

Novel Structural Principles in Poly-lithium Chemistry. Predicted Structures and Stabilities of XLi_3 , XLi_5 ($\text{X} = \text{F}, \text{Cl}$), YLi_6 ($\text{Y} = \text{O}, \text{S}$), SLi_8 and SLi_{10}

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High-level theoretical calculations are reported which indicate substantial thermodynamic stability and novel molecular structures for many 'hyperlithiated' compounds of F, Cl, O and S.

Lithium derivatives of main-group elements do not follow normal chemical rules. Extraordinary structures and stoichiometries have been predicted for CLi_6 (octahedral),¹ OLi_4 (tetrahedral),² SiLi_4 (not tetrahedral),³ PLi_5 (square-pyramidal rather than trigonal-bipyramidal)⁴ and SLi_6 (D_{3d} rather than octahedral),⁴ amongst others, using the methods of computational quantum chemistry. Experimental mass spectral results confirm the gas-phase existence of CLi_6 ,⁵ OLi_4 ,⁶ PLi_5 ⁷ and SLi_4 ,⁸ and are beginning to provide thermodynamic stability data, which generally agree well with computational predictions, but no experimental structural data are yet available. In all the ALi_n compounds considered above, all the Li atoms are directly bonded to the central A atom. In this communication we report new classes of poly-lithium clusters, which have substantial thermodynamic stability. They contain small clusters of Li atoms, such as triangular Li_3 , which encapsulate hetero-elements. These small fragments may combine by vertex-sharing, to build up larger polydentate ligands. For example, two Li_3 groups may condense to yield a planar tridentate Li_5 unit.

Geometry optimizations were performed at SCF and MP2 levels of theory from analytical first derivatives. 3-21G*, DZP and TZ2P basis sets were used. Vibrational frequencies were calculated from analytical SCF second derivatives or MP2 first derivatives. All electrons and orbitals were active in these MP2 calculations. Some final energies were obtained at the QCISD and QCISD(T) levels of theory, adopting geometries optimized with MP2 theory; for these calculations, excitations out of core orbitals and into their virtual counterparts were excluded. The DZP basis was built on the Huzinaga–Dunning (9s5p)/[4s2p] DZ set for O and F,⁹ the Huzinaga–Dunning (9s)/[4s] DZ set for Li⁹ and the Huzinaga–Dunning and Hay (11s7p)/[6s4p] DZ set for S and Cl.¹⁰ Exponents were

optimized at the SCF level for two Li p functions (0.11 and 0.44 in OLi_4 or 0.07 and 0.28 in SLi_6 ; a factor of four between the higher and lower exponents was assumed¹¹) and for the spherical harmonic components of d-type polarization functions (0.2 for Li and 0.53 for O in OLi_4 , 0.6 for F in LiF, 0.2 for Li and 0.28 for S in SLi_6 and 0.4 for Cl in LiCl). The DZP lithium basis set contained a d exponent of 0.2 for both F- and Cl-containing compounds. The TZ2P basis was obtained from the Huzinaga–Dunning (10s)/[4s] set for Li,¹² the Huzinaga–Dunning (10s6p)/[5s3p] set for F¹² and the McLean–Chandler (12s9p)/[6s5p] set for Cl.¹³ These basis sets were augmented by adding p exponents of 0.07, 0.22 and 0.66 to Li in fluorine compounds, or 0.05, 0.15 and 0.45 in chlorine compounds, and d exponents of 0.3 and 1.2 for F, 0.2 and 0.8 for Cl and 0.2 for Li. The Gaussian 90 program¹⁴ was used for all calculations.

A triangular bidentate Li_3 unit is found in planar C_{2v} isomers of FLi_3 and CLi_3 , which are shown in Fig. 1. Optimized geometrical parameters are presented in Table 1. There are only modest changes in structure as the level of theory is improved from 3-21G*/SCF through DZP/SCF to TZ2P/SCF or DZP/MP2. Addition of diffuse s and p functions to the F DZP basis produced only trivial changes to the optimized structure of C_{2v} FLi_3 . After extensive searching, just one additional stationary point was located for both FLi_3 and CLi_3 ; it is pyramidal, with C_{3v} symmetry. Both isomers proved to be true minima, with all real vibrational frequencies at 3-21G*/SCF, DZP/SCF and DZP/MP2 levels of theory. Energies for the two isomers are reported in Table 2, and binding energies for XLi_3 compared to ($\text{XLi} + \text{Li}_2$) are presented in Table 3. The planar C_{2v} isomer containing the bidentate unit is more stable than the pyramidal C_{3v} species at every level of theory considered here, for both FLi_3 and CLi_3 .

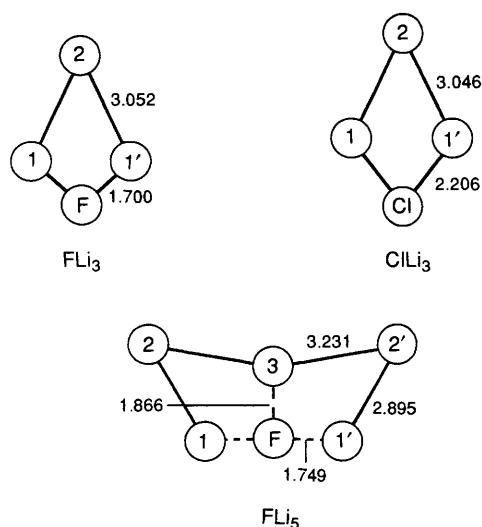


Fig. 1 Scaled diagrams of C_{2v} isomers of FLi_3 , CLi_3 and FLi_5 . Principal bonded distances, optimized at the DZP/MP2 level of theory, are indicated in Å. Solid (dashed) lines indicate the main (subsidiary) bonding interactions, but do not necessarily imply the presence of a traditional two-electron bond.

Table 1 Structures predicted for XLi_3 and XLi_5^a

		3-21G*/SCF	DZP/SCF	TZ2P/SCF	DZP/MP2
FLi_3	F-Li ¹	1.631	1.680	1.676	1.700
	F-Li ²	3.927	4.019	4.031	3.926
	Li ¹ -F-Li ²	52.2	48.5	48.3	47.6
CLi_3	Cl-Li ¹	2.265	2.215	2.210	2.206
	Cl-Li ²	4.641	4.622	4.609	4.509
	Li ¹ -Cl-Li ²	36.8	36.9	36.7	36.8
FLi_5	F-Li ¹	1.687	1.738	1.733	1.749
	F-Li ²	4.051	4.107	4.114	4.011
	F-Li ³	1.762	1.829	1.827	1.866
	Li ³ -F-Li ¹	98.7	94.2	93.8	92.3
	Li ³ -F-Li ²	58.0	55.1	54.9	52.4
CLi_5	Cl-Li ¹	2.316	2.275	2.262	2.256
	Cl-Li ²	2.514	2.489	2.501	2.450
	Cl-Li ³	4.732	4.720	4.706	4.594
	Li ³ -Cl-Li ¹	72.5	72.4	71.9	72.2
	Li ³ -Cl-Li ²	41.7	42.3	42.0	41.1

^a Distances in Å, angles in degrees. Refer to Fig. 1 for atomic numbering scheme.

Table 2 Absolute energies^a for XLi_3 and XLi_5

	3-21G*/SCF	DZP/SCF	TZ2P/SCF	DZP/MP2	DZP/QCISD ^b	DZP/QCISD(T) ^b
$FLi_3 (C_{2v})$	-121.21614	-121.90947	-121.92451	-122.14728	-122.11683	-122.11971
$FLi_3 (C_{3v})$	-121.21194	-121.89222	-121.90670	-122.13569	-122.10366	-122.10832
FLi_5	-136.03943	-136.81955	-136.83446	-137.10190	-137.06166	-137.06592
$CLi_3 (C_{2v})$	-479.70637	-481.92589	-481.96326	-482.18222	-482.10567	-482.10863
$CLi_3 (C_{3v})$	-479.68099	-481.89936	-481.93514	-482.16326	-482.08465	-482.08931
CLi_5	-494.50716	-496.82365	-496.86116	-497.12352	-497.04022	-497.04482

^a In Hartree. ^b At DZP/MP2 geometries.

Table 3 Binding energies^a for XLi_3 and XLi_5

	3-21G*/SCF	DZP/SCF	TZ2P/SCF	DZP/MP2	DZP/QCISD ^b	DZP/QCISD(T) ^b
$FLi_3 (C_{2v})$	246	184	179	196	198	200
$FLi_3 (C_{3v})$	235	138	133	166	163	171
FLi_5	142	107	103	126	125	128
$CLi_3 (C_{2v})$	143	141	131	154	164	168
$CLi_3 (C_{3v})$	76	72	57	104	109	117
CLi_5	83	75	71	91	98	102

^a Energy changes for loss of Li_2 , in kJ mol^{-1} . ^b At DZP/MP2 geometries.

Since neither basis extension from DZP to TZ2P at the SCF level, nor improving the treatment of correlation with the DZP basis from MP2 to QCISD(T), makes much difference to the C_{2v} - C_{3v} energy separation, we are confident that the greater stability of the C_{2v} geometry is firmly established. We are not aware of any previous discussion of a C_{2v} isomer for XLi_3 , though the C_{3v} isomer of FLi_3 has been reported briefly.¹⁵ Binding energies of FLi_3 and CLi_3 with respect to loss of Li_2 are substantial, at about 200 kJ mol^{-1} or 170 kJ mol^{-1} , respectively, with our most elaborate calculations. It is noteworthy that the thermodynamic stabilities of both FLi_3 and CLi_3 are increased slightly by the effects of electron correlation, and they continue to increase gradually as the treatment of correlation is improved, from MP2 to QCISD to QCISD(T). The 3-21G* basis is clearly too small to give reliable binding energies, but basis extension beyond DZP has little effect.

A tridentate Li_5 group is seen in the planar C_{2v} structures of FLi_5 and CLi_5 . FLi_5 is illustrated in Fig. 1 and optimized structural parameters for both FLi_5 and CLi_5 are displayed in Table 1. As for the XLi_3 systems, only minor structural differences are found as the level of theory is improved. An extensive search was carried out for further isomers of both FLi_5 and CLi_5 ; several additional stationary points were located, but the C_{2v} isomer shown in Fig. 1 was the only true minimum found, with all real frequencies at the 3-21G*/SCF, DZP/SCF and DZP/MP2 levels of theory for both FLi_5 and CLi_5 . Absolute energies for the FLi_5 and CLi_5 molecules are presented in Table 2, and binding energies with respect to loss of Li_2 to give C_{2v} XLi_3 are listed in Table 3. These XLi_5 compounds have high binding energies, with our best calculations predicting values of 128 kJ mol^{-1} and 102 kJ mol^{-1} for FLi_5 and CLi_5 respectively. Basis extension beyond DZP has little effect on the predicted stability, and successive improvements in the application of electron correlation are of minor consequence, so these XLi_5 compounds are unquestionably bound with respect to loss of Li_2 . The relatively slight decrease in binding energies from XLi_3 to XLi_5 suggests that the halogen atoms are not coordinatively saturated in XLi_5 . We have located thermodynamically and structurally stable structures for XLi_7 , which will be described elsewhere.¹⁶

Two of the bidentate Li_3 groups are seen in D_{2d} isomers of OLi_6 and SLi_6 . Both structures are illustrated in Fig. 2 and optimized geometrical parameters are reported in Table 4. Again, as in the halogen systems, there are only relatively minor changes in structure as the level of theory is improved from 3-21G*/SCF to DZP/MP2. Vibrational frequencies have

been calculated at all these levels of theory for OLi_6 and at the 3-21G*/SCF and DZP/SCF levels for SLi_6 . All these calculations predict the D_{2d} structure for both molecules to be true

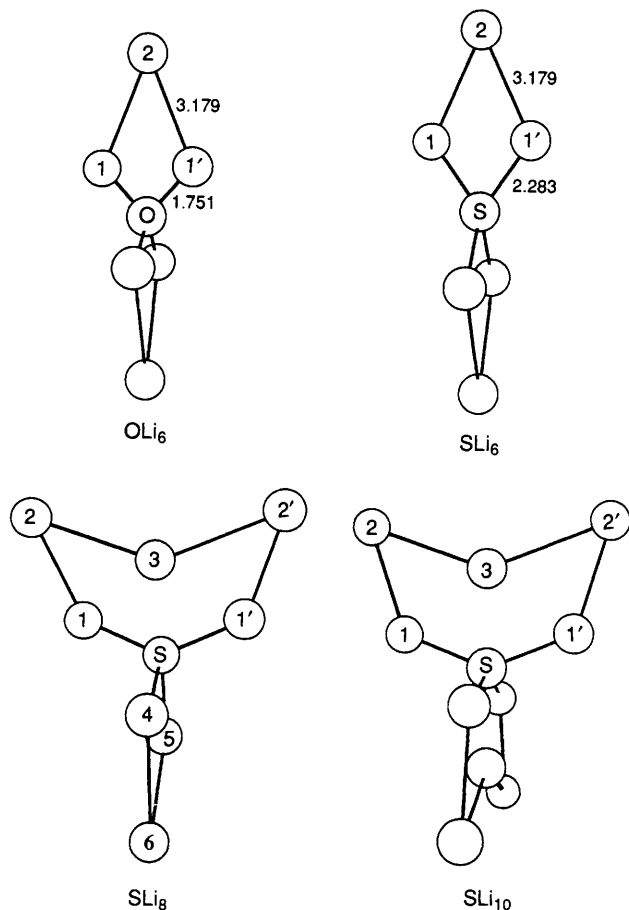


Fig. 2 Scaled diagrams of OLi_6 , SLi_6 (both D_{2d}), SLi_8 (C_s) and SLi_{10} (D_{2d}). Solid lines indicate the main bonding interactions, but do not necessarily imply the presence of a traditional two-electron bond.

Table 4 Structures predicted for YLi_6^a

		3-21G*/SCF	DZP/SCF	DZP/MP2
OLi_6	O-Li ¹	1.739	1.751	1.783
	O-Li ²	4.188	4.215	4.103
	Li ¹ -O-Li ²	44.3	43.4	43.0
SLi_6	S-Li ¹	2.315	2.284	2.283
	S-Li ²	4.747	4.744	4.612
	Li ¹ -S-Li ²	35.9	35.7	35.8

^a Distances in Å, angles in degrees. Refer to Fig. 2 for atomic numbering scheme.

Table 5 Absolute^a and binding energies for YLi_6 , SLi_8 and SLi_{10}

	3-21G*/SCF	DZP/SCF	DZP/MP2	DZP/QCISD ^c	DZP/QCISD(T) ^c
OLi_6	-119.00307	-119.68926	-120.01491	-119.93109	-119.93723
Δ^b	133	128	123	130	126
SLi_6	-440.19848	-442.33623	-442.62793	-442.53907	-442.54548
Δ^b	155	149	153	169	169
SLi_8	-455.00247	-457.23600			
Δ^b	91	80			
SLi_{10}	-469.80407	-472.13334			
Δ^b	85	74			

^a In Hartree. ^b Energy changes for loss of Li_2 , in kJ mol^{-1} . ^c At DZP/MP2 geometries.

minima. It has previously been reported that OLi_6^{15} and SLi_6^4 adopt D_{3d} structures based on a distorted octahedron, but more recent work,¹⁷ at less rigorous levels of theory than that used here, has suggested that the D_{2d} isomers illustrated in Fig. 1 are more stable. Our results show that the D_{2d} structures lie significantly lower than the D_{3d} , by approximately 170 kJ mol^{-1} for OLi_6 and 122 kJ mol^{-1} for SLi_6 at the DZP/SCF level of theory. Binding energies for the D_{2d} XLi_6 compounds with respect to loss of Li_2 are presented in Table 5. The stability of OLi_6 is quoted for dissociation to $\text{OLi}_4(T_d)^2$ and Li_2 . Consistent results for OLi_6 are obtained at all levels of theory employed, our most rigorous being DZP/QCISD(T) which predicts a thermodynamic stability of 126 kJ mol^{-1} . The stability of SLi_6 is also determined relative to SLi_4 and Li_2 . However, there are many isomers for SLi_4 which lie extremely close in energy, and the apparent ground state changes with the level of theory employed.^{4,16,18} Therefore, in calculating the stability of SLi_6 , we have considered dissociation to the most stable isomer of SLi_4 at that particular level of theory. It is noteworthy that the binding energy predicted for SLi_6 increases as the calculations become more accurate, with a thermodynamic stability of 169 kJ mol^{-1} indicated at our highest level.

Just as SLi_6 contains two of the Li_3 units found in FLi_3 , so there is a stationary point of D_{2d} symmetry for SLi_{10} , which contains two of the Li_5 clusters found in FLi_5 . Additionally, we have located a C_s structure for SLi_8 which contains one Li_3 unit and one Li_5 group. Structures for SLi_8 and SLi_{10} are presented in Fig. 2, and energies may be found in Table 5. The two Li_5 units are planar in SLi_{10} , and are arranged in perpendicular planes, but the Li_5 group in SLi_8 is slightly puckered. Both SLi_8 and SLi_{10} are true minima at both 3-21G*/SCF and DZP/SCF levels of theory. Correlated calculations were not performed for these larger systems. DZP/SCF binding energies with respect to loss of Li_2 at 80 kJ mol^{-1} for SLi_8 and 74 kJ mol^{-1} for SLi_{10} . While these are appreciably less than the binding energy calculated for SLi_6 , they do not suggest that the Li binding limit has been reached at SLi_{10} . In view of the low sensitivity of the calculated binding energies of the other poly-lithiated molecules described in this report to the level of theory used, we expect that these results for SLi_8 and SLi_{10} are fairly reliable. Structures for OLi_8 and OLi_{10} were also investigated. The most stable isomers turn out to be quite different from their sulfur counterparts, and they will be described elsewhere.¹⁶

It does not seem possible to give a simple, accurate description of the bonding in these XLi_n and YLi_m hyper-coordinate families. The Li_3 and Li_5 cluster units contain extensively delocalized Li-Li bonding interactions, as indicated by the overlap populations,¹⁹ and there is a considerable ionic component to the X-Li and Y-Li interactions. It is noticeable that the Li atom (or atoms in the case of Li_5 groups) farthest from the central F, Cl, O or S carries a substantial negative charge, of the order of -0.2 or -0.3 e (DZP/SCF), whereas the 'inner' Li atoms have the more usual positive net charges. There is little bonding between the inner Li atoms, even though they are closer together than the inner-outer

separation. The Li-Li bonding in the Li₅ units in XLi₅ or SLi_{8/10} is similar, with the two outer Li atoms bonding to the two neighbouring inner ones. The negative charges on these outer Li atoms are unusual. We do not know of any other Li derivatives where any of the lithium atoms are predicted to bear negative charge (with the possible exception of cases where Li is bonded to other alkali metals).

In view of their high thermodynamic stabilities, we believe that the XLi_n and YLi_m compounds described here could be detected by mass spectrometry, as has already happened for CLi₆⁵ and SLi₄.⁸ It should also be possible to detect them by matrix-isolation IR spectroscopy. No major differences were found in calculated vibrational frequencies obtained at the 3-21G*/SCF, DZP/SCF or DZP/MP2 levels of theory. Our analysis indicates that matrix IR spectra should distinguish between the two isomers of FLi₃. From our DZP/MP2 data, which should be the most reliable of those we have, the C_{3v} species has a very intense band at 189 cm⁻¹ and its highest frequency at 571 cm⁻¹, whereas the C_{2v} species is predicted to have relatively intense bands at both 192 and 328 cm⁻¹, and its highest frequency at 706 cm⁻¹. The C_{3v} isomer is predicted to have no bands near 328 cm⁻¹, while the C_{2v} isomer should have no bands near 571 cm⁻¹. The distinction between the isomers of CLi₃ should also be possible; the C_{2v} species has an intense band at 191 cm⁻¹ and its highest frequency at 429 cm⁻¹, whereas the C_{3v} system has intense bands at 192, 319 and 517 cm⁻¹. Vibrational spectra for the more complex XLi₅ or YLi₆ molecules are naturally more cluttered; the most intense IR bands are predicted at 187, 261, 314, 350 and 651 cm⁻¹ for FLi₅, 179, 238, 307, 337 and 431 cm⁻¹ for CLi₅, and 163, 264, 382 and 738 cm⁻¹ for OLi₆. These predicted wavenumbers are likely to be overestimated by about 5% compared to gas-phase values, though the differences compared to matrix data may be slightly larger.²⁰

It seems probable that the systematic exploration of the structural principles suggested by the results in this communication will lead to the discovery of many new compounds.

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