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Isomers of *cyclo*-Heptasulfur and Their Coordination to Li^+: an Ab Initio Molecular Orbital Study

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The potential energy hypersurfaces (PESs) of heptasulfur (S_7) and of $[LiS_7]^+$ have been investigated by ab initio molecular orbital calculations at the G3X(MP2) level of theory. Besides the chairlike seven-membered ring (**1a**) as the global minimum structure, eight local minimum structures and one transition state have been located on the PES of S_7. The barrier for pseudorotation of **1a** is only 5.6 kJ mol^{-1}. The boatlike S_7 ring (**1b**) is 12.1 kJ mol^{-1} less stable than **1a**, followed by three isomers of connectivity $S_6{=}S$ and four open-chain isomers. On the basis of multireference calculations at the MRCI(4,4)+Q/6-311G(d) level, the most stable open-chain form of S_7 is a triplet of relative energy 133.1 kJ mol^{-1}. Thus, the reaction energy (ΔE_0) for the ring opening of **1a** is 133.1 kJ mol^{-1}, halfway between those of the highly symmetrical rings S_6 and S_8. Because of their strong multireference characters, the stabilities of the biradicalic singlet chains are significantly overestimated by the single-reference-based G3X(MP2) method. The calculated vibrational spectrum of **1a** is in good agreement with experimental data. The various isomers of S_7 form stable complexes with Li^+ with coordination numbers of 1–4 for the metal atom and binding energies in the range of –93.8 to –165.7 kJ mol^{-1}. A total of 15 isomeric complexes have been located, with 13 of them containing cyclic ligands. The global minimum structure (**2a**) is composed of **1a**, with the Li^+ cation linked to the four negatively charged sulfur atoms (symmetry C_s). The corresponding complex **2c** containing the ligand **1b** is by 23.4 kJ mol^{-1} less stable than **2a**, and a bicyclic crown-shaped LiS_7 cation (**2e**) is by 34.9 kJ mol^{-1} less stable than **2a**. Even less stable are four complexes with the branched $S_6{=}S$ ligand. SS bond activation by polarization of the valence electrons takes place on coordination of Li^+ to *cyclo*-S_7 (**1a**).

1. Introduction

Heptasulfur (*cyclo*-S_7) is a component of liquid[1] and gaseous[2] sulfur (under equilibrium conditions) and of many synthetic mixtures of elemental sulfur.[3] S_7 is also formed on thermal decomposition of polymeric sulfur,[4,5] a process important for the vulcanization of rubber. From solutions in organic solvents, S_7 crystallizes as four allotropes, which all consist of chairlike ring molecules of C_s symmetry.[6,7] The most striking feature of the S_7 structure is one unique torsion angle of 0° resulting in a length of 218 pm of the corresponding bond, while "normal" bonds between two-coordinate sulfur atoms are ca. 205 pm long and are characterized by torsion angles near 90°.[8] Therefore, it was to be expected that S_7 is more reactive than any other solid allotrope of sulfur all exhibiting S−S−S−S torsion angles of $>60°$. In fact, crystalline S_7 is less stable at 298 K than all other cyclic sulfur allotropes, decomposing within several hours to a mixture of *cyclo*-S_8 and polymeric sulfur.[4] The

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mechanism of this low-temperature decomposition reaction is unknown, and less stable isomers of S_7 may play a role as intermediates.

The possible higher-energy isomers of the S_7 molecule have not yet been studied systematically at a correlated level of theory (for both the geometry and energy calculations) although some isomeric structures have been established by theoretical methods.[9,10] In addition to the ground-state exo or chair structure, present in the solid allotropes, there exists an endo or boat structure of C_s symmetry on the potential energy surface (PES), which is only slightly less stable by ca. 13 kJ mol^{-1} at the MP2/6-311G(d) level of theory.[10] Both conformers undergo facile pseudorotation through transition states of C_2 symmetry with barriers of less than 15 kJ mol^{-1}. The barrier for the chair → boat transformation is much higher, ca. 85 kJ mol^{-1}. According to density functional theory (DFT) calculations at the B3LYP/6-31G(d) level, branched ring structures of the type $S_6{=}S$ as well as diradicalic open chains are much less stable than the two seven-membered rings,[11] but reliable thermodynamic data are missing and details of the geometries have not been released yet. Therefore, we have investigated the PES of S_7 at the G3X(MP2) level of theory.[12]

The chemical reactivity of sulfur homocycles is strongly influenced by the presence of nucleophilic or electrophilic reagents. While the impact of nucleophiles (especially organic amines and phosphines) has been studied many times,[13] the interaction with electrophiles is less well understood. In previous publications, we have investigated the protonation of the sulfur molecules S_2-S_8 [14] as well as the addition of lithium cations to the homocycles S_6 [15] and S_8.[16] In the present work, we report on the corresponding coordination compounds between various S_7 isomers and Li^+. Numerous polysulfido complexes of main-group and transition metals have been reported in the literature, but in most cases, the ligands are anionic.[17] Species with neutral S_n ligands are rare,[18] and complexes with the ligand *cyclo*-S_7 are unknown. The interaction of elemental sulfur with cationic reagents is, however, of general interest in connection with the large-scale vulcanization of rubber, a process with involves zinc oxide as an activator. Gas-phase experiments with reactions between *cyclo*-S_8 and univalent cations of Ca, Cu, V, and many other metals have demonstrated that $[MS_n]^+$ ions with $n = 1-12$ are readily formed (detection by ion cyclotron resonance mass spectrometry).[19]

2. Computational Details

Standard ab initio calculations were carried out with the *Gaussian 98* series of programs[20] at the G3X(MP2) level of theory.[21] This theory corresponds effectively to the QCISD(T)/G3XL//B3LYP/6-31G(2df,p) energy together with zero-point vibrational and isogyric corrections. The G3X(MP2) theory represents a modification of the G3(MP2) theory[22] with three important changes: (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. All three features are particularly important for the proper description of the sulfur-containing compounds examined in this work. For instance, the geometries and stabilities of several cluster species are poorly predicted by the MP2 theory.[23] Restricted Hartree−Fock was used for closed-shell species, and the unrestricted Hartree−Fock formalism was employed for the open-shell systems. For the singlet- and triplet-chain isomers of S_7, multiconfiguration self-consistent field (SCF) calculations, including complete active space SCF (CASSCF)[24] and multireference configuration interaction (MRCI),[25] were also carried out, using the *MOLPRO* program.[26] Harmonic fundamental vibrations were calculated at the B3LYP/6-31G(2df,p) level to characterize stationary points as equilibrium

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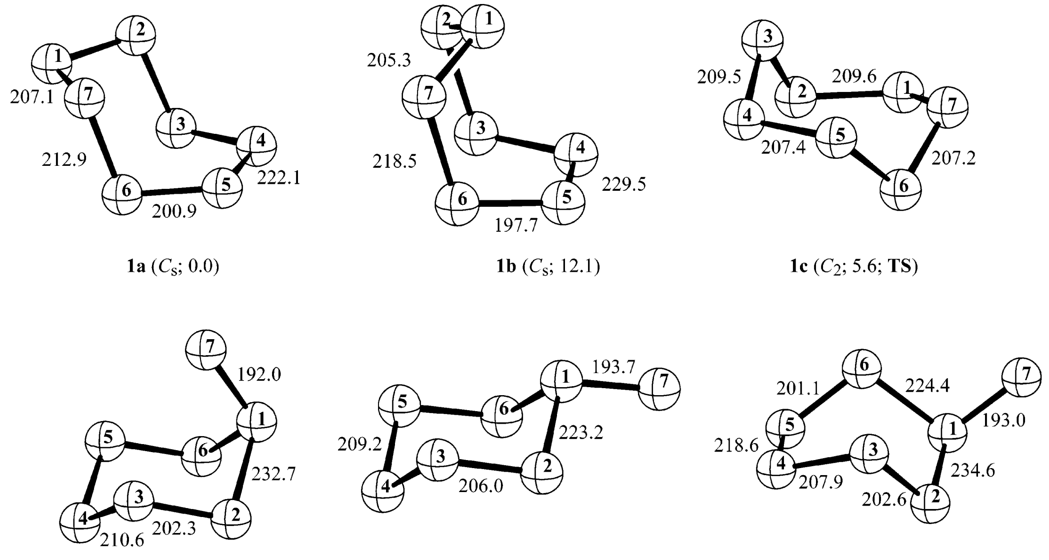
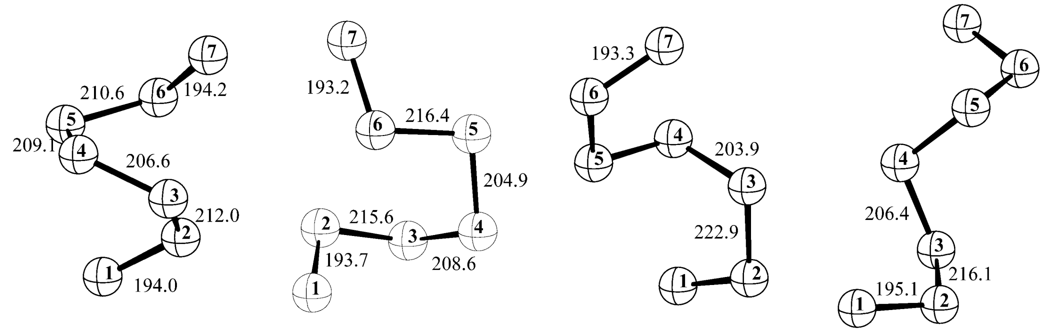


1a (C_s; 0.0) **1b** (C_s; 12.1) **1c** (C_2; 5.6; **TS**)

1d (C_s; 58.1) **1e** (C_s; 71.4) **1f** (C_1; 95.5)

Figure 1. Structures of the cyclic isomers of the S_7 molecule and of the transition state (TS) for pseudorotation with symmetries and relative energies ΔE_0 (kJ mol^{-1}) calculated at the G3X(MP2) level. Bond lengths are in picometers.



1g (C_1; 111.9 [163.6]) **1h** (C_1; 121.7 [151.3]) **1i** (C_2; 135.3 [133.1]) **1j** (C_2; 149.9)

Figure 2. Structures of the chainlike isomers of the S_7 molecule with symmetries and relative energies ΔE_0 (kJ mol^{-1}) calculated at the G3X(MP2) level. Energies obtained at the MRCI(4,4)+Q/6-311G(d) level are given in brackets (see Table 1). Bond lengths are in picometers.

structures, with all frequencies real, and transition states, with one imaginary frequency. To calculate the Gibbs energy of the lithium ion, a value of 6.197 kJ mol^{-1} was used for the temperature correction ($H_{298} - H_0$) and a value of 133.017 J mol^{-1} K^{-1} for the entropy (S_{298}).[27] The binding energies are defined as the difference between the energy of the complex and the combined energies of Li^+ and the corresponding S_7 ligand.

For all investigated molecules, a charge density analysis was performed using the natural bond orbital (NBO) approach based on the B3LYP/6-31G(2df,p) wave function.[28] NBO atomic charges of small molecules have recently been demonstrated to agree well with experimental values obtained from X-ray diffraction data.[29] Unless otherwise noted, all relative energies reported in this publication are given as ΔE_0 and correspond to the G3X(MP2) level.

3. Results and Discussion

3.1. Isomers of S_7. We have located seven local energy minima on the singlet PES of S_7 and two on the triplet PES. Their geometrical structures are shown in Figures 1 and 2, and their relative energies are given in Table 1. Absolute energies as well as atomic coordinates are given in the Supporting Information. The chairlike seven-membered ring is confirmed as the global minimum structure (**1a**), while the boatlike isomer (**1b**) is by 12.1 kJ mol^{-1} less stable. Both species are of C_s symmetry. The calculated structure of **1a** is in excellent agreement with the experimental structure of the solid-phase γ-S_7, which has been studied by X-ray crystallography.[6] Calculated bond distances are 1.2−4.6 pm longer, but the bond and torsion angles deviate by less than 3° from the experimental values. The most remarkable features of the two rings are the torsion angles of 0° at the unique bond. The other torsion angles of **1a** are as follows:

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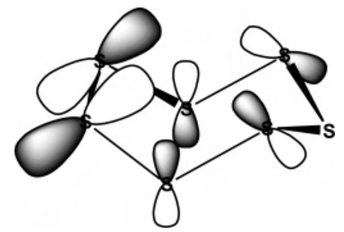
Table 1. Relative Energies ΔE_0,[a] Enthalpies $\Delta H°_{298}$,[a] and Gibbs Energies $\Delta G°_{298}$[a] (All in kJ mol^{-1}) and Dipole Moments μ[b] (D) of the Nine Isomeric Structures of S_7 and of the Transition State (**1c**) for the Pseudorotation of **1a**

species	symmetry	relative energy ΔE_0	relative enthalpy, $\Delta H°_{298}$	relative Gibbs energy, $\Delta G°_{298}$	μ
chair **1a**	C_s	0.0 [0.0][c]	0.0	0.0	0.17
boat **1b**	C_s	12.1	12.4	8.4	0.09
transition state **1c**	C_2	5.6	3.4	10.7	0.26
branched ring **1d**	C_s	58.0	58.2	58.1	0.74
branched ring **1e**	C_s	71.4	71.7	70.9	1.79
branched ring **1f**	C_1	95.5	96.3	92.2	1.22
singlet chain **1g**	C_2	111.9 [163.6][c]	113.1	107.5	0.64
singlet chain **1h**	C_1	121.7 [151.3][c]	122.9	117.1	1.44
triplet chain **1i** (^{3}**B**)	C_2	135.5 [133.1][c]	138.2	121.3	0.22
triplet chain **1j** (^{3}**B**)	C_2	149.9	153.1	129.5	0.71

[a] G3X(MP2) level unless otherwise noted. Absolute G3X(MP2) energy E_0 of the chair form (**1a**): −2784.357 89 hartree. [b] B3LYP/6-31G(2df,p) level. [c] MRCI+Q/6-311G(d) levels, based on an active space of 4 electrons in four orbitals, are given in brackets.

Chart 1



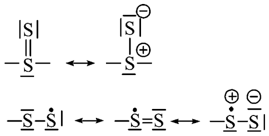
76.3° (bond between atoms 1 and 2), −104.8° (between atoms 2 and 3), and 81.3° (between atoms 3 and 4).

Seven-membered rings are known to undergo facile pseudorotation, i.e., a concerted torsional motion that transforms one C_s-symmetrical structure into an equivalent one through a transition state of C_2 symmetry. In the case of S_7 and its derivative 1,2-Se_2S_5, this process has been studied by Raman and ^{77}Se NMR spectroscopy.[30] Our data show that the barrier for the pseudorotation of **1a** is only 5.6 kJ mol^{-1} high. Previous calculations at MP2 and B3LYP levels of theory had resulted in similarly low barriers.[10] The transition-state structure (**1c**) is also shown in Figure 1. The torsion angles within this homocycle are between 45° and 102° (absolute values), and the spread of bond distances is much smaller (207.2−209.6 pm) than those in the C_s-symmetrical rings **1a** (200.9−222.1 pm) and **1b** (197.7−229.5 pm).

The variation of the S−S bond lengths in **1a** and **1b** can be understood readily in terms of the interaction of the various 3p orbitals in the occupied molecular orbitals. The highest occupied molecular orbital (HOMO) of **1a** involves the interaction of the 3p orbitals of atoms 2−7. The largest coefficients are located in atoms 4 and 5, which interact in an antibonding fashion, leading to the unusually long S−S bond of 222.1 pm (Chart 1).

The atomic charges of all S_7 isomers are given in Table S4 (Supporting Information). For the two-coordinate atoms of the homocycles, the charges are close to zero (−0.07 to +0.06), but three-coordinate atoms are considerably positive (0.28−0.34), and exocyclic atoms are always negatively charged (−0.23 to −0.29). As a consequence, the branched rings **1d**−**f** show larger dipole moments (0.74−1.79 D) than the two unbranched rings **1a** and **1b** (0.09−0.17 D). The chainlike isomers **1g**−**j** have negatively charged chain-terminating atoms (−0.10 to −0.23), while their neighbors are positively charged (0.12−0.19). These findings may be rationalized by the Lewis structures depicted in Scheme 1.

Scheme 1



Accordingly, the spin densities of the two most stable S_7 chains **1g** (singlet) and **1i** (triplet) are mainly located at the two chain-terminating atoms ($-S_b-S_a$):

1g: S_a 0.57, S_b 0.39 **1i**: S_a 0.65, S_b 0.32

Sulfur rings can be oxidized by trifluoroperoxoacetic acid to give homocyclic oxides such as $S_6{=}O$, $S_7{=}O$, and $S_8{=}O$.[31] Similarly, there exist isoelectronic branched rings $S_5{=}S$ and $S_7{=}S$ as higher-energy isomers on the PESs of S_6 [32] and S_8.[33] Here, we have found three branched ring structures of the type $S_6{=}S$ on the PES of S_7, two derived from the S_6 chair and one related to the boat form. The most stable of these (**1d**) with a relative energy of 58.1 kJ mol^{-1} has the exocyclic atom in an axial position, obviously stabilized by the well-known anomeric effect. There is a pronounced C_s-symmetrical bond-length alternation on proceeding from the formal double bond of length 192.0 pm at the exocyclic atom via the two longest bonds of 232.7 pm originating from the three-coordinate atom toward the unique atom no. 4 (Figure 1). The related isomer **1e** with the equatorial position for the exocyclic atom is by 13.3 kJ mol^{-1} less stable. Its chairlike ring is quite similar to that of **1d** with all torsion angles between 72° and 76° (absolute values). However, the exocyclic atom of **1e** is coplanar with two sets of three neighboring atoms (all except no. 4). In other words, the torsion angles τ_{7123} and τ_{7165} are both 180°. In contrast, the asymmetrical isomer **1f** exhibits an unusual rooflike conformation for the six-membered ring, which is not a local minimum structure on the PES of S_6.[14] This structure is characterized by two relatively small torsion angles of −17.7° and −21.2°. Consequently, the bond lengths in this species vary between 193.0 pm for the exocyclic bond and 234.6 pm for the neighboring bond with the smallest torsion angle of the ring.

We did not search for doubly and triply branched isomers such as $S_5({=}S)_2$ and $S_4({=}S)_3$ because these are expected to be very unstable.

At the G3X(MP2) level, the most stable form of an open-chain S_7 isomer is a singlet state (**1g**), only 111.9 kJ mol^{-1}

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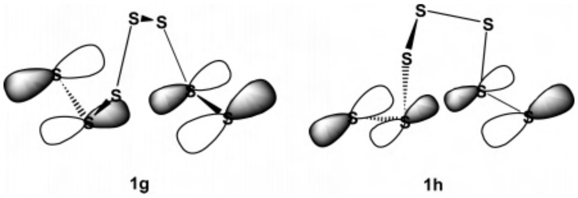
Chart 2



1g **1h**

less stable than the global minimum structure (Figure 2). This singlet S_7 chain is a slightly asymmetric spiral of approximate C_2 symmetry with torsion angles of −37.4°, −35.0°, −80.1°, and −42.2° from one end to the other (atoms 1 → 7). The terminal bonds are much shorter (194.1 ± 0.1 pm) than the remaining bonds (206.6−212.0 pm), a feature that is typical for all homoatomic sulfur chains regardless of their spin state. The species **1g** may be an intermediate in the thermal reactions of *cyclo*-S_7. Another asymmetrical singlet chain **1h** (Figure 2) also lies close in energy, 121.7 kJ mol^{-1} above **1a**. As with **1g**, **1h** is characterized by two short SS terminal bonds. The geometry of **1h** resembles a doubly branched five-membered ring with a long SS bond (281.5 pm) between atoms 2 and 6. What is the source of the apparent stabilization of the singlet chains **1g** and **1h**? Inspection of the HOMO of these species shows that the π^* orbitals of the two terminal units interact favorably at atoms 2 and 6 (Chart 2). As a consequence, these atoms are in relatively close contact, with distances of 303.1 and 281.5 pm for **1g** and **1h**, respectively. These distances are smaller than the van der Waals distance of 350 pm.

At the G3X(MP2) level, the two most stable triplet chains of S_7 (**1i** and **1j**) are 135.5 and 149.9 kJ mol^{-1} above the global minimum. Both molecules are of C_2 symmetry, but only **1j** is a spiral with all torsion angles of equal sign. In structure **1i**, two almost planar S_4 units are connected to each other, sharing one atom and oriented almost perpendicular to each other. The planar S_4 unit is commonly found in the long-chain $S_n^{\bullet\bullet}$ biradicals.[34] We found several other higher-energy singlet- and triplet-chain isomers, but they are not reported here.

It is important to note that both the singlet-chain isomers **1g** and **1h** are best considered as biradicalic species. The strong muliterference characters of these species are indicated by their significantly spin-contaminated wave functions ($\langle S^2 \rangle = 1.00$ and 0.99 for **1g** and **1h**, respectively) when an unrestricted Kohn−Sham-based method is employed. Therefore, the predicted relative energies of the two open-shell singlet chains using the single-reference-based G3X(MP2) method may not be reliable. Thus, we have examined also the relative stability of **1a**, the two singlet-chain isomers (**1g** and **1h**), and the triplet-chain isomer **1i** using the CASSCF[24] approach, which is expected to provide a proper description of the degeneracy problem involved. An active space of four electrons in four orbitals, i.e., CASSCF(4,4), is chosen to provide a balance description for all species. Dynamic electron correlation effects were included by carrying out MRCI[25] single-point energy calculations in conjunction with the 6-311G(d) basis set, based on the B3LYP-optimized geometries. Our best relative energies correspond to the MRCI+Q level, MRCI with Davidson correction (Table 1). The calculated relative energy of the triplet isomer **1i** is in good agreement with the single-reference method (Table 1). This result is not unexpected because the $\langle S^2 \rangle$ value of **1i** (2.01) is close to the expectation value. However, the relative energies of both **1g** and **1h** are substantially higher, by 30−50 kJ mol^{-1}, compared to the G3X(MP2) values. These large errors are due to their very strong multireference characters, as reflected by the two dominant configurations in the MRCI wave function, (0.73, −0.49) and (0.74, −0.48) for **1g** and **1h**, respectively. There are two major differences between the MRCI+Q and G3X(MP2) results. At the MRCI+Q level, the triplet-chain isomer **1i** is more stable than the two singlet chains. Furthermore, there is a change in the stability order of the two singlet chains, with **1h** favored over **1g**. In summary, the multireference calculations indicate that the triplet open-chain isomer **1i** is preferred and the single-reference method grossly overestimates the stabilities of the biradicalic singlet-chain isomers.

Table 2. Calculated [B3LYP/6-31G(2df,p)] and Experimental Vibrational Spectra of S_7 (**1a**)[a]

symmetry	calcd wavenumbers[b]	calcd IR/ Raman intensities	exptl IR spectrum	exptl Raman spectrum
a″	531 (531)	2.5/2.8	526 sh	525 w
a′	523 (520)	9.5/9.7	*518* vs	*520* m
a′	481 (487)	2.5/16.3	*482* m	*485* s
a″	453 (474)	2.2/2.0	*463* s	*462* w
a′	380 (426)	6.3/14.6	400 vs	*402* m−s
a″	372 (426)	0.2/1.4		396 sh
a′	342 (374)	0.8/31.4	357 vw	*362* s
a″	289 (291)	0.1/5.4	*288* vw	*289* w
a′	267 (280)	1.0/2.8	*270* s	*274* w
a′	233 (240)	1.9/19.5	*236* s	*238* vs
a″	193 (194)	3.0/0.8	*195* m	
a′	168 (177)	0.4/8.9	180 m	*174* m
a″	154 (158)	0.0/13.3		*153* s
a′	126 (134)	0.4/2.4	146 m	147 w
a″	54 (28)	0.0/0.3		*c*

[a] Wavenumbers in cm^{-1}; IR intensities in km mol^{-1}; Raman intensities in A^4 amu^{-1}. Experimental intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. Solution data (CS_2) are in italics. All Others are from Solid S_7.[7] [b] QCISD/6-31G(d) values are given in parentheses. [c] Obscured by lattice modes.

According to these results, the ring-opening reaction energy of *cyclo*-S_7 (**1a**) to produce the expected triplet chain **1i** is 133.1 kJ mol^{-1}, and this process involves a spin-crossover as in the case of the related homocycles S_6 [29] and S_8 ,[30] which also produce triplet-chain molecules. For comparison, the reaction energies for the homolytic ring opening of S_6 and S_8 are 116.8 and 151.2 kJ mol^{-1}, respectively.[29,30] The energy calculated here for *cyclo*-S_7 is exactly halfway between the two values of S_6 and S_8.

The vibrational frequencies of selected S_7 isomers are given in Tables 2 and S3 (Supporting Information). The IR and Raman spectra of the stable form of S_7 (**1a**) are well-known[7] and are compared to the calculated wavenumbers and intensities in Table 2. In general, the agreement is excellent, although the calculated assignment to the two

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(34) Wong, M. W. *Top. Curr. Chem.* **2003**, *231*, 1−29.

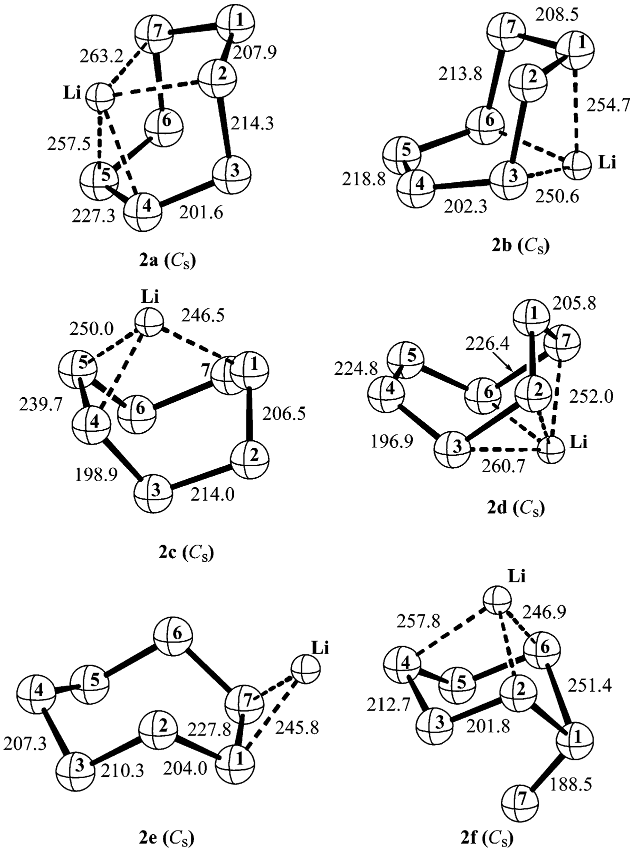
Table 3. Relative Energies[a] ΔE_0 (kJ mol^{-1}), Binding Energies[a] (kJ mol^{-1}), and Dipole Moments μ[b] (D) of Various Isomers of Composition $[LiS_7]^+$

species	symmetry	CN(Li)[c]	relative energy, ΔE_0	binding energy[d]	μ
$[LiS_7]^+$ **2a**	C_s	4	0.0	−151.2 (**1a**)	3.86
$[LiS_7]^+$ **2b**	C_s	2 + 1	20.7	−130.5 (**1a**)	5.12
$[LiS_7]^+$ **2c**	C_s	3	23.4	−139.9 (**1b**)	5.43
$[LiS_7]^+$ **2d**	C_s	2 + 2	28.1	−135.2 (**1b**)	4.48
$[LiS_7]^+$ **2e**	C_s	2	34.9	−116.1 (**1a**)	9.34
$[LiS_6{=}S]^+$ **2f**	C_s	2 + 1	43.3	−165.7 (**1d**)	4.88
$[S_6{-}SLi]^+$ **2g**	C_s	1 + 2	55.8	−153.2 (**1d**)	4.12
$[LiS_7]^+$ **2h**	C_1	1	57.4	−93.8 (**1a**)	13.36
$[S_6{-}SLi]^+$ **2i**	C_s	1 + 2	71.4	−151.1 (**1e**)	4.18
$[LiS_6{=}S]^+$ **2j**	C_s	2 + 1	82.7	−139.8 (**1e**)	4.43
$[S_6{-}SLi]^+$ **2k**	C_1	1 + 1	102.0	−144.5 (**1f**)	6.74
$[LiS_6{=}S]^+$ **2l**	C_1	2 + 1	109.0	−137.5 (**1f**)	5.86
$[S_6{-}SLi]^+$ **2m**	C_1	1	113.2	−133.3 (**1f**)	11.15

[a] G3X(MP2) level; absolute G3X(MP2) energies E_0 of **2a** and Li$^+$ are −2791.651 30 and −7.235 84 hartree, respectively. [b] B3LYP/6-31G(2df,p) level. [c] CN is the coordination number of the metal atom. [d] The S_7 isomer used as a reference is given in parentheses.

symmetry species a′ and a″ is slightly different from the previously published assignment, which was based on a normal-coordinate analysis. The main difference between the two sets of data concerns the lowest torsional mode, which is calculated at 54 cm^{-1}, while previously signals at 146 cm^{-1} have been assigned to this mode. As a consequence, the previously calculated thermodynamic functions $S°$, C_p, $(H_T - H_0)/T$, and $(G_T - H_0)/T$ for S_7 are slightly in error. For instance, the entropy $S°$ of **1a** at 298.2 K is now obtained as 414.3 J mol^{-1} K^{-1} rather than 398.6 J mol^{-1} K^{-1}, in perfect agreement with the experimental value of 408 J mol^{-1} K^{-1} derived from vapor-pressure measurements over liquid sulfur.[35] The molar heat capacity is now calculated as C_v = 127.1 J mol^{-1} K^{-1} at 298.2 K. In addition to the DFT result, we have calculated the vibrational frequencies of **1a** at the QCISD/6-31G(d) level. The QCISD frequencies (Table 2) are in good accord with the DFT values. This lends confidence to our assignment of the vibrational frequencies of **1a**. Unexpectedly, two SS vibrations (a′ and a″) are predicted to have similar wavenumbers at the QCISD level (426 cm^{-1}).

3.2. Coordination of Li$^+$ to S_7 Isomers. In our previous work, we have shown that the coordination of Li$^+$ to the various isomers of the homocycles S_6 and S_8 produces a large number of isomeric complexes: 15 minimum-energy structures have been located on the PES of $[LiS_6]^+$[15] and 23 on the PES of $[LiS_8]^+$.[16] In this work, we did not intend to fully explore the PES of $[LiS_7]^+$. Rather, we wanted to identify just the global minimum structure as well as those isomers that are of similarly low energy. Guided by the experiences made with the species $[LiS_6]^+$ and $[LiS_8]^+$, we have nevertheless located 15 isomers on the PES of $[LiS_7]^+$. The energies of most of them are given in Table 3, and the optimized geometries are shown in Figures 3 and 4. In agreement with our earlier results (topological analysis),[15] all Li−S distances above 280 pm are treated as nonbonding.



2a (C_s) **2b** (C_s) **2c** (C_s) **2d** (C_s) **2e** (C_s) **2f** (C_s)

Figure 3. Structures of the isomers **2a**−**f** of composition $[LiS_7]^+$ with symmetry and numbering of atoms, ordered by increasing relative energy (bond lengths are in picometers).

The most stable $[LiS_7]^+$ structure (**2a**) is of C_s symmetry (Figure 3), with the metal atom linked to four sulfur atoms of the global minimum structure of S_7, which has the same symmetry. The coordination takes place at those sulfur atoms that are negatively charged (Table S4 in the Supporting Information), resulting in a binding energy of −151.2 kJ mol^{-1}. The Li−S bonds are pairwise 257.5 and 263.2 pm long. Compared to the free S_7 molecule, the bond-length alternation within the seven-membered ring of **2a** is slightly enhanced by the interaction with the Li$^+$ ion, with S−S distances ranging from 201.6 to 227.3 pm, compared to free S_7, for which a bond-length range of 200.9−222.1 pm has been calculated (Figure 1). The average S−S bond length increased from 209.1 pm in S_7 (**1a**) to 210.7 pm in **2a**, which may be taken as a sign of activation of the ligand. The torsion angles are similar to those of **1a**: 76.3° (bond between atoms 1 and 2), −106.7° (between atoms 2 and 3), and 81.6° (between atoms 3 and 4).

The HOMO of S_7 is centered at the two atoms forming the unique bond, which is the longest in the molecule (see Chart 1). The main reason for the unusual length of this bond is the repulsion between the two 3p lone pairs of local π symmetry. The removal of electron density from these orbitals should increase the bond strength and shorten the bond length. Surprisingly, the opposite effect is observed in $[LiS_7]^+$ because the corresponding S−S distance increases from 222.1 pm in S_7 (**1a**) to 227.3 pm in **2a**. To understand this apparent contradiction, one needs to examine the atomic

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(35) Rau, H.; Kutty, T. R. N.; Guedes de Carvalho, J. R. F. *J. Chem. Thermodyn.* **1973**, *5*, 833−844.

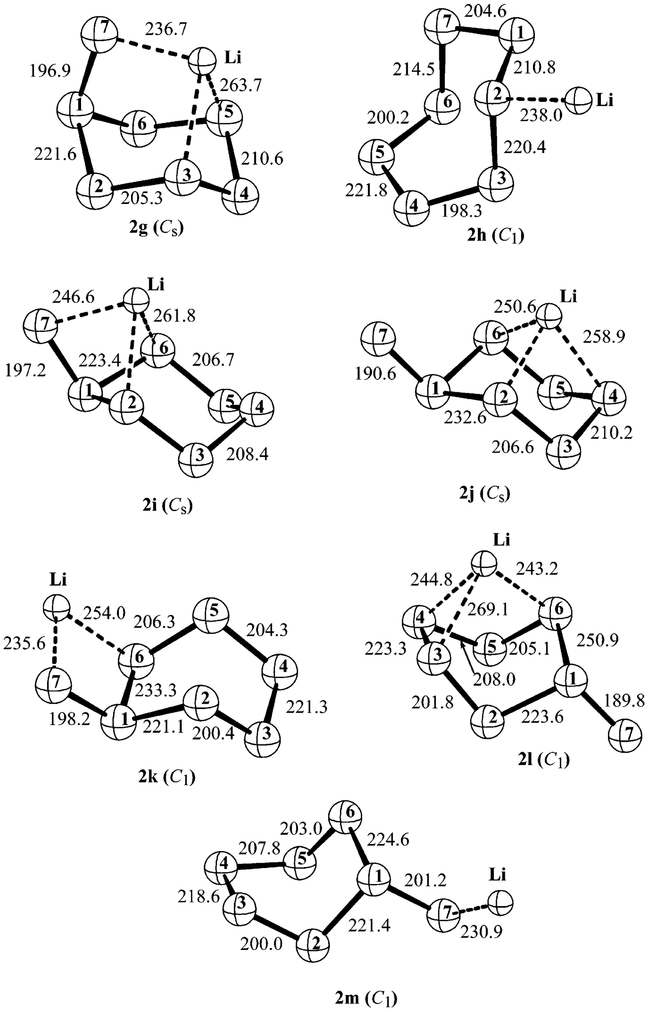

Figure 4. Structures of the isomers **2g**–**m** of composition $[LiS_7]^+$ with symmetry and numbering of atoms, ordered by increasing relative energy (bond lengths are in picometers).

charges. The NBO charge of Li in **2a** is +0.86, the smallest value of all $[LiS_7]^+$ complexes investigated (Table S5 in the Supporting Information). In other words, 0.14 electrons have been transferred from the four sulfur atoms that Li^+ is coordinated to. Unexpectedly, this electron density comes mainly from the three atoms that Li^+ is *not* coordinated to because their positive NBO charges increase from 0.01 to 0.11 (atom 1) and from 0.03 to 0.12 (atoms 3 and 6). The negative charges at atoms 4 and 5 forming the very long S−S bond increase from −0.02 in S_7 to −0.05 in **1a**. In other words, the polarization of the valence electrons by the Li^+ ion is responsible for the longer S−S bonds in the complex.

The vibrational spectrum of **2a** is very similar to the spectrum of **1a** except for the three additional modes introduced by the Li^+ ion, which are calculated at 279, 257, and 205 cm^{-1} and characterized by very high IR intensities (Table S3 in the Supporting Information).

The comparison of $[LiS_7]^+$ (**2a**) with the global minimum structures of $[LiS_6]^+$ and $[LiS_8]^+$ in Table 4 demonstrates that the binding energy increases with the size of the ligand but the bond energy, i.e., the binding energy per bond, of the Li−S interaction is greatest in the case of S_6. Accordingly, the Li−S distances are smallest in $[LiS_6]^+$. However, an even stronger metal−ligand interaction as judged by the bond energy is calculated for $[LiS_3]^+$, $[LiS_4]^+$, and $[LiS_5]^+$ (Table 4).

The $[LiS_7]^+$ isomer **2b** contains the metal atom attached to the three slightly positively charged atoms of **1a**. Accordingly, the relative energy is by 20.7 kJ mol^{-1} higher compared to the global minimum.

In the $[LiS_7]^+$ isomer **2c**, the seven-membered sulfur ring is in the endo- or boatlike conformation **1b** and functions as a tridentate ligand (symmetry C_s). Accordingly, the binding energy (−139.9 kJ mol^{-1}) is slightly smaller than that in **1a** and the charge transfer from the ligand to the metal atom is only 0.10 electrons. The Li atom is linked to the ring atoms 1, 4, and 5 with bond lengths of 246.5 and 250.0 pm, respectively (Figure 3). This almost spherical structure may be considered as a cluster. Its relative energy of 23.4 kJ mol^{-1} is about twice the relative energy of the boatlike S_7 (**1b**). Isomer **2d** is another derivative of the boatlike S_7 ring, but the metal atom is now attached to the underside of the boat.

Isomer **2e** is an eight-membered bicyclic system of C_s symmetry and similar in conformation to the crown-shaped S_8 molecule. In other words, replacement of one sulfur atom of S_8 by Li^+ has formally taken place. However, in reality, this complex is composed of the chairlike S_7 ring (**1a**) coordinated to Li^+ as a bidentate ligand. The two coordinating atoms are the most negatively charged ones in the homocycle. The bond angle at the lithium atom is 55.2°, and the Li−S bonds (245.8 pm) are slightly shorter than those in the related complexes **2a** and **2c**. The length of the S−S bond bridged by Li^+ (227.8 pm) has slightly increased from the value of free S_7 (222.1 pm), and the same holds for the other SS bonds, but the charge transfer from the heptasulfur ligand to the metal ion is only 0.05 electrons. Thus, the interaction will be mainly ion−dipole attraction rather than of the covalent type. This has already been demonstrated for the various $[LiS_6]^+$ complexes on the basis of a topological analysis.[15] Species **2e** has a rather high dipole moment of 9.34 D (Table 3). Its binding energy with repect to **1a** was calculated as −116.1 kJ mol^{-1}. In the related isomer **2h**, the metal atom is attached to just one ring atom of **1a**, resulting in a relative energy of 57.4 kJ mol^{-1} and a binding energy of −93.8 kJ mol^{-1}, the lowest value of all complexes studied in this work. This species has the highest dipole moment of all $[LiS_7]^+$ complexes investigated (13.36 D).

The most stable branched isomer of heptasulfur (**1d**) is a component of the four structures $[LiS_6{=}S]^+$ (**2f**,**j**) and $[S_6{-}SLi]^+$ (**2g**,**i**), which are all of C_s symmetry (Figures 3 and 4). Because the exocyclic sulfur atom of $S_6{=}S$ bears the highest negative charge (Table S4, in the Supporting Information), the metal atom forms short bonds of lengths 236.7 and 246.6 pm respectively to that atom in the structures **2g** and **2i**, while in the cations **2f** and **2j**, Li^+ prefers to bind exclusively to three ring atoms with distances of 246.9−258.9 pm. However, the coordination number (CN) of Li is 3 in all cases. The S−S bonds within the ring of **2f** alternate in length, and two bonds are remarkably long (251.4 pm),

Table 4. Comparison of the Properties of the Most Stable Complexes $[LiS_n]^+$ with $n = 3-8$ (CN = Coordination Number; d = Bond Length)

	$[LiS_3]^+$	$[LiS_4]^+$	$[LiS_5]^+$	$[LiS_6]^+$	$[LiS_7]^+$ (**2a**)	$[LiS_8]^+$
symmetry	C_{2v}	D_{2d}	C_s	C_{3v}	C_s	C_{4v}
CN(Li)	2	2	2+1	3	2+2	4
d(Li−S) (pm)	252.1	242.1	250.2/260.7	255.6	257.5/263.2	263.1
binding energy (kJ mol^{-1})	−112.1	−124.7	−134.3	−133.9	−151.2	−156.5
bond energy (kJ mol^{-1})	56.1	62.4	44.8	44.6	37.8	39.1
reference	this work	16	this work	15	this work	16

while the neighboring exocyclic S═S bond is as short (188.5 pm) as the bond in the triplet $S_2(^3\Sigma_g^-)$ molecule (188.9 pm[36]). The relative energy of S_6═S (**1d**) is 58.0 kJ mol^{-1}, but in the complex **2f**, this isomer is stabilized with a relative energy of only 43.3 kJ mol^{-1}.

There are three isomers that contain the isomer S_6═S with the six-membered ring in a rooflike conformation (**1f**). These asymmetrical complexes, **2k**−**m** (Figure 4), are of very similar energy despite the differing CNs of the metal atom: CN(Li) = 1 + 1 in **2k**, CN = 2 + 1 in **2l**, and CN = 1 in **2m**. The bicyclic structure **2k** is most interesting. Lithium and three sulfur atoms form an almost planar four-membered ring with torsion angles of ±3.0 (±0.4)° and sharing one edge with the roof-shaped "condensed" S_6 homocycle. The S−S−S−S torsion angles at the bonds between atoms 3 and 4 and atoms 1 and 6 are −10 ± 2°, resulting in two very long bonds while all other S−S bond distances have normal values. Structure **2l** demonstrates that the coordination of Li^+ to two ring atoms can successfully compete thermodynamically with the coordination to the more negatively charged exocyclic atom. Additionally, there may be a weak bond between Li^+ and sulfur atom no. 3 with a distance of 269 pm. In structure **2m**, the Li−S bond is pointing away from the S_6 ring and the CN of the metal atom is therefore just 1. The two torsion angles Li−S−S−S are ±127.7 ±0.2°.

Our results obtained previously for complexes of compositions $[LiS_6]^+$ and $[LiS_8]^+$ indicated that $[LiS_7]^+$ isomers of the types $[Li(S_3)(S_4)]^+$ and $[Li(S_2)(S_5)]^+$, i.e., with two separate neutral sulfur ligands, would be very unstable. Therefore, we did not search the PES of $[LiS_7]^+$ for such species. However, we did find two minima for complexes of C_1 symmetry derived from the chainlike S_7 ligands **1g** and **1h** but with relative energies of 123.8 and 150.1 kJ mol^{-1}. We will not discuss these species here.

4. Summary

We have shown that the S_7 molecule like the related S_6 and S_8 species forms at least six isomers on the potential energy surface that are more stable than several open-chain isomers. The most stable S_7 chain has a triplet configuration based on multireference calculations. The ring-opening energy ($\Delta E°$) of S_7 is 133.1 kJ mol^{-1}. The calculated vibrational spectrum of the chair form of *cyclo*-S_7 is in good agreement with experimental IR and Raman spectra. Upon coordination to lithium cations, this chair functions as a tetradentate ligand, but there are several higher-energy isomers of $[LiS_7]^+$ with CNs of Li^+ of between 1 and 4 and absolute binding energies in the range of 94−166 kJ mol^{-1}. The metal ion polarizes the various S_7 ligands and in this way activates the S−S bonds.

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Supporting Information Available: Total energies and atomic coordinates of all structures shown in Figures 1−4; vibrational frequencies of selected S_7 isomers and of **2a**; NBO atomic charges of all S_7 and S_7Li^+ isomeric structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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