are still far from being good models for the ionic crystal. However, we can find some aspects in the geometrical parameters and IP's for the oligomers that point already to those properties in the crystal.

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Registry No. LiH, 7580-67-8; $(LiH)_2$, 78715-95-4; $(LiH)_3$, fence, 78715-96-5; $(LiH)_3$, ring, 65219-65-0; $(LiH)_4$, fence, 78715-97-6; $(LiH)_4$, ring, 78715-98-7; $(LiH)_4$, ring dimer, 78715-99-8; $(LiH)_5$, fence, 78716-00-4; $(LiH)_5$, ring, 78716-01-5; $(LiH)_5$, fence, 78716-02-6; $(LiH)_6$, ring, 78716-03-7; $(LiH)_6$, ring dimer, 78716-03-7; $(LiH)_6$, ring dimer, 78716-04-8; $(LiH)_6$, fence dimer, 78716-05-9; $(LiH)_7$, fence, 78716-06-0; $(LiH)_7$, ring, 78716-07-1; $(LiH)_8$, fence, 78716-08-2; $(LiH)_8$, ring, 78716-09-3; $(LiH)_3$, ring dimer, 78716-10-6; $(LiH)_8$, fence dimer, 78716-11-7.

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Structures of Complex Beryllium Hydrides and Fluorides, $LiBeX_3$ and Li_2BeX_4

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Alternative structural possibilities for $LiBeX_3$ and for Li_2BeX_4 (X = H or F) monomers were examined at various levels of ab initio molecular orbital theory. For $LiBeX_3$, there is a decided preference for attachment of lithium at the edges of BeX_3 triangles (II), rather than to corners (I) or to faces (III). For Li_2BeX_4, the results are not as clear-cut. At the highest theoretical level employed, MP2/6-31G*//4-31G, Li_2BeH_4 prefers lithium attachment to two faces of a BeH_4 tetrahedron (VII); the opposite edge arrangement (V) is next best energetically. Planar six-membered ring structures (IV) for both Li_2BeF_4 and Li_2BeH_4 are preferred at the 4-31G//4-31G level (the highest feasible for the former species). The corresponding anions BeX_3^- and BeX_4^{2-} (in both planar and tetrahedral geometries) were also examined, and the energies of various possible dissociation reactions were calculated.

Introduction

Analogous to boron and aluminum which form the well-known complex hydrides and fluorides MBX_4 and $MAlX_4$, beryllium also forms similar complex salts with alkali metals, $nMX{\cdot}BeX_2$ (n = 1 or 2).[2-7] The 1:1 complexes, e.g., $LiBeH_3$[5] and $LiBeF_3$,[4,7] are simplest; 2:1 complexes (Li_2BeH_4[5] and Li_2BeF_4[4,6,7]) also are known. Li_2BeF_4 is of technical interest; its molten salt might find use as a superior cooling and breeding agent in nuclear technology, especially in fusion reactors.[8]

The infinite-lattice crystal structures of these species are well established.[4-6] Moreover, the existence of monomeric $LiBeF_3$ and Li_2BeF_4 in the gas phase has been demonstrated mass spectroscopically.[3b] IR studies by Snelson and Cyvin[4] on matrix-isolated monomeric species led to the interesting and unusual proposal that planar IV, rather than an alternative, tetrahedral BeF_4-based geometry, represented the structure of Li_2BeF_4.

We have examined various structural possibilities for $LiBeH_3$, Li_2BeH_4, $LiBeF_3$, and Li_2BeF_4 by means of ab initio molecular orbital calculations. The parent anions, BeH_3^-, BeH_4^{2-}, BeF_3^-, and BeF_4^{2-}, were also included in this study. Structures of $LiBeH_3$ and $LiBeF_3$ have been calculated before;[9,10] for uniformity, we reexamined these species employing higher levels of theory.

Computational Methods

The structures of the fluorides and hydrides were first optimized with use of the minimal STO-3G basis set.[11] Geometry optimizations were then carried out with the small split-valence basis 4-31G[12a] (5-21G for lithium and beryllium is implied[12c]). The structures of BeH_2 and the anions BeH_3^- and BeH_4^{2-} were also calculated with the small

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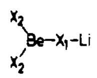
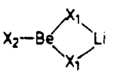


I

C_{2v}

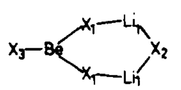


II

C_{2v}

III

C_{3v}



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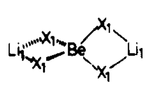
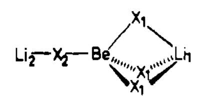


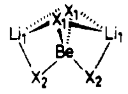
V

D_{2d}



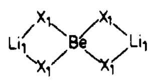
VI

C_{3v}



VII

C_{2v}



VIII

D_{2h}

split-valence basis 4-31G[12a] and with the diffuse function-augmented 4-31+G basis set, which is especially successful in treating anions.[10f,13] For the hydrides, single-point calculations were carried out on the 4-31G optimized geometries with use of the 6-31G* basis set[12b] (a split-valence basis set including d-type polarization functions on the heavy atoms). Estimates of correlation energy were made with use of second-order Møller–Plesset theory (MP2).[14] Results are designated, e.g., MP2/6-31G*//4-31G (this indicates a single-point MP2/6-31G* calculation carried out on the 4-31G-optimized geometry). Mulliken population analyses[15] employed STO-3G wave functions with STO-3G optimum geometries. All singlet spin states were calculated with use of closed-shell spin-restricted Hartree–Fock theory (RHF)[16] employing the Gaussian 76 series of programs.[17]

Tables I–V summarize the calculated energies and geometries. For $LiBeF_3$, LiF, and $(LiF)_2$ comparisons of theoretical with experimental reaction energies are possible; these data (included in Table VI) allow an evaluation of the accuracy of the various theoretical levels employed.

Results and Discussion

A. Anion Energies and Structures. We first examined the parent anions, BeH_3^-, BeF_3^-, BeH_4^{2-}, and BeF_4^{2-}. Starting from linear BeH_2[9] and BeF_2, trigonal (D_{3h}) BeH_3^- and BeF_3^- are formed by the formal addition of a hydride or a fluoride anion. Further addition of a second hydride or a fluoride anion leads to the dianions BeH_4^{2-} and BeF_4^{2-} for which square-planar (D_{4h}) as well as the classical tetrahedral (T_d) geometries were considered.[18] The calculated structures and energies (4-31+G//4-31+G and 6-31G*//6-31G* for hydrides; 4-31+G//4-31+G for fluorides) are summarized in Table I. The STO-3G results do not appear to be as reliable as those at higher levels and will not be discussed.

The Be–H bond lengths increase regularly in going from BeH_2 (1.33 Å) to BeH_3^- (1.43 Å) to T_d BeH_4^{2-} (r_{Be-H} = 1.58 Å). The fluorinated species show analogous trends: BeF_2 (r_{Be-F} = 1.40 Å), BeF_3^- (1.50 Å), and T_d BeF_4^{2-} (1.61 Å). The hydride ion affinity of BeH_2 is 55.5 kcal/mol (4-31+G//4-31+G), but BeH_3^- resists further attachment of H^- (to give T_d BeH_4^{2-}) by 77.9 kcal/mol. Because of this endothermicity, the structure of BeH_4^{2-} (and BeF_4^{2-}) has been calculated by the imposition of symmetry. The fluoride affinity of BeF_2 is −96.1 kcal/mol; the second F^- attachment (to T_d BeF_4^{2-}) is endothermic by +54.5 kcal/mol (4-31+G//4-31+G).

	ΔH_R
$BeH_2 + H^- \rightarrow BeH_3^-$	−55.5
$BeH_3^- + H^- \rightarrow BeH_4^{2-}$	77.9
$BeF_2 + F^- \rightarrow BeF_3^-$	−96.1
$BeF_3^- + F^- \rightarrow BeF_4^{2-}$	54.5

Our previous examination of tetrahedral, planar (D_{4h}), and pyramidal (C_{4v}) ZH_4 structures[18] prompted us to include planar BeH_4^{2-} and BeF_4^{2-} in the present study (Table I). On the basis of our previous conclusions, only a relatively small difference in energy between tetrahedral and planar forms was to be expected for these species. Indeed, planar (D_{4h}) BeH_4^{2-} is only 61.8 kcal/mol (MP2/6-31G*//6-31G*) less stable than the tetrahedral form; this value is considerably lower than that for BH_4^- (127.6 kcal/mol, at the same level) and only about two-fifths of the corresponding difference calculated for methane (159.7 kcal/mol). The T_d–D_{4h} energy difference for BeF_4^{2-} also is about 51 kcal/mol (4-31+G//4-31+G).

The bond lengths of the planar species are longer than in the tetrahedral forms. All data for these D_{4h} beryllium compounds refer to the δ lumomer, which has a HOMO of d-type symmetry. The corresponding π lumomers are expected to be several hundreds of kcal/mol higher in energy.[18]

B. Energies and Structures of the 1:1 Complexes, $LiBeX_3$ (X = H or F). On the basis of the trigonal-planar (D_{3h}) anions BeH_3^- and BeF_3^-, three types of geometries were examined as possible candidates for the global minimum of each $LiBeX_3$ species. In principle, the lithium cation might be located at a corner, at an edge, or at a face of a BeX_3^- triangle.[9,10] Corner complexation leads to the C_{2v} structure I with a single interaction between lithium and X. Complexation at a BeX_3^- edge gives the C_{2v} structure II, characterized by a bridging lithium. The third possibility, location of the lithium cation on a BeX_3^- face, results in C_{3v} symmetry and triple Li–X coordination. The BeX_3^- unit in III can no longer be expected to be planar but bends toward lithium.

Calculations at various theoretical levels for the $LiBeX_3$ species are summarized in Table II (energies) and Table III (geometries). The data at the highest levels, MP2/6-31G*//4-31G for the hydrides and 4-31G//4-31G for the fluorides, will be discussed. Using various double-ζ basis sets, Charkin et al. obtained similar results.[10]

For both $LiBeH_3$ and $LiBeF_3$, type II structures with doubly coordinated lithium atoms are lowest in energy, reflecting the favorable, planar BeX_3 arrangements.[3a] For X = H, structure III is second best. In spite of the higher coordination of the Li cation, the pyramidalization of the BeX_3^- unit is unfavorable. Structures I and III for $LiBeF_3$ are of comparable energy, whereas structure I for $LiBH_3$ is not a minimum on the potential energy surface.

Some general trends in the bond lengths of I–III are apparent. Be–H bonds involving unbridged hydrogen atoms (1.35–1.38 Å) are slightly shorter than the corresponding bond lengths in the parent anion (BeH_3^-, r_{Be-H} = 1.43 Å). The Be–H bond lengths involving lithium-bridged hydrogens are much more variable (1.41–1.52 Å) and depend on the coordination number of the neighboring lithium atoms: the higher the lithium coordination, the shorter the Be–H bond. The Be–F bond lengths in the corresponding $LiBeF_3$ isomers follow the same trends (Table III).

A similar degree of pyramidalization around Be in structure III is indicated for both X = H and X = F; the X–Be–X bond angles are reduced to 110.9° (X = H) and to 107.7° (X = F) because of the bending of the BeX_3^- unit toward the lithium

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Table I. Calculated Total Energies *E* (hartrees) and Optimized Geometries[a] for BeX_2, BeX_3^-, and BeX_4^{2-} Molecules

molecule	symm	STO-3G//STO-3G		4-31G//4-31G		4-31+G//4-31+G		MP2/4-31+G//4-31+G	6-31G*//6-31G*		MP2/6-31G*//6-31G*
		E	Be-X	*E*	Be-X	*E*	Be-X	*E*	*E*	Be-X	*E*
BeH_2	$D_{\infty h}$	−15.561 35	1.291	−15.754 61	1.332	−15.755 95	1.333	−15.785 88	−15.765 93	1.334	
BeF_2	$D_{\infty h}$	−210.644 47	1.329	−213.442 25	1.390	−213.462 83	1.401				
BeH_3^-	D_{3h}	−16.040 31	1.313	−16.312 46	1.436	−16.326 76	1.438	−16.373 53	−16.326 90	1.434	
BeF_3^-	D_{3h}	−308.618 48	1.406	−312.893 17	1.480	−312.942 25	1.497				
BeH_4^{2-}	T_d	−16.180 51	1.385	−16.627 06	1.594	−16.682 22	1.575	−16.748 61	−16.642 99	1.584	−16.713 67
BeH_4^{2-}	D_{4h}	−15.983 21	1.556	−16.537 81	1.721	−16.577 11	1.738	−16.634 38	−16.551 73	1.717	−16.615 19
BeF_4^{2-}	T_d	−406.244 17	1.519	−412.081 96	1.584	−412.181 64	1.614				
BeF_4^{2-}	D_{4h}	−406.127 44	1.593	−411.985 53	1.653	−412.100 78	1.682				

[a] Bond lengths in Å.

Table II. Calculated Total Energies E_{tot} (hartrees) and Relative Energies E_{rel} (kcal/mol) for the $LiBeX_3$ Molecules

X	structure	STO-3G//STO-3G		4-31G//4-31G		6-31G*//4-31G		MP2/6-31G*//4-31G	
		E_{tot}	E_{rel}	E_{tot}	E_{rel}	E_{tot}	E_{rel}	E_{tot}	E_{rel}
H	I	−23.442 47	24.7	−23.762 23	18.1	−23.777 65	20.8	−23.838 60	22.6
	II	−23.481 86	0.0	−23.791 14	0.0	−23.810 81	0.0	−23.874 56	0.0
	III	−23.458 04	15.0	−23.768 96	13.9	−23.788 70	13.9	−23.856 68	11.2
F	I	−316.130 34	46.2	−320.354 51	20.1				
	II	−316.204 02	0.0	−320.386 47	0.0				
	III	−316.178 23	16.2	−320.349 11	23.4				

Table III. Optimized Geometries[a] of the $LiBeX_3$ Molecules

X	structure	symm	Li-Be	$Be-X_1$	$Be-X_2$	$Li-X_1$	X_1-Be-X_2	X-Li-X
				STO-3G				
H	I	C_{2v}	3.124	1.568	1.292	1.555	110.7	
	II	C_{2v}	2.158	1.440	1.286	1.694	128.4	83.5
	III	C_{3v}	1.842	1.358		1.908	110.3	71.5
F	I	C_{2v}	2.992	1.509	1.361	1.483	113.3	
	II	C_{2v}	2.178	1.461	1.334	1.638	131.3	84.2
	III	C_{3v}	1.787	1.430		1.763	103.9	79.4
				4-31G				
H	I	C_{2v}	3.117	1.522	1.377	1.595	111.7	
	II	C_{2v}	2.285	1.470	1.353	1.788	128.6	80.1
	III	C_{3v}	1.980	1.411		2.045	110.9	69.2
F	I	C_{2v}	3.178	1.563	1.445	1.615	114.1	
	II	C_{2v}	2.334	1.535	1.419	1.762	131.0	82.3
	III	C_{3v}	1.991	1.491		2.011	107.7	73.6

[a] Bond lengths in Å; angles in deg.

Table IV. Calculated Total Energies E_{tot} (hartrees) and Relative Energies E_{rel} (kcal/mol) for the Li_2BeX_4 Molecules

X	structure	STO-3G//STO-3G		4-31G//4-31G		6-31G*//4-31G		MP2/6-31G*//4-31G	
		E_{tot}	E_{rel}	E_{tot}	E_{rel}	E_{tot}	E_{rel}	E_{tot}	E_{rel}
H	IV	−31.419 60	0.0	−31.837 65	0.0	−31.858 57	0.0	−31.939 05	8.0
	V	−31.406 54	8.2	−31.827 61	6.3	−31.853 51	3.2	−31.944 04	4.9
	VI	−31.363 55	35.3	−31.793 64	27.6	−31.816 06	26.7	−31.908 76	27.0
	VII	−31.402 83	10.5	−31.829 57	5.1	−31.855 91	1.7	−31.951 85	0.0
	VIII	−31.336 23	52.3	−31.767 09	44.3	−31.877 89	41.1	−31.877 89	46.4
F	IV	−421.784 15	11.6	−427.325 73	0.0				
	V	−421.752 96	31.1	−427.315 97	6.1				
	VI	−421.701 78	63.3	−427.272 04	33.7				
	VII	−421.802 58	0.0	−427.303 94	13.7				
	VIII	−421.689 78	70.8	−427.257 86	42.6				

atom. The X–Li bonds are much longer than in the other forms, I and II. However, the very short distance between lithium and beryllium (ca. 2.0 Å for both X = H and X = F) suggests that significant Li–Be interactions must be present. Interestingly the interaction is bonding in the hydride (overlap population = 0.40) but is antibonding in the fluoride (overlap population = −1.15); due to the fluorine electronegativity, positive charges result on *both* Li and Be, 0.38+ and 0.27+, respectively. The planar structures I and II for $LiBeF_3$ show modest pπ–pπ interactions among fluorine, beryllium, and lithium. The π-overlap population involving terminal fluorine and beryllium is 0.14–0.16, whereas values for the bonds between bridged fluorine and beryllium or lithium are 0.04–0.06.

C_{3v} structures similar to III were also found for the carbenoids CX_3Li (X = Cl or F), but the two additional electrons in these species permit a considerably greater degree of bending toward the lithium atom than in III (X = F).[19]

C. Structures and Energies of the 1:2 Complexes, Li_2BeX_4 (X = H or F). Five structural types, IV–VIII, were considered for $LiBeX_4$ (X = H or F). Structure IV is based on the interesting and unusual geometry proposed by Snelson et al.;[4]

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[19] Clark, T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**, *101*, 7747.

Table V. Optimized Geometries for the Li_2BeX_4 Molecules[a]

X	structure	symm	Li-Be	Be-X_1	Be-X_2	Be-X_3	Li_1-X_1	Li_1-X_2	Li_2-X_2	X_1-Be-X_1	Be-X-Li	X-Li-X
						STO-3G						
H	IV	C_{2v}		1.421	3.490	1.289	1.668	1.679		116.1	124.9	126.7
	V	D_{2d}	2.135	1.449			1.671			102.6		85.2
	VI	C_{3v}	1.849	1.405	1.457		1.759		1.540	101.9		76.7
	VII	C_{2v}	1.965	1.511	1.380		1.837	1.782		89.8	139.4[b]	97.6[c]
	VIII	D_{2h}	2.230	1.566			1.587			90.8		89.2
F	IV	C_{2v}		1.442	3.170	1.341	1.581	1.553		109.5	131.5	86.8
	V	D_{2d}	2.183	1.482			1.620			95.8		87.2
	VI	C_{3v}	1.833	1.474	1.472		1.714		1.484	98.9		81.6
	VII	C_{2v}	1.909	1.581	1.427		1.741	1.694		84.8	150.6[b]	91.5[c]
	VIII	D_{2h}	2.320	1.541			1.603			87.0		83.0
						4-31G						
H	IV	C_{2v}		1.449	3.628	1.359	1.747	1.761		113.3	129.0	122.7
	V	D_{2d}	2.250	1.494			1.760			102.8		83.1
	VI	C_{3v}	2.001	1.482	1.452		1.900		1.573	102.4		89.1
	VII	C_{2v}	2.083	1.578	1.418		1.933	1.879		88.3	139.0[b]	98.1[c]
	VII	D_{2h}	2.386	1.601			1.699			90.7		84.3
F	IV	C_{2v}		1.520	3.508	1.428	1.722	1.676		109.0	131.1	
	V	D_{2d}	2.319	1.575			1.737			96.9		85.5
	VI	C_{3v}	1.997	1.569	1.547		1.869		1.611	99.6		79.7
	VII	C_{2v}	2.091	1.682	1.499		1.895	1.872		85.1	148.0[b]	91.6[c]
	VIII	D_{2h}	2.463	1.642			1.701			87.0		83.3

[a] Bond lengths in Å; angles in deg. [b] X_2-Be-X_2. [c] Li-Be-Li.

Table VI. Heats of Dissociation and Ionization Reactions, ΔH_R (kcal/mol)

reaction[a]	4-31G// 4-31G	6-31G*// 4-31G	exptl
$Li_2BeH_4 \rightarrow LiBeH_3 + LiH$	43.4	42.0	...
$LiBeH_3 \rightarrow BeH_2 + LiH$	37.1	40.2	...
$Li_2BeF_4 \rightarrow LiBeF_3 + LiF$	72.3		...
$LiBeF_3 \rightarrow BeF_2 + LiF$	75.4	65.3[e]	59.4[b]
$(LiH)_2$ $(D_{2h}) \rightarrow 2LiH$	45.0	46.8[c]	...
$(LiF)_2$ $(D_{2h}) \rightarrow 2LiF$	76.1	68-70[d]	61.4[b]
$LiBeH_3 \rightarrow Li^+ + BeH_3^-$	154.0	146.8[e]	...
$LiBeF_3 \rightarrow Li^+ + BeF_3^-$	163.2	147.6[e]	...
$LiH \rightarrow Li^+ + H^-$	201.9	161.9[e]	162.9[b]
$LiF \rightarrow Li^+ + F^-$	215.3	178.5[e]	182.7[b]

[a] Data for lowest energy structures were employed. [b] Calculated from ref 7. [c] 6-31G*//STO-3G, calculated from data in ref 9a. [d] Higher level calculation values from ref 10c. [e] 4-31+G//4-31+G. Diffuse orbitals on the first-row atoms (and on the hydrogen in H^-) have been added to the 4-31G basis set. See text.

C_{2v} symmetry was indicated by the IR spectrum of matrix-isolated $LiBeF_3$. Structure IV is based on the trigonal-planar BeX_3^- anion rather than on the tetrahedral geometry of the BeX_4^{2-} dianion from which alternative structures V–VII can be derived. Trial geometry VIII was based on planar BeX_4^{2-}.

Many studies of the coordination of metal cations to tetrahedral AX_4 units have been reported.[20,21] In general, corner attachment (monocoordination) is less favorable than edge (dicoordination) or face (tricoordination) alternatives. Lithiation of two opposite edges of the BeX_4^{2-} tetrahedron leads to structure V, a spiro[4.4] complex of D_{2d} symmetry. In the C_{3v} structure VI, the tricoordinated lithium atom is located on one face of the BeX_4^{2-} tetrahedron; the other lithium, on the corner opposite to the lithiated face, is monocoordinated. Structural type VII results from lithiation of two faces of the BeX_4^{2-} tetrahedron (C_{2v}). Here both lithiums achieve the highest possible coordination (three) in this series of compounds. The lithium atoms in VIII are located at two opposite edges of the BeX_4^{2-} square. The resulting arrangement has D_{2h} symmetry and is the planar analogue of the spiro structure V.

The computational results are summarized in Table IV (energies) and Table V (geometries). An unusually large dependence of the calculated relative energies on the theoretical level was found. Nevertheless, the five isomeric structures can be classified into two sets: IV, V, and VII are low in energy and are candidates for the global minimum of Li_2BeX_4. Members of the other set, VI and VIII, are high in energy and are unlikely. Results at the highest computational levels (for hydrides MP2/6-31G*//4-31G and for fluorides 4-31G//4-31G) should be the most reliable and provide the basis for the following discussion.

Within the set of favorable isomers, structure IV (X = F) is lowest in energy for Li_2BeF_4 but IV (X = H) is 8 kcal/mol higher in energy than the best Li_2BeH_4 structure (VII). This low energy is somewhat surprising, since one of the four X atoms is monocoordinated and beryllium does not utilize the tetrahedral four-coordination found in the majority of known crystal structures.[20] However, tricoordinate beryllium also is known.[21] The larger angles around lithium in the planar six-membered ring are favored. A relatively flexible (Li–F–Li) unit bridges an edge of trigonal BeX_3^-. The bond angles around Be in the ring are reduced to 113.3° in Li_2BeH_4 and to 109.0° in Li_2BeF_4. As in $LiBeX_3$, coordination of X with Li increases the BeX bond lengths.

For both $LiBeH_4$ and Li_2BeF_4, the spiro structure V (X = H or F) is second lowest in energy (E_{rel} = +5 and +6 kcal/mol, respectively). Lithiation of two opposite edges of the BeX_4^{2-} tetrahedron results in compression of the X–Be–X bond angles of 102.8° (X = H) and to 96.9° (X = F). Compared to the ring Be–X_1 bonds of IV, the Be–X_1 bonds in V are lengthened considerably to 1.49 Å (X = H) and 1.58 Å (X = F); this shows that coordination in four-membered rings is less favorable than in six-membered rings. The relative short Be–Li distances in V (X = H or F) (2.25 Å in Li_2BeH_4 and 2.32 Å in Li_2BeF_4) indicate significant interaction (BeLi overlap populations: +0.33 (bonding) in Li_2BeH_4 but −0.61 (antibonding) in Li_2BeF_4).

The third favorable C_{2v} structural type, VII (X = H or F), was lowest in energy for Li_2BeH_4 but only third best (E_{rel} = 13.7 kcal/mol) for Li_2BeF_4. As in structure V, the ideal BeX_4^{2-} tetrahedron suffers significant distortions due to lithiation: the X_2BeX_2 angles, involving *doubly* coordinated X_2 atoms, are widened to 139° (X = H) and to 148° (X = F), whereas the X_1BeX_1 angles involving triply coordinated X_1

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(20) Snow, A. J.; Rundle, R. E. *Acta Crystallogr.* **1951**, *4*, 348.
(21) Hall, B.; Farmer, J. B.; Shearer, H. M. M.; Sowerby, J. D.; Wade, K. *J. Chem. Soc., Dalton Trans.* **1979**, *102*.

atoms are reduced to 88.3° (X = H) and to 85.1° (X = F). Again reflecting the coordination, the Be–X_1 bonds are lengthened compared to the Be–X_2 bonds. In addition to Snelson's structure IV (X = F), VII is also a possible candidate for the C_{2v} Li_2BeF_4 isomer.

On the basis of the structural details found for IV, V, and VII, it is easy to understand why isomers VI and VIII are higher in energy. The C_{3v} structures (VI, X = H or F) (E_{rel} = 27 kcal/mol for Li_2BeH_4 and 34 kcal/mol for Li_2BeF_4) are unfavorable because one of the lithium atoms is only attached to only a single X atom. The $LiBeX_3$ forms, I, similar in this respect, are also high in energy. VI was examined by imposing C_{3v} symmetry, but this structure is more likely to be a saddle point than a mimimum on the potential energy surface. The structural alternative VIII (X = H or F), obtained by imposing D_{2h} symmetry, was highest in energy (E_{rel} = 46 kcal/mol for Li_2BeH_4 and 43 kcal/mol for Li_2BeF_4). Compared to the corresponding D_{2d} isomers V, the BeX bonds in VIII are lengthened considerably: Be–H, 1.60; Be–F, 1.64 Å. In addition to the unfavorable four-membered ring (also present in V), structure VIII suffers from the planar BeX_4^{2-} arrangement. However, lithium coordination *reduces* the tetrahedral/planar energy difference from about 60 kcal/mol for both BeH_4^{2-} and BeF_4^{2-} to about 40 kcal/mol (V vs. VIII).

The pπ–pπ STO-3G overlap populations for planar Li_2BeF_4 structures IV and VI are 0.16 (terminal F–Be) and 0.06–0.08 (bridging F to Be or Li).

D. Dissociation and Ionization Reactions. Mass spectroscopic studies[3b] of $LiBeF_3$ and Li_2BeF_4 suggest the possibility of thermal dissociation of these species in the gas phase. The calculated heats of dissociation for Li_2BeH_4, $LiBeH_3$, Li_2BeF_4, and $LiBeF_3$ (based on the lowest energy structures for each species) are summarized in Table VI, along with comparison data for $(LiH)_2$ and $(LiF)_2$.

Similarly large energies (40–47 kcal/mol at 6-31G*//4-31G) are needed to dissociate the lithium hydride dimer (D_{2h}) or to remove a LiH molecule from either $LiBeH_3$ or Li_2BeH_4. The fluoride complexes are even more stable toward dissociation; about 70 kcal/mol (4-31G//4-31G) is needed to split off LiF from D_{2h} Li_2F_2,[22] $LiBeF_3$, or Li_2BeF_4.[9a,10c] These data suggest that equilibria involving BeX_2 and LiX should lie entirely on the side of the complexes. Except at extremely high temperatures, the vapor pressure of BeX_2 in the presence of LiX should not be measurable.

The complexes might dissociate into ions under mass spectroscopic conditions. We calculated the heats of ionization only for the $LiBeX_3$ species (Table VI); the energies for ionization of Li_2BeX_4 into Li^+ and $LiBeX_4^-$ are expected to be of similar magnitude. Such ionic dissociations are highly endothermic; the 4-31+G//4-31+G values are 147 kcal/mol for $LiBeH_3$ and 148 kcal/mol for $LiBeF_3$. Nevertheless, some stabilization by charge delocalization in the complex anions is shown by the comparison of the data for the dissociation of LiH and LiF into ions, indicated experimentally to require 163 and 183 kcal/mol, respectively. (The calculated values at the 4-31+G level are in very good agreement.) The electronegative fluorine atoms in BeF_3^- accept and distribute the extra charge somewhat better than the hydrogen atoms in BeH_3^-. Thus, the difference in ionization energies between LiF and $LiBeF_3$, 31 kcal/mol, is larger than the 15 kcal/mol difference calculated for LiH vs. $LiBeH_3$ (4-31+G).

Conclusions

Several factors compete in determining the most stable structures. Higher coordination is favorable, but this is often achieved at the expense of smaller angles and longer distances. For tetracoordination, tetrahedral, rather than planar, arrangements around beryllium are preferred; for tricoordination, trigonal planar is better than pyramidal. Metal–metal interaction is indicated in many of the structures, despite expectations based on simple electrostatic considerations.

Structure II for $LiBeX_3$ is most favorable both for X = H and X = F. Insertion of an additional LiX unit into a LiX bond to give planar IV combines the favorable features of I with better angular arrangements. Despite the lower coordination of all the metal atoms in IV, this structure competes well against the best alternatives based on tetrahedral tetracoordinate beryllium, V and VII. Li_2BeH_4 is indicated to prefer structure IV at the MP2/6-31G*//4-31G level; the Li_2BeF_4 ordering is IV (best) > V > VII (4-31G//4-31G), but higher levels of theory are needed to verify this conclusion. Although we have emphasized the energies of various forms, these molecules are likely to have fluxional character.

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Registry No. $LiBeH_3$, 25282-11-5; $LiBeF_3$, 15552-34-8; Li_2BeH_4, 19321-21-2; Li_2BeF_4, 13874-36-7.

Supplementary Material Available: Listings of Mulliken analysis data (dipole moments, charges, overlap populations (STO-3G)) and calculated total energies needed to determine the values in Table VI (2 pages). Ordering information is given on any current masthead page.

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(22) Kollman, P. A.; Liebman, J. F.; Allen, L. C. *J. Am. Chem. Soc.* **1970**, *92*, 1142. Baskin, C. P.; Bender, C. F.; Kollman, P. A. *Ibid.* **1973**, *95*, 5868.

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Vaporization Characteristics of Ammonium Tetrachloroferrate(III). The Monoammine of Iron(III) Chloride in the Vapor Phase

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The behavior of NH_4FeCl_4 on heating is found to be complex. The iron(III) tends to be reduced by ammonia; however as HCl, a product of the reduction reaction, accumulates, the system stabilizes sufficiently to permit the study of vaporization equilibria. Absorption spectroscopy, mass spectrometery, and diaphragm gauge measurement of total pressures have been used to determine the composition of the vapor phase, and thermodynamic data for the reactions $NH_4FeCl_4(C) = NH_3FeCl_3(g) + HCl(g)$ and $NH_4FeCl_3(C) = FeCl_2(s) + NH_3(g) + HCl(g)$ are reported. The UV–visible absorption spectrum of NH_3FeCl_3 between 240 and 500 nm is given.

Ammonium tetrachloroferrate(III) is easily prepared by reaction of ammonium chloride and ferric chloride and has been studied by a number of investigators.[1-7] In the present work, the molecular composition of the vapor phase formed