of the lithium atom).

Species	Symmetry	CN(Li)	Relative energy ΔE_o	Binding energy[a]	Dipole moment[b]
$[LiS_8]^+$ (**8a**)	C_{4v}	4	0.0	–156.5 (**1**)	3.15
$[LiS_8]^+$ (**8b**)	C_1	2+2	34.4	–141.2 (**4**)	3.64
$[S_7SLi]^+$ (**8c**)	C_1	1+2	37.5	–151.8 (**2**)	3.43
$[LiS_8]^+$ (**8d**)	C_s	3	50.0	–141.2 (**3**)	4.41
$[LiS_8]^+$ (**8e**)	C_2	2	57.4	–99.2 (**1**)	12.25
$[LiS_8]^+$ (**8f**)	C_{2v}	4	60.4	–140.2 (**5**)	3.86
$[LiS_8]^+$ (**8g**)	C_s	4	60.5	–152.1 (**6**)	3.68
$[LiS_8]^+$ (**8h**)	C_s	1	61.6	–94.9 (**1**)	14.04
$[S_7\text{–Sli}]^+$ (**8i**)	C_1	1+2	65.6	–182.9 (**7**)	2.93
$[LiS_8]^+$ (**8j**)	C_1	2	71.3	–104.2 (**7**)	10.27
$[S_7\text{–Sli}]^+$ (**8k**)	C_1	1+1	72.3	–176.3 (**4**)	7.05
$[LiS_8]^+$ (**8l**)	C_1	2	84.3	–116.2 (**5**)	11.26
$[LiS_8]^+$ (**8m**)	C_s	2	91.9	–120.7 (**6**)	9.77
$[S_7\text{–Sli}]^+$ (**8n**)	C_s	1+2	93.4	–155.2 (**7**)	3.69
$[LiS_8]^+$ (**8o**)	C_1	2	104.4	–108.2 (**6**)	11.77
$[S_7\text{–Sli}]^+$ (**8p**)	C_s	1	116.4	–132.2 (**7**)	13.68
$[LiS_7 = S]^+$ (**8q**)	C_1	2+1	121.9	–126.6 (**7**)	5.16
$[LiS_7 = S]^+$ (**8r**)	C_s	2	129.0	–119.6 (**7**)	8.95
$[Li(\eta^2\text{-}S_4)_2]^+$ (**8s**)	D_{2d}	4	132.9	–216.7	0.0
$[LiS_8]^+$ (**8t**)	C_2	2+2	142.5	–165.3	1.05
$[Li(\eta^1\text{-}S_4)_2]^+$ (**8u**)	C_2	2	146.0	–203.6	0.63
$[Li(\eta^2\text{-}S_4)(\eta^1\text{-}S_4)]^+$ (**8v**)	C_1	3	178.9	–212.0	3.12

[a] The numbers in parentheses indicate the S_8 isomer (Figure 1), which has been used to calculate the binding energy. [b] B3LYP/6-31G(2df,p) values.

bonds of length 263.1 pm (Figure 2). The metal atom is located on the upper lobes of the lone-pair orbitals of the four ring atoms no. 1, 3, 5, and 7. These orbitals form the HOMO of the S_8 molecule. In this way, the HOMO(S_8)–LUMO(cation) interaction is maximized, resulting in a binding energy of $-156.5\ kJ\cdot mol^{-1}$. The calculated S–S bond length of 209.1 pm is slightly larger than that calculated for the free S_8 molecule (208.0 pm), indicating a certain degree of activation. Bond angles and torsion angles of the Li^+ complexes are presented in Table 2.

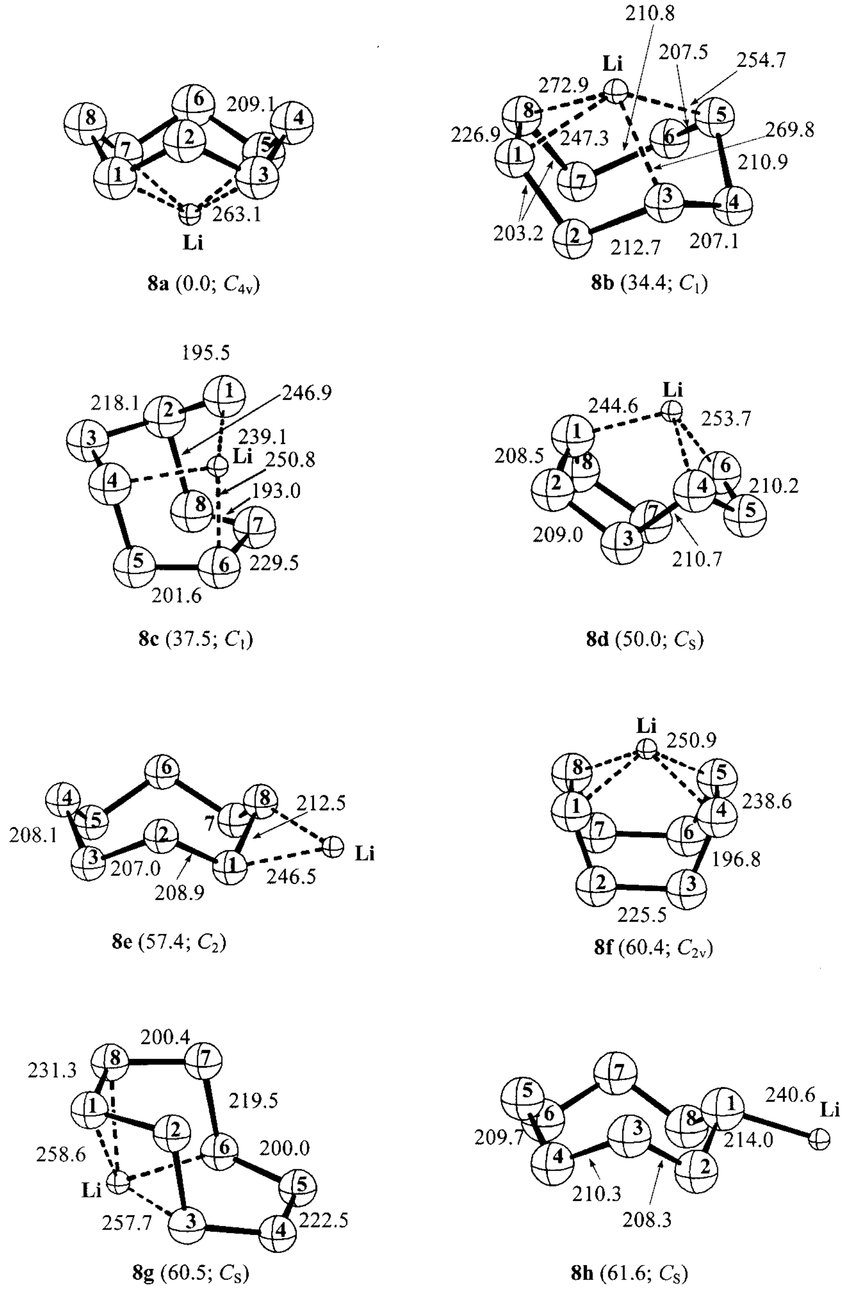
The calculated structure of isomer **8a** is in agreement with the experimentally determined structure of the cation $[AgS_8]^+$, which is also of C_{4v} symmetry in solid $[AgS_8]$-[Al(hfip)] (hfip = hexafluoroisopropanolate)[3], and with the theoretically predicted structure of $[Ca(S_3)(S_8)]^+$.[10] On the other hand, the cation $[VS_8]^+$ has been predicted by density functional calculations to prefer the connectivity $[V(S_2)_4]^+$ (assuming a singlet electronic state) while a structure analogous to **8a** was not considered.[9] Below we show that the latter results are probably incorrect.

A structure with the Li^+ ion at the geometrical center of the S_8 ring is a first-order saddle point of D_{4d} symmetry (**TS1**) which connects two equivalent structures of the global minimum **8a** with a barrier height of $72.5\ kJ\cdot mol^{-1}$ (Figure 2). Via this transition state the Li^+ ion is able to oscillate back and forth through the center of the S_8 ligand. In **TS1**, Li^+ has the coordination number 8 with Li–S distances of 247.9 pm. A structure analogous to **TS1** with CN(V) = 8 was predicted as a high-energy minimum on the singlet PES of $[VS_8]^+$,[9] but we were unable to reproduce this result (see below).

The first equilibrium structure (**8b**) above the global minimum consists of an asymmetric twisted ring with the Li cation coordinated to four sulfur atoms with distances of between 247.3 and 272.9 pm (Figure 2). To a first approximation, this structure of relative energy $34.4\ kJ\cdot mol^{-1}$, derived from the twist-form of S_8 (**4**), can be considered as a distortion of structure **8a**. The S–S bond lengths vary between 203.2 and 226.9 pm; the longest bond is characterized by an unusually small SSSS torsion angle of 6.3°. The overall motif of the homocycle (the order of signs of the torsion angles) is –+–++–++. The coordination pattern of the metal atom is pyramidal and the sum of the four neighboring SLiS angles is 303.3° (360° would result in a planar coordination sphere).

The second structure above the global minimum of $[LiS_8]^+$ is a complex containing the cluster-like S_8 ligand **2** (see Figure 1) with the Li atom coordinated to three sulfur atoms (isomer **8c** in Figure 2). The ligand has the same conformation as the related molecule $S_7{=}O$ which has been studied by X-ray crystallography of single crystals.[14] The Li–S distances below 280 pm are 239.1, 250.8 and 260.8 pm. There are two S–S–S–S torsion angles close to zero (–2.6° at atoms 5678 and 7.4° at atoms 1287) while S–S bonds usually prefer a torsion angle close to 90°.[15] As a consequence, the S–S bond lengths vary between 193.0 and 246.9 pm. Structure **8c** is less stable than **8a** by only $37.5\ kJ\cdot mol^{-1}$, while the cluster-like S_8 isomer **2** is less stable than the crown **1** by only $32.8\ kJ\cdot mol^{-1}$. The binding energy with respect to **2** is $-151.8\ kJ\cdot mol^{-1}$. For the bond angles of **8c**, see Table 2.

The $[LiS_8]^+$ structure **8d** contains the eight-membered sulfur ring in an *exo–endo* conformation resulting in CN = 3 for the metal atom (Figure 2). This ion is of C_s symmetry and less stable than **8a** by $50.0\ kJ\cdot mol^{-1}$. In this case, the metal atom is approximately located on the upper lobes of



8a (0.0; C_{4v}) **8b** (34.4; C_1)

8c (37.5; C_1) **8d** (50.0; C_S)

8e (57.4; C_2) **8f** (60.4; C_{2v})

8g (60.5; C_S) **8h** (61.6; C_S)

Figure 2. Structures of the eight lowest-energy isomers (**8a**–**h**) of composition $[LiS_8]^+$ (relative energies in kJ·mol^{-1} and symmetries are given in parentheses). Bond lengths in pm.

the lone-pair orbitals of the three ring atoms 1, 4, and 6. The three shortest Li–S distances are 244.6 pm (1) and 253.7 pm (2). As a consequence of the asymmetric coordination, the S–S bonds are no longer equivalent but their lengths range from 208.5 to 210.7 pm. This range is narrower than in the free ligand of identical conformation containing S–S bonds of between 205.9 and 213.9 pm. The free *exo–endo* shaped ligand is less stable than the crown structure by 34.7 kJ·mol^{-1}.[13] In other words, the coordination to Li$^+$ destabilizes the *exo–endo* form by 15.3 kJ·mol^{-1} because only three Li–S bonds are formed compared to four in **8a**. The binding energy of **8d** is –141.2 kJ·mol^{-1}.

The $[LiS_8]^+$ isomer **8e** consists of a crown-shaped S_8 ring with the Li cation located on one of the C_2 axes of the ring and bridging just one S–S bond, which becomes the longest bond in the ligand (212.5 pm). Because of the lower coordination number of 2, the binding energy of –99.2 kJ·mol^{-1} is significantly smaller (by 37%) than in the case of **8a** with CN = 4.

There are two $[LiS_8]^+$ isomers formally derived from the tub- or boat-like S_8 isomer **5** shown in Figure 1. Structure **8f** is of C_{2v} symmetry with CN(Li) = 4 and Li–S distances of 250.9 pm (Figure 2). The S–S bond lengths range from 196.8 to 238.6 pm. This structure is less stable than isomer

Table 2. Selected bond angles and torsional angles [°] of the $[LiS_8]^+$ isomers **8a**–**v** [B3LYP/6-31G(2df,p) optimized geometries]. For the numbering of the sulfur atoms, see Figures 2–5.

Species	Bond angles (α) and torsion angles (τ)
8a	$\alpha_{123} = 105.6$, $\alpha_{234} = 110.2$, $\alpha_{1\mathrm{Li}3} = 78.6$, $\tau_{1234} = -98.9$
8b	$\alpha_{123} = 104.7$, $\alpha_{234} = 108.8$, $\alpha_{345} = 102.7$, $\alpha_{456} = 109.3$, $\alpha_{567} = 109.3$, $\alpha_{678} = 108.1$, $\alpha_{782} = 105.9$, $\alpha_{812} = 109.2$, $\alpha_{1\mathrm{Li}3} = 78.8$, $\alpha_{1\mathrm{Li}5} = 125.9$, $\alpha_{1\mathrm{Li}8} = 51.3$, $\tau_{1234} = -107.9$, $\tau_{2345} = 83.8$, $\tau_{3456} = -108.1$, $\tau_{4567} = 64.4$, $\tau_{5678} = 59.5$, $\tau_{6781} = -108.1$, $\tau_{7812} = 6.3$, $\tau_{8123} = 92.9$
8c	$\alpha_{123} = 112.2$, $\alpha_{234} = 106.9$, $\alpha_{345} = 107.6$, $\alpha_{456} = 103.9$, $\alpha_{567} = 105.2$, $\alpha_{678} = 107.0$, $\alpha_{782} = 101.4$, $\alpha_{1\mathrm{Li}6} = 119.0$, $\alpha_{1\mathrm{Li}4} = 96.1$, $\alpha_{21\mathrm{Li}} = 103.4$, $\tau_{1234} = -38.1$, $\tau_{2345} = -76.1$, $\tau_{3456} = 108.8$, $\tau_{4567} = -83.9$, $\tau_{5678} = -2.4$, $\tau_{6782} = 88.0$, $\tau_{7821} = 7.5$
8d	$\alpha_{123} = 108.6$, $\alpha_{234} = 106.7$, $\alpha_{345} = 103.9$, $\alpha_{456} = 110.0$, $\alpha_{1\mathrm{Li}4} = 98.3$, $\alpha_{4\mathrm{Li}6} = 85.4$, $\tau_{1234} = 50.6$, $\tau_{2345} = -116.2$, $\tau_{3456} = 84.3$, $\tau_{56\mathrm{Li}1} = 110.6$
8e	$\alpha_{123} = 105.6$, $\alpha_{234} = 108.6$, $\alpha_{345} = 107.9$, $\alpha_{812} = 108.5$, $\alpha_{1\mathrm{Li}8} = 51.1$, $\tau_{1234} = -93.4$, $\tau_{2345} = 100.1$, $\tau_{3456} = -103.6$, $\tau_{1876} = 97.9$, $\tau_{2187} = -106.1$
8f	$\alpha_{123} = 110.4$, $\alpha_{812} = 104.1$, $\alpha_{1\mathrm{Li}8} = 56.8$, $\alpha_{1\mathrm{Li}4} = 92.5$, $\tau_{1234} = 0$, $\tau_{2345} = -84.6$, $\tau_{3456} = 0$
8g	$\alpha_{123} = 101.3$, $\alpha_{234} = 108.3$, $\alpha_{345} = 110.0$, $\alpha_{812} = 107.2$, $\alpha_{1\mathrm{Li}3} = 77.9$, $\alpha_{1\mathrm{Li}8} = 53.1$, $\alpha_{3\mathrm{Li}6} = 88.4$, $\alpha_{6\mathrm{Li}8} = 77.9$, $\tau_{1234} = -141.0$, $\tau_{2345} = 81.6$, $\tau_{8123} = 87.8$
8h	$\alpha_{123} = 106.9$, $\alpha_{234} = 107.9$, $\alpha_{345} = 108.0$, $\alpha_{456} = 108.1$, $\alpha_{21\mathrm{Li}} = 99.4$, $\alpha_{218} = 110.7$, $\tau_{1234} = 96.1$, $\tau_{2345} = -98.7$, $\tau_{3456} = 100.6$, $\tau_{321\mathrm{Li}} = 155.1$, $\tau_{2187} = 99.5$
8i	$\alpha_{123} = 111.1$, $\alpha_{234} = 104.9$, $\alpha_{345} = 105.4$, $\alpha_{456} = 105.3$, $\alpha_{567} = 104.5$, $\alpha_{678} = 103.3$, $\alpha_{781} = 112.5$, $\alpha_{821} = 99.3$, $\alpha_{1\mathrm{Li}8} = 81.8$, $\tau_{1234} = -30.8$, $\tau_{2345} = -106.0$, $\tau_{3456} = 80.5$, $\tau_{4567} = -77.6$, $\tau_{5678} = 105.0$, $\tau_{6782} = -82.6$, $\tau_{821\mathrm{Li}} = -36.9$, $\tau_{3287} = 5.4$, $\tau_{\mathrm{Li}123} = 73.6$
8j	$\alpha_{123} = 109.1$, $\alpha_{234} = 109.6$, $\alpha_{345} = 107.0$, $\alpha_{456} = 103.4$, $\alpha_{567} = 108.5$, $\alpha_{678} = 105.8$, $\alpha_{781} = 109.0$, $\alpha_{78\mathrm{Li}} = 101.2$, $\alpha_{1\mathrm{Li}8} = 56.5$, $\tau_{1234} = -64.1$, $\tau_{2345} = -62.8$, $\tau_{3456} = 110.9$, $\tau_{4567} = -82.9$, $\tau_{5678} = 103.2$, $\tau_{6781} = -99.3$, $\tau_{678\mathrm{Li}} = -163.0$, $\tau_{7812} = 4.0$, $\tau_{\mathrm{Li}123} = 165.8$
8k	$\alpha_{123} = 107.6$, $\alpha_{234} = 105.2$, $\alpha_{345} = 103.7$, $\alpha_{456} = 105.6$, $\alpha_{567} = 105.8$, $\alpha_{678} = 109.4$, $\alpha_{782} = 106.4$, $\alpha_{1\mathrm{Li}7} = 93.4$, $\alpha_{21\mathrm{Li}} = 102.7$, $\tau_{1234} = -37.0$, $\tau_{2345} = -79.9$, $\tau_{3456} = 112.1$, $\tau_{4567} = -84.6$, $\tau_{5678} = 0.4$, $\tau_{6782} = 92.0$, $\tau_{1287} = 8.4$, $\tau_{\mathrm{Li}128} = 29.1$
8l	$\alpha_{123} = 104.0$, $\alpha_{234} = 106.4$, $\alpha_{345} = 105.5$, $\alpha_{456} = 105.5$, $\alpha_{567} = 106.4$, $\alpha_{678} = 104.0$, $\alpha_{781} = 103.1$, $\alpha_{78\mathrm{Li}} = 135.8$, $\alpha_{1\mathrm{Li}8} = 48.1$, $\tau_{\mathrm{Li}123} = 72.8$, $\tau_{1234} = 83.9$, $\tau_{2345} = -2.2$, $\tau_{3456} = -85.2$, $\tau_{4567} = -2.0$, $\tau_{5678} = 83.9$, $\tau_{6781} = 3.8$, $\tau_{7812} = -91.0$, $\tau_{8123} = 4.0$, $\tau_{678\mathrm{Li}} = 72.6$
8m	$\alpha_{812} = 106.8$, $\alpha_{123} = 103.9$, $\alpha_{234} = 104.1$, $\alpha_{345} = 108.0$, $\alpha_{1\mathrm{Li}8} = 57.8$, $\tau_{8123} = 85.0$, $\tau_{1234} = -143.9$, $\tau_{2345} = 86.0$
8n	$\alpha_{123} = 109.3$, $\alpha_{234} = 104.7$, $\alpha_{354} = 109.1$, $\alpha_{456} = 109.9$, $\alpha_{21\mathrm{Li}} = 97.0$, $\alpha_{4\mathrm{Li}7} = 86.7$, $\tau_{\mathrm{Li}123} = -57.6$, $\tau_{1234} = 45.3$, $\tau_{2345} = 103.5$, $\tau_{3456} = -81.2$, $\tau_{4567} = 0.0$
8o	$\alpha_{812} = 1105.4$, $\alpha_{123} = 105.4$, $\alpha_{234} = 1104.8$, $\alpha_{345} = 1108.2$, $\alpha_{456} = 1107.5$, $\alpha_{567} = 103.0$, $\alpha_{678} = 104.5$, $\alpha_{781} = 104.5$, $\alpha_{1\mathrm{Li}2} = 48.8$, $\tau_{7812} = -14.8$, $\tau_{8123} = 96.7$, $\tau_{1234} = -136.2$, $\tau_{2345} = 87.1$
8p	$\alpha_{123} = 107.0$, $\alpha_{234} = 105.4$, $\alpha_{345} = 107.1$, $\alpha_{456} = 108.5$, $\alpha_{21\mathrm{Li}} = 99.6$, $\tau_{1234} = 47.6$, $\tau_{2345} = 103.5$, $\tau_{3456} = -84.2$, $\tau_{4567} = 0.0$, $\tau_{321\mathrm{Li}} = 121.6$
8q	$\alpha_{123} = 109.2$, $\alpha_{234} = 101.1$, $\alpha_{345} = 106.7$, $\alpha_{456} = 103.5$, $\alpha_{567} = 105.6$, $\alpha_{678} = 107.5$, $\alpha_{782} = 100.3$, $\alpha_{821} = 112.0$, $\alpha_{4\mathrm{Li}7} = 106.5$, $\alpha_{6\mathrm{Li}7} = 53.5$, $\tau_{1234} = 170.0$, $\tau_{5678} = 7.7$
8r	$\alpha_{123} = 106.2$, $\alpha_{234} = 99.0$, $\alpha_{345} = 107.8$, $\alpha_{456} = 113.2$, $\alpha_{45\mathrm{Li}} = 101.4$, $\tau_{1234} = 24.7$, $\tau_{2345} = 103.7$, $\tau_{3456} = -79.1$, $\tau_{4567} = 2.7$, $\tau_{345\mathrm{Li}} = -143.9$
8s	$\alpha_{123} = 112.6$, $\alpha_{21\mathrm{Li}} = 112.1$, $\alpha_{1\mathrm{Li}4} = 90.6$, $\alpha_{1\mathrm{Li}8} = 119.7$
8t	$\alpha_{1\mathrm{Li}8} = 153.7$, $\alpha_{4\mathrm{Li}5} = 51.3$, $\alpha_{\mathrm{Li}12} = 112.5$, $\alpha_{123} = 112.4$, $\alpha_{234} = 108.0$, $\alpha_{345} = 104.5$, $\tau_{\mathrm{Li}123} = -8.6$, $\tau_{1234} = -8.4$, $\tau_{2345} = 88.3$, $\tau_{3456} = 148.7$, $\tau_{8\mathrm{Li}12} = 174.8$
8u	$\alpha_{123} = 109.2$, $\alpha_{234} = 104.7$, $\alpha_{34\mathrm{Li}} = 99.5$, $\tau_{34\mathrm{Li}5} = -117.1$
8v	$\alpha_{123} = 112.9$, $\alpha_{234} = 112.9$, $\alpha_{21\mathrm{Li}} = 110.6$, $\alpha_{1\mathrm{Li}4} = 92.8$, $\alpha_{1\mathrm{Li}5} = 149.3$, $\alpha_{567} = 110.5$, $\alpha_{678} = 112.3$

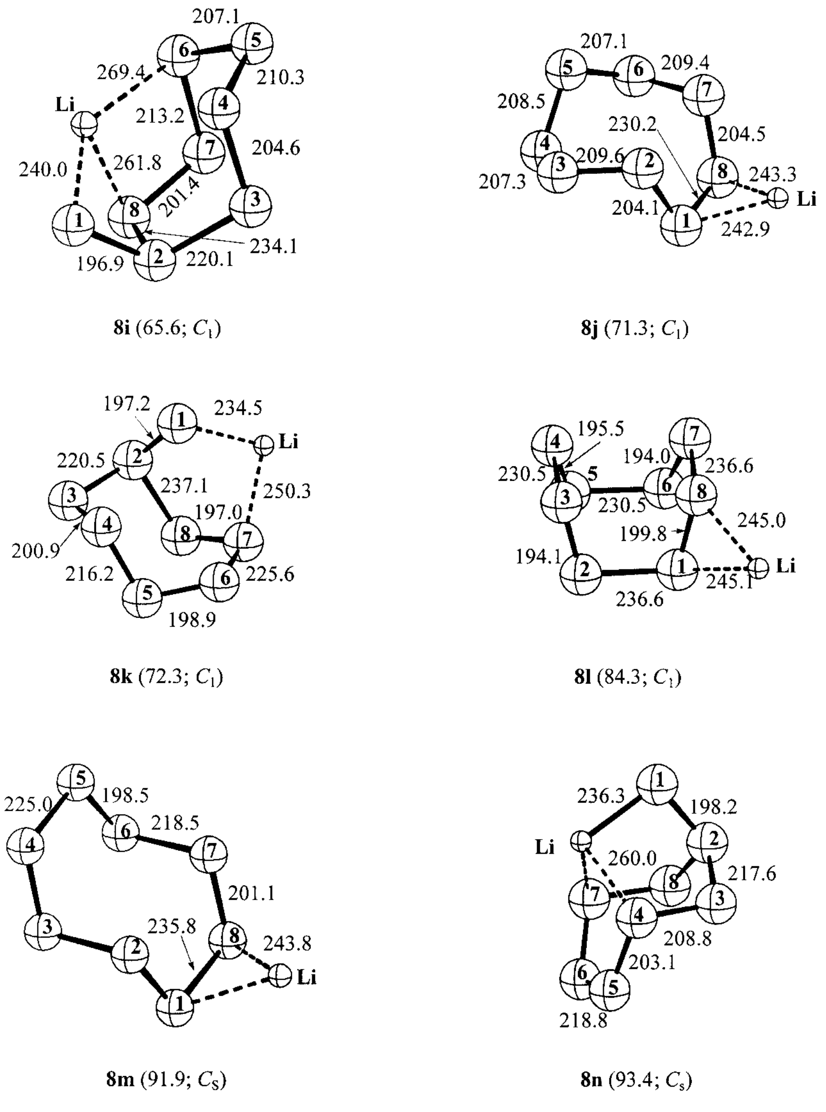
8a by 60.4 kJ·mol^{-1} compared to the relative energy of only 44.1 kJ·mol^{-1} for the free ligand.[13] The other isomer with a boat-shaped S_8 ligand (**8l**) has a relative energy of 84.3 kJ·mol^{-1}. This structure has no symmetry at all and contains a two-coordinate Li^+ ion with Li–S distances of 245.0 and 245.1 pm. The tub-like S_8 rings in **8f** and **8l** can approximately be thought of as being composed of four S_2 units because the S–S bond lengths alternate between rather small (194.0–199.8 pm) and much larger values (230.5–238.6 pm). As expected, the binding energy of **8l** (–116.2 kJ·mol^{-1}) is smaller than that of **8f** (–140.2 kJ·mol^{-1}). When we tried to optimize the geometry of a cube-like structure with connectivity $[Li(S_2)_4]^+$ (metal ion at the center of an arrangement of four parallel but independent S_2 molecules; starting symmetry D_{4h}) in analogy to the reported $[V(S_2)_4]^+$ structure,[9] we obtained structure **8f** instead.

A crown-shaped S_8 ring is also present in structure **8h** which is of C_s symmetry and less stable than **8a** by 61.6 kJ·mol^{-1} (see Figure 2). This structure resembles that of the $S_8{=}O$ molecule[16] but the metal atom is in an equatorial position with an Li–S distance of 240.6 pm. Owing to the lower coordination number of 1, the binding energy is only –94.9 kJ·mol^{-1}, the lowest value among all complexes studied in this work. As expected, the distortion of the eight-membered ring by the metal ion induces a symmetrical S–S bond length alternation with the two longest bonds (214.0 pm) neighboring the Li–S bond (Figure 2). The average S–S bond length of 210.6 pm is now considerably larger than in free S_8 (208.0 pm). Attempts to optimize a similar structure with Li^+ in an axial position (as the oxygen atom in solid S_8O) resulted in isomer **8a**.

We found three isomeric $[LiS_8]^+$ cations derived from the chair conformation of S_8 (structure **6** in Figure 1; motif00–+–0+–+). The most stable of these, **8g**, with a relative energy of 60.5 kJ·mol^{-1}, contains the Li cation pyramidally coordinated to four sulfur atoms with distances in the narrow range of 257.7–258.6 pm (Figure 2). The other two isomers with CN = 2 (**8m** and **8o**) are considerably less stable than **8g**, by 31.5 and 44.0 kJ·mol^{-1}, respectively (see Figure 3). The binding energies decrease in the order of decreasing relative stability (Table 1).

As has been shown previously, a characteristic feature of Li^+ complexes with sulfur-rich ligands is the bridging of single S–S bonds by the metal ion.[11] This type of bonding can also be seen in structure **8j** (Figure 3), which is a derivative of the twisted S_8 isomer **4** shown in Figure 1. Complex **8j** is characterized by an LiS_2 triangle with Li–S bonds of lengths 242.9 and 243.3 pm bridging a dramatically lengthened S–S bond of 230.2 pm. The remaining S–S bonds alternate in length symmetrically to a plane through the lithium atom and the midpoint of bond S4–S5 (symmetry C_s). This isomer with a binding energy of –104.2 kJ·mol^{-1} is less stable than **8a** by 71.3 kJ·mol^{-1}.

The asymmetrical structure **8i** is the most stable $[LiS_8]^+$ isomer with an S_7=S ligand with a relative energy of 65.6 kJ·mol^{-1}. It has the largest binding energy (–182.9 kJ·mol^{-1}) among all the $[LiS_8]^+$ structures. The metal ion coordinates to the exocyclic sulfur atom and very weakly also to two ring atoms. The seven-membered ring is considerably distorted compared to free S_7 and free S_7=S (**7**), as the SS bond lengths vary between 201.4 and 234.1 pm (Figure 3). The related isomer **8k** with the relative energy of 72.3 kJ·mol^{-1} contains the S_7 = S ligand in another connectivity (Figure 3). The metal atom is linked by a short bond (234.5 pm) to the exocyclic sulfur atom and by a much longer bond (250.3 pm) to one of the two atoms at which the HOMO of the S_7=S molecule is centered, resulting in a bicyclic structure similar to that of isomer **8c**. There are four additional complex cations containing various conformations and isomers of the S_7=S ligand. As a free molecule, S_7=S exists as two conformers (Figure 1) which are less stable then the S_8 crown (**1**) by 92.1 and 94.8 kJ·mol^{-1}, respectively.[13] The ion **8n** is of C_s symmetry (Figure 3). The metal atom is linked to the exocyclic sulfur atom with a rather short bond of 236.1 pm and to two ring



8i (65.6; C_1)

8j (71.3; C_1)

8k (72.3; C_1)

8l (84.3; C_1)

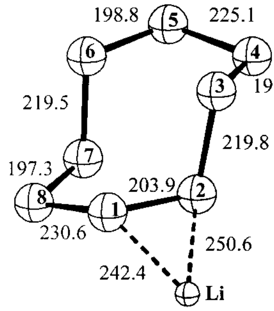
8m (91.9; C_S)

8n (93.4; C_s)

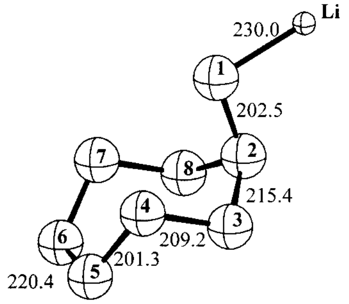
Figure 3. Isomeric structures **8i**–**n** of composition $[LiS_8]^+$ (relative energies in kJ·mol^{-1} and symmetries are given in parentheses). Bond lengths in pm.

atoms with bond lengths of 260.1 pm forming a tricyclic structure. This type of interaction results in a binding energy of –155.2 kJ·mol^{-1}. The conformation of the seven-membered ring is very similar to that of the free S_7 molecule,[17] with one torsion angle of zero and a strong and symmetrical bond length alternation. The compact and cluster-like geometry of **8n** is less stable than **8a** by 93.4 kJ·mol^{-1}. This relative energy is practically identical to the relative energy of the most stable conformation of the free $S_7{=}S$ ligand compared to the crown-shaped S_8 molecule.[13] Structure **8p** contains the metal atom coordinated just to the exocyclic sulfur atom of $S_7{=}S$, which carries the highest negative charge in the free ligand.[13] The exocyclic sulfur atom is in an axial position which is stabilized by the anomeric effect. The corresponding structure with the LiS group in an equatorial position (**8p′**) is also a minimum on the PES but slightly less stable than **8p**. Interestingly, on the PES of $[HS_8]^+$ a structure similar to **8p** with the hydrogen atom coordinated just to the exocyclic sulfur atom represents the global minimum structure.[18] We notice that the field strength of Li^+ is evidently not high enough to stabilize the $S_7{=}S$ structure over the crown-shaped eight-membered ring as the proton does. Even less stable than **8p** are two isomers with other coordination patterns (structures **8q,r** in Figure 4 and Table 1). These structures will not be discussed in detail.

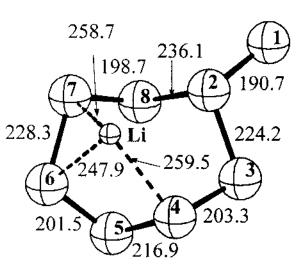
We found three minimal energy structures of composition $[LiS_8]^+$, each containing two S_4 ligands (Figure 5). However, these isomers are much less stable than all the complexes with the undissociated S_8 ligand, despite their larger binding energies (Table 1). This finding is in agreement with the corresponding results obtained for $[LiS_6]^+$ complexes.[11] The most stable of the $[Li(S_4)_2]^+$ complexes (isomer **8s**), with a relative energy of 132.9 kJ·mol^{-1}, is of D_{2d} symmetry with two planar LiS_4 heterocycles joined by a common Li atom. These two rings are perpendicular to each other. The *cis*-planar conformation of the two S_4 ligands corresponds to the global minimum structure of the free S_4 molecule.[19] The same holds for the most remarkable structure **8u** in which the two S_4 ligands are monodentate. This nine-atomic chain of C_2 symmetry consists of two planar segments of six atoms each, having the central three-atom unit S–Li–S in common. The torsion angle between the two planes is 126.5°. The relative energy of **8u** is 146.0 kJ·mol^{-1}. Complex **8v**, on the other hand, contains one chelating and one open-chain S_4 ligand, the latter in the *trans*-planar conformation (Figure 4) resulting in a relative energy of 178.9 kJ·mol^{-1}. In species **8v** the torsion angle between the two planar S_4 units is 159.8°. The binding energies of **8s,u,v** (–216.7, –203.6, and –212.0 kJ·mol^{-1}, respectively) are much higher than for the $[LiS_8]^+$ complexes with the eight-atomic ligands.



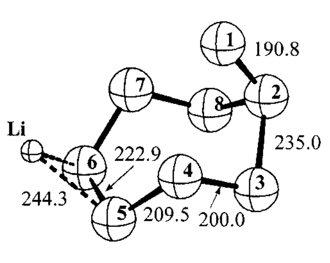
8o (104.4; C_1)



8p (116.4; C_s)



8q (121.9; C_1)



8r (129.0; C_s)

Figure 4. Isomeric structures **8o**–**r** of composition $[LiS_8]^+$ (relative energies in kJ·mol^{-1} and symmetries are given in parentheses). Bond lengths in pm.

It is worth noting that the related complex of composition $[LiS_4]^+$ also exists as two isomers with either a monodentate or a bidentate S_4 ligand (see Figure 5). Both isomers are planar. The five-membered heterocycle **4a** (binding energy –124.7 kJ·mol^{-1}) is more stable than **4b** (binding energy –113.2 kJ·mol^{-1}). Addition of another S_4 to **4a** with formation of **8s** liberates –92.0 kJ·mol^{-1}.

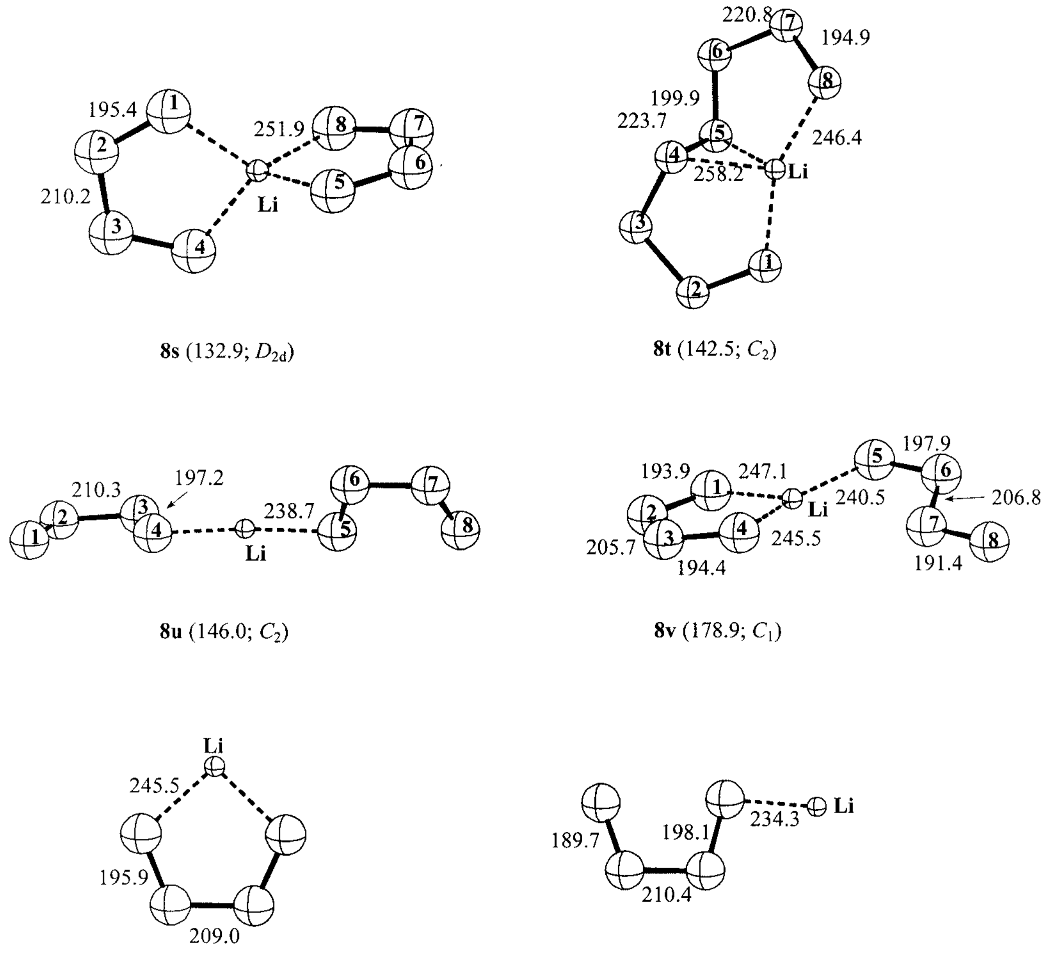
Because the S_8 molecule can also exist as a triplet chain (structure **9** in Figure 1), we have investigated its ability to coordinate to Li^+. The resulting triplet cation (**8t**) forms an eight-membered heterocycle with CN(Li) = 2+2 (Figure 5). Six torsion angles of this ring are within 10° of either 0° or 180°, that is, planarity (Table 2). Thus, this heterocycle is rather flat. The relative energy of 142.5 kJ·mol^{-1} is slightly lower than the corresponding energy of **9** (151.2 kJ·mol^{-1}). However, the binding energy (–165.3 kJ·mol^{-1}) is higher than in the case of the global minimum structure **8a** by 10 kJ·mol^{-1}. We did not consider other possible triplet chain structures with lower coordination numbers as they are expected to have lower binding energies. However, a singlet nine-membered $[LiS_8]^+$ heterocycle is less stable than the global minimum structure **8a** by only 81.7 kJ·mol^{-1}. Finally, we would like to mention that the connectivity $[Li(S_6)(S_2)]^+$ represents also a minimum on the PES of $[LiS_8]^+$, but this structure is even less stable than **8v**.

The present results and the calculations on complexes of the types $[LiS_6]^{+[11]}$ and $[LiS_7]^{+[20]}$ indicate that the global minimum structures always contain the most stable conformation of the ligand donating electron density to the metal atom through three or four atoms. Hence, we expect that other alkali metal cations form analogous symmetrical complexes with sulfur homocycles. However, univalent transition-metal polysulfur cations seem to prefer other structures and different compositions (see below).

Our present data together with previous results[11] allow the calculation of the reaction energy of the following gasphase sulfurization reaction between the most stable species involved:

$[LiS_6]^+$ (**6a**) + ¼ S_8 (**1**) → $[LiS_8]^+$ (**8a**)

ΔE_o = –49.0 kJ·mol^{-1}, $\Delta H°_{298}$ = –47.8 kJ·mol^{-1}, $\Delta G°_{298}$ = –33.5 kJ·mol^{-1}



8s (132.9; D_{2d})

8t (142.5; C_2)

8u (146.0; C_2)

8v (178.9; C_1)

4a (0.0; C_{2v})

4b (11.5; C_S)

Figure 5. Isomeric structures **8s**–**v** of composition $[LiS_8]^+$ and **4a**–**b** of composition $[LiS_4]^+$, all containing chain-like ligands (relative energies in kJ·mol^{-1} and symmetries are given in parentheses). Bond lengths in pm.

One, therefore, would expect the cation $[LiS_6]^+$ to be unstable in the presence of an excess of S_8, for example in a mass spectrometric experiment. The lithium cation basicity of S_8 (**1**), that is, the negative Gibbs energy of the addition of Li^+ to S_8 producing **8a** at 298 K, is 122.7 kJ·mol^{-1}.

Atomic Charges

The atomic charges of the 23 complexes of composition $[LiS_8]^+$ calculated by the NBO approach are listed in Table S2 in the Supporting Information. The charge transfer from the polysulfur ligand(s) to the metal atom varies between 0.04 and 0.27 electrostatic units. In the various isomers all sulfur atoms linked to Li^+ are negatively charged while all others are positive or practically neutral, with the exception of exocyclic and terminal atoms, which are always negative. The metal ion clearly polarizes the valence electrons of the ligand(s) and thus induces dipole moments directed towards this cation. This can be seen, for example, in the charge distribution of the global minimum structure **8a**. The three-coordinate sulfur atoms bear a small negative charge of –0.03, while the two-coordinate atoms have a positive charge of +0.07 and Li^+ has gained 0.18 electrons from the ligand. Exocyclic sulfur atoms as in $S_7{=}S$ are always negatively charged; therefore, Li^+ prefers to bind to these atoms except in the high-energy isomers **8q** and **8r**. A high degree of charge separation is also found in the three cations with S_4 ligands **8s**,**u**,**v**. In these complexes the charge differences between the metal atom and the coordinating sulfur atoms are considerably larger than 1 electrostatic unit. The structures of the latter three ions can be reproduced readily using point-charge model calculations.

Vibrational Spectra

To identify the species **8a** or similar cations containing crown-shaped S_8, one may use vibrational spectroscopy, as the bonds between two-coordinate sulfur atoms are excellent Raman scatterers and the metal–sulfur bonds will give rise to vibrations of high infrared intensity. In addition, the vibrational spectrum of a ligand contains information about the influence of the metal ion on the ligand. Therefore, we have compared the vibrational spectra of S_8 (**1**) and $[LiS_8]^+$ (**8a**) in Table 3. The additional atom increases the number of vibrational degrees of freedom by 3. Taking the lowering of the symmetry from D_{4d} to C_{4v} into account, the irreducible representation $2A_1 + B_1 + B_2 + 2E_1 + 3E_2 + 2E_3$ of S_8[21] changes to $4A_1 + A_2 + 3B_1 + 3B_2 + 5E$ for $[LiS_8]^+$. The three E_2 modes of S_8 split into B_1 and B_2 modes in $[S_8Li]^+$ while all E_1 and E_3 modes of S_8 end up as E modes in the cation. The vibrational transitions introduced by the Li atom are calculated at 254 cm^{-1} (A_1) and 222 cm^{-1} (E). As can be seen from the data in Table 3, the wavenumbers of the S_8 ligand are very similar to those of the free S_8 molecule in agreement with the weak interaction deduced above from the internuclear distances and the atomic charges.

Table 3. Calculated harmonic fundamental vibrations (cm^{-1}) of S_8 (D_{4d} symmetry) and of $[S_8Li]^+$ (C_{4v}) as well as infrared intensities (km·mol^{-1}) of the latter. Observed wavenumbers of S_8 (dissolved in CS_2) are given in parentheses (according to ref.[21]).

S_8	Symmetry	$[S_8Li]^+$	Symmetry	Infrared intensity
474 (476)	A_1	465	A_1	0.0
466 (471)	E_1	462	B_1	0.0
462 (476)	E_2	460	E	0.9
		453	B_2	0.0
415 (444)	E_3	415	E	2.2
389 (–)	B_1	385	A_2	0.0
		254	A_1 (LiS_3)	20.7
247 (248)	E_3	251	E	5.5
		222	E (LiS_3)	19.4
241 (243)	B_2	220	A_1	12.9
213 (218.5)	A_1	196	A_1	45.0
189 (191)	E_1	171	E	4.7
145 (152.5)	E_2	155	B_1	0.0
		141	B_2	0.0
72 (86)	E_2	94	B_2	0.0
		68	B_1	0.0

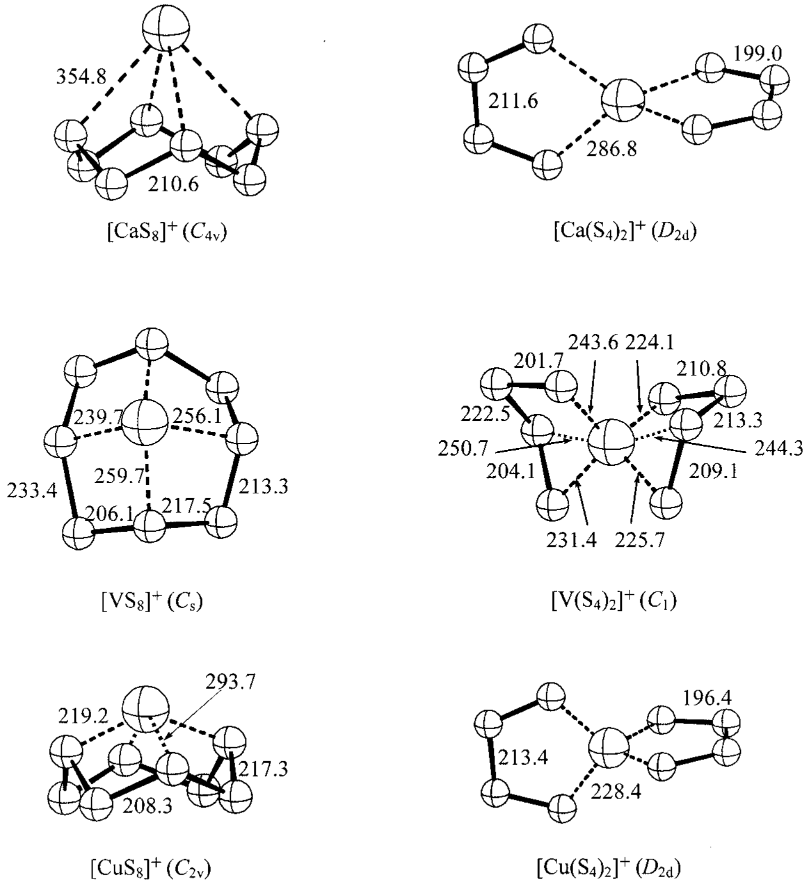
Other Metal Ions

To investigate the dependence of the reported structures on the metal ion, we have carried out preliminary calculations on some ions of composition $[MS_8]^+$ with M = Ca, V, and Cu using calculations at the CCSD(T)/6-31G*//B3LYP/6-31G*+ZPE level after mass spectrometric observations of such species have been reported (see Introduction). In particular, we were interested in the relative stabilities of isomeric complexes containing either one crown-shaped S_8 ligand or two chain-like chelating S_4 ligands. The thermodynamic results are summarized in Tables 4 and S3 (Supporting Information), and the molecular structures are shown in Figure 6. For the free metal ions, the most stable electronic configuration[22] was used to calculate the binding energies. It turned out that for all three cations, the complex with the connectivity $[M(S_4)_2]^+$ is more favorable energetically than the structures analogous to **8a**. The binding energy for $[Li(S_8)]^+$ is now obtained as –164.3 kJ·mol^{-1} rather than –156.5 kJ·mol^{-1} at the G3X(MP2) level (Table 1). The interaction of Ca^+ with S_8 (**1**) is relatively weak (binding energy only –71.4 kJ·mol^{-1}). In the case of Cu^+, the symmetry of the S_8 complex is only C_{2v} rather than C_{4v}, and $[V(S_8)]^+$ is even of C_s symmetry. The complexes $[Ca(S_2)_4]^+$ and $[Cu(S_2)_4]^+$ contain planar S_4 ligands and the metal atoms are tetrahedrally coordinated. $[V(S_4)_2]^+$ has an interesting although asymmetrical geometry (Figure 6) with the higher coordination number 6 for the metal atom and two tridentate S_4 ligands explaining its remarkable binding energy of –586.5 kJ·mol^{-1}. This nonplanar ion with SSSS torsion angles of 57° and 63° has a triplet ground state while the isomeric complex with the eight-atomic crown-shaped ligand is a quintet (Table 4), as is the free V^+ ion. Even more stable than $[V(S_4)_2]^+$ are the isomeric complexes $[V(S_2)(S_6)]^+$ and $[V(S_3)(S_5)]^+$ (not shown) which both prefer the singlet state. In contrast to the report by Dance et al.,[9] we could not locate a minimum structure

Table 4. Relative energies ΔE_o and binding energies ($kJ \cdot mol^{-1}$) of complexes of composition $[MS_8]^+$ with M = Li, Ca, V, Cu calculated at the CCSD(T)/6-31G*//B3LYP/6-31G*+ZPE level of theory. The relative energy of the complex with an eight-atomic crown-shaped S_8 ligand was set equal to zero in all cases.

Metal ion	Relative energy of $[M(S_4)_2]^+$	Binding energy of $[M(S_8)]^+$	Binding energy of $[M(S_4)_2]^+$
Li^+ (^1S)	+73.4	–164.3	–269.1
Ca^+ (^2S)	–49.0	–71.4	–298.6
V^+ (^5D)	–213.3	–195.0[a]	–586.5[b] –656.6[c]
Cu^+ (^1S)	–58.2	–304.5	–540.9

[a] Quintet ground state. [b] Triplet ground state. [c] Calculated with respect to triplet V^+.



$[CaS_8]^+$ (C_{4v})

$[Ca(S_4)_2]^+$ (D_{2d})

$[VS_8]^+$ (C_s)

$[V(S_4)_2]^+$ (C_1)

$[CuS_8]^+$ (C_{2v})

$[Cu(S_4)_2]^+$ (D_{2d})

Figure 6. Structures of the complexes $[M(S_8)]^+$ and $[M(S_4)_2]^+$ with M = Ca, V, Cu, calculated at the B3LYP/6-31G* level. Bond lengths in pm.

for $[V(S_2)_4]^+$. More details on the polysulfur complexes of transition metals will be published elsewhere.

Conclusions

Lithium cations form stable complexes with neutral sulfur molecules such as various isomers of S_8 and S_4 with binding energies ranging from –95 to –217 $kJ \cdot mol^{-1}$. The crown-shaped S_8 ring of D_{4d} symmetry coordinates to Li^+ as a tetradentate ligand resulting in a complex of C_{4v} symmetry, which represents the global minimum on the PES of $[LiS_8]^+$. The interaction is explained by ion–dipole attraction with a charge transfer of only 0.18 electrostatic units. Consequently, the vibrational spectrum of the S_8 ligand changes only slightly on complex formation, reflecting however the lower symmetry. Higher-energy conformers and isomers of *cyclo*-S_8 such as twisted, chair- and tub-like eight-membered rings, branched seven-membered rings (S_7=S) as well as the triplet and singlet chains also form complexes with Li^+ with the coordination number of the metal atom varying between 1 and 4. In general, the conformation of the ligand changes only very little on complex formation but the relative energy changes are sometimes considerable. Complexes of composition $[LiS_8]^+$ containing two S_4 ligands are much less stable than those with one S_8 or S_7=S ligand. The planar S_4 unit may coordinate either as a chelating dihapto ligand or as a chain-like monohapto ligand of either *cis*- or *trans*-conformation. Consequently, there are several types of $[Li(S_4)_2]^+$ complexes. We should note that our calculations may relate directly to experiments in the gas phase, but not in a condensed phase, as Li^+ is strongly solvated in a dielectric medium. As a result, the lithium binding energies are expected to be absolutely smaller in solution. Complexes of composition $[MS_8]^+$ with M = Ca, V, and Cu prefer the connectivity $[M(S_4)_2]^+$ over $[M(S_8)]^+$ with CN(M) = 4 or 6 and binding energies in the range –266 to –586 kJ·mol^{-1}, but in the case of vanadium even more stable isomers of connectivities $[V(S_2)(S_6)]^+$ and $[V(S_3)(S_5)]^+$ have been located on the PES.

Computational Methods

Standard ab initio and density functional calculations were carried out with the GAUSSIAN 98 and 03 series of programs[23] at the G3X(MP2) level of theory.[24] This theory corresponds effectively to QCISD(T)/G3XL//B3LYP/6-31G(2df,p) energy together with zero-point vibrational and higher-level corrections. The G3X(MP2) theory represents a modification of the G3(MP2) theory,[25] with three important modifications: (1) B3LYP/6-31G(2df,p) geometry, (2) B3LYP/6-31G(2df,p) zero-point energy, and (3) addition of a *g* polarization function to the G3Large 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.[13,18,19] For instance, the geometries and stabilities of several cluster species are poorly predicted by the MP2 theory.[13]

Harmonic frequencies were calculated at the B3LYP/6-31G(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 metal ion complexes were computed as the difference between the energy of the lithiated species and the total energy of the two free monomers in the same conformation as found in the complex. The Gibbs energy differences (ΔG) were computed from the equation $\Delta G_T = \Delta H_T - T\Delta S$, where ΔS is the entropy change and $\Delta H_T = \Delta H_0 + (H_T - H_0)$. The thermal correction ($H_{298} - H_0 = 6.197$ kJ·mol^{-1}) and the entropy value ($S_{298} = 133.017$ J·mol^{-1}·K^{-1}) of the lithium cation were taken from the JANAF compilation.[26] Unless otherwise noted, all relative energies of S_n molecules and $[LiS_8]^+$ ions reported in this publication are given as ΔE_o and correspond to the G3X(MP2) level, while all reported structural parameters of these species correspond to the B3LYP/6-31G(2df,p) level. The structures of all complexes of composition $[MS_8]^+$ (M = Ca, V, Cu) were examined by the density functional method B3LYP with the 6-31G* basis set with higher-level single-point energy calculations obtained at the CCSD(T)/6-31G* level. All structures were optimized initially without any symmetry constraint and were reoptimized with a higher symmetry after a local energy minimum was obtained. In the case of vanadium, the singlet, triplet, and quintet states have been investigated for both $[M(S_8)]^+$ and $[M(S_4)_2]^+$ species.

Supporting Information (see also footnote on the first page of this article): Absolute energies and atomic charges of the isomers of composition $[LiS_8]^+$ and total energies as well as zero-point energies (ZPE) of the complexes $[M(S_8)]^+$ and $[M(S_4)_2]^+$ and related species.

Acknowledgments

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