Molecular Lattice Fragment of LiI. Crystal Structure and ab Initio Calculations of $[LiI(NEt_3)]_4$

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Numerous crystal structures of donor-stabilized LiX species are known, but only two of them show a heterocubane arrangement $[LiX(Do)]_4$ (X = Cl, Br; Do = donor) in the solid state. Herein we report the X-ray crystal structure of $[LiI(NEt_3)]_4$ (**1**), obtained by the reaction of $LiN(SiMe_3)_2$ with either GaI or AlI in the presence of NEt_3. The structural backbone of **1** is a $[LiI]_4$ heterocubane core, which is compared to $[LiX]_4$ (X = Cl, Br) as well as to $[Li(CH_3)]_4$. The energetics of the formation of **1** and its stability with respect to solid LiI is rationalized and additionally supported by DFT (density functional theory) calculations.

Introduction

Lithium compounds, such as lithium alkyl and lithium amide species, are frequently used as starting materials in metathesis reactions with elemental halides, e.g., MX (M = Al, Ga; X = Cl, Br, I).[1] The driving force behind these reactions is the formation of the solid lithium halides.

Although a variety of donor-stabilized lithium halides containing monomeric, dimeric, tetrameric, larger oligomeric, and polymeric units have been characterized, only two examples with a heterocubane LiX structure are known to date: $[LiCl(HMPTA)]_4$ (**2**)[2] and $[LiBr(Et_2O)]_4$ (**3**).[3] Many Li halide structures have been published[3] as well as a comparison of various oligomeric Li halide structures including a detailed analysis of $[LiCl]_4$.[4]

Herein, we report the solid-state structure of $[LiI(NEt_3)]_4$ (**1**) that was obtained by reacting a solution of metastable MI (M = Al, Ga) with $LiN(SiMe_3)_2$ in the presence of NEt_3. The structure of the respective crystalline Al or Ga amide could as yet not be determined.

Many tetrameric organolithium compounds with a heterocubane structure are known.[5] Therefore, we discuss **1** in comparison to the homologous $[LiX]_4$ (X = Cl, Br) tetramers as well as to $[LiCH_3]_4$, the simplest organolithium compound.[6]

Experimental Section

All reactions were carried out in an atmosphere of dry nitrogen or argon using standard Schlenk techniques. The compound $LiN(SiMe_3)_2$ was prepared from $HN(SiMe_3)_2$ and ^nBuLi in hexane.[7]

Synthesis of $[LiI(NEt_3)]_4$ (1). A solution of GaI (3 mL, 1.1 mmol) in toluene/NEt_3 (4:1) was added to 165 mg (1.0 mmol) of $LiN(SiMe_3)_2$ in 5 mL of toluene at −78 °C.[8] The dark-red reaction mixture was allowed to warm to room temperature (12 h). Within a few days colorless crystals of **1** precipitated upon cooling to −30 °C. Filtration and recrystallization of the precipitate gave **1** in 95% yield.

Recently, **1** was also obtained by using AlI as starting material.[9] To a mixture of AlI (3 mL, 1.0 mmol) in toluene/Et_2O (3:1) 150 mg $LiN(SiMe_3)_2$ (0.9 mmol) was added, heated to 65 °C, and subsequently cooled to room temperature in several cycles. Addition of 3 mL of toluene/NEt_3 (1:1) led to the immediate precipitation of a brown amorphous solid. After several months at −30 °C colorless crystals of **1** were formed.

X-ray Crystallography. The X-ray crystallographic data for **1** were obtained from a single crystal mounted on a glass fiber using a STOE STADI4 four-circle diffractometer. The cell parameters were refined from 59 reflections with $20° < 2\theta < 33°$ scanned at positive and negative 2θ positions. Two standard reflections were recorded every 2 h and showed no decay during the entire measurement. Intensity measurements were performed by ω-scans in the range $3° < 2\theta < 55°$ and 5600 (1222 independent) reflections. An empirical absorption correction on the data set was carried out on the basis of 10 reflections measured at different Ψ-angles. LP correction was performed by the STOE software XRED. The structure was solved by direct methods (SHELXS86), and 109 parameters were refined by full matrix least squares against F^2 (SHELXL-93) with anisotropic thermal parameters for all non-hydrogen atoms.[10,11] The hydrogen atoms were found from the difference Fourier maps and refined freely with isotropic thermal parameters. I, Li, and N atoms lie on 8-fold special positions, thus forming two heterocubane units per unit cell. One of the ethyl groups is disordered over two positions. R1 = 0.018 and wR2 = 0.0349 (for 905 reflections with $F > 4\sigma(F)$), where R1 and wR2 are defined as

$$R1 = \frac{\sum ||F_o| - |F_c||}{\Sigma |F_o|}$$

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Table 1. Crystallographic Data for **1**

chemical formula	$I_4Li_4N_4C_{24}H_{60}$
fw	940.12
space group	$P4_2/nmc$ (no. 137)
a/Å	13.007(2)
c/Å	11.581(2)
V/Å^3	1959.4(5)
Z	2
T/K	200(2)
λ/Å	0.710 73
ρ_{calcd}/g cm^{-3}	1.593
μ/mm^{-1}	3.197
$R1^a$	0.0180
$wR2^b$	0.0349

[a] $R1 = (\sum||F_o| - |F_c||)/(\sum|F_o|)$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2]^{1/2}$; $w = 1/[(\sigma^2(F_o^2)] + (0.115)P^2 + 0.4631P)$.

and

$$wR2 = [\sum w(F_o^2 - F_c^2)^2]^{1/2}$$

Table 1 provides a summary of the crystal data, data collection, and refinement parameters.

DFT Calculations. The DFT calculations (functional BP86) were carried out using the RI-DFT (RI = resolution of identity) implementation of the TURBOMOLE[12,13] suite of programs using the SV(P) [split valence (polarization)][14] basis set for C, H, N, Li as implemented within TURBOMOLE. The relativistic 46-electron ECP (effective core potential)−46-MWB reported by Dolg et al.[15] was used for I. All species were fully optimized at the given level and are true minima with no imaginary frequencies. The SV(P) basis set is known to slightly overestimate lithium-element bond distances with respect to experimental data.[16] An Ahlrichs−Heinzmann population analysis[17,18] was performed using the minimum geometry and the BP86/SV(P) electron density. The validity of our DFT calculations is established by the excellent agreement between the calculated (177 kJ/mol) and the experimentally observed (179 kJ/mol) dimerization energy[19] of two gaseous LiX molecules to give the D_{2h} symmetric $[LiI]_2$ dimer.

Results and Discussion

The metathesis reaction of GaI and $LiN(SiMe_3)_2$ was designed to yield $GaNR_2$ species. However, only an orange oil sensitive to oxygen and moisture could be obtained, which disproportionates to metallic Ga and $Ga\{N(SiMe_3)_2\}_3$ upon warming to 0 °C. From the mother liquor of this reaction, crystals of **1** precipitated. More recently, crystals of **1** could also be isolated from a similar reaction of AlI with $LiN(SiMe_3)_2$, which finally leads to the formation of an Al_{77} cluster ion[1] as the aluminum-containing species. An X-ray crystal structure analysis of **1** shows a distorted $[LiI]_4$ heterocubane in which the Li and I atoms alternately occupy the corners of a cube. The principal bond distances and angles are summarized in Figure 1.

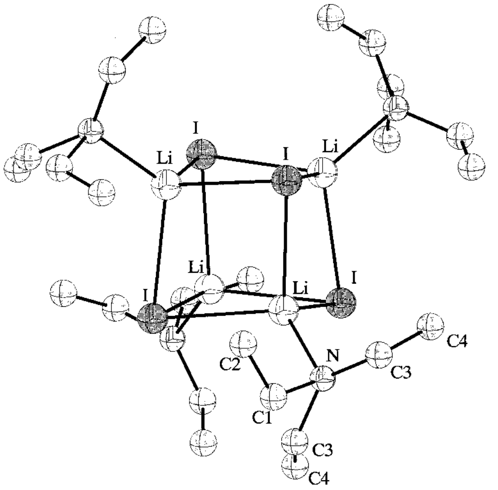

Figure 1. Molecular structure of $[LiI(NEt_3)]_4$ (**1**) shown as 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected distances [pm] and angles [deg] (min, max) are the following: Li−Li 357.5(6), 363.7(6); Li−I 282.2(6), 284.0(6); I−I 431.6(6), 436.4(6); Li−N 210.4(6); Li−I−Li 78.3(2), 79.6(2); I−Li−I 98.9(2), 100.8(2); N−Li−I 115.1(2), 118.9(2).

Table 2. Experimental Li−X, Li−Li, and X−X Distances (X = Cl, Br, I, CH_3) [pm] in LiX, $[LiX]_2$, $[LiX]_4$ and Solid LiX

		LiX^{a,28}	$[LiX]_2$^{a,29}	[LiX(Do)]$_4$		solid LiX^{29}
LiCl	d(Li−Cl)		217	235.7/244.1		257
		202				
	d(Li−Li)		230	306/312	(**2**)	363
	d(Cl−Cl)		363	366		363
LiBr	d(Li−Br)	217	235	254/262		275
	d(Li−Li)		270	331	(**3**)	389
			388	390/400		389
	d(Br−Br)					
LiI	d(Li−I)	239	254	284/282		303
	d(Li−Li)		269	361	(**1**)	428
	d(I−I)		431	432/436		428
$[LiCH_3]_4$	d(Li−C)					231 (236)^b
	d(Li−Li)					268 (**4**)
	d(C−C)					368 (389)^b

[a] Gaseous. [b] The value in parentheses represent the distance between the $[LiCH_3]_4$ units.

Each Li atom is coordinated pseudotetrahedrally by three I atoms and one N atom of the triethylamine ligand. A similar heterocubane-like arrangement as in **1** was found in the $[LiCl]_4$ and $[LiBr]_4$ entities of **2** and **3**, and therefore, their structural data are compared to **1** in Table 2. For comparison we also present the data of solid $LiCH_3$ and the monomeric, dimeric, and solid lithium halides.

The Li−X distances increase from the monomer to the solid as a consequence of the increasing coordination number (1 → 2→ 3 → 6, only Li−X contacts). All oligomers show X−X distances that are almost identical, implying that the X−X contacts govern the formation of the overall structure by repulsive forces. As a consequence of growing Li−X and constant X−X separations, the Li−Li distances increase to a maximum in crystalline LiX, where the Li−Li and X−X separations are equal. The bonding in all these species appears to be highly ionic and is dominated by the electrostatic Coulomb repulsion of the large anions. This interpretation is analogous to the ligand close packing model as proposed by R. J. Gillespie.[20]

Comparison of 2 with Solid $LiCH_3$ (4) by DFT Calculations.[6] Although the Li−C and the C−C distances in the

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[19] In this paper we do not distinguish between energy and enthalpy because the errors associated with the calculated values and also with the experimental data (e.g., for $[LiI]_2$, it is ±16 kJ/mol)[23] are much larger than errors due to the neglect of zero-point energies and thermal corrections to the enthalpy.

Table 3. Selected Distances [pm], Charges (*Q*), and Shared Electron Numbers (SEN) of the Tetrameric LiX Molecules [BP86/SV(P)]

	$[LiCl]_4$ (**2a**)	$[LiCl(NH_3)]_4$ (**2b**)	$[LiCH_3]_4$ (**4a**)	$[LiCH_3(NH_3)]_4$ (**4b**)	$[LiCH_3(LiCH_3)_2]_4$ (**4c**)[a]
d(Li−X)	235.0	239.9	223.7	230.7	230.6
d(Li−Li)	290.5	297.5	245.6	255.7	259.5
d(X−X)	365.6	372.7	364.4	374.8	372.8
Q(Li)	0.40	0.40	0.46	0.39	0.44
SEN(Li−Li)	0.11	0.03	0.27	0.13	0.09
SEN(Li−X)	0.01	0.02	0.22	0.10	0.06

[a] See text.

$[LiCH_3]_4$ entity of **4** are similar to the Li−Cl and Cl−Cl distances in the $[LiCl]_4$ unit of **2** (Table 2), the Li−Li distances of **4** (268 pm) are much shorter than those found in **2** (306/312 pm). However, this comparison is misleading, since solid $LiCH_3$ exhibits a polymeric structure in which the Li−C distances between the "tetramers" are only 5 pm longer than those within the "tetramers".[6] Therefore, one would expect the Li−Li distances to be shorter in isolated molecular $[LiCH_3]_4$ units than in solid **4**.

To elucidate the differences in bonding, especially the amount of ionic and covalent contribution in both $[LiCl]_4$ and $[LiCH_3]_4$, we optimized the geometries of the following molecules in T_d symmetry: $[LiCl]_4$ (**2a**), $[LiI(NH_3)]_4$ (**2b**), $[LiCH_3]_4$ (**4a**), $[LiCH_3(NH_3)]_4$ (**4b**), $[LiCH_3(LiCH_3)_2]_4$ (**4c**). Selected distances, shared electron numbers (SEN),[21] and the partial charge (*Q*) residing on the Li atom of **2a**, **2b**, **4a**−**c** are summarized in Table 3.

As already noted for **2** and **4**, similar pairs of molecules show similar X−X distances, e.g., 365.6/364.4 pm (**2a**/**4a**) and 372.7/374.8 pm (**2b**/**4b**). The coordination of a donor molecule at the Li atoms leads to greater X−X and Li−Li distances. An indication of the good quality of our calculations is the good agreement between the calculated distances in **4b** and the separations within the $[Li_4(CH_3)_4(tmeda)_2]$ molecule.[22] However, Li−Li contacts in **4b** are much shorter than in **4** (255.7/268.0 pm). To approach the bonding in solid $LiCH_3$, we chose the hypothetical molecule **4c** in which each corner of the $[LiCH_3]_4$ cube is coordinated by an additional $LiCH_3$ molecule, either via Li atoms or via a methyl group (see Figure 2). However, even the Li−Li distances (259.5 pm) in **4c** do not reach those found in solid $LiCH_3$ (268.0 pm).

Although the Li−Li distances in Table 3 vary considerably, there is nearly no change in the polarity of the Li atoms in all molecules listed. This implies that these compounds are similarly polar-bonded. Therefore, the differences in Li−Li bond distances may possibly be attributed to the small but significant covalent contribution in the $LiCH_3$ species; the Li−Li SENs of the methyllithium complexes are 3−4 times larger than the Li−Li SENs of the LiCl species (**2a** compared to **4a**, **2b** compared to **4b** and **4c**).

Comparison of 1 with Solid LiI (4) by DFT Calculations. To understand the bonding in **1**, we performed DFT calculations on LiI, $[LiI]_4$, $[LiI(NH_3)]$, $[LiI(NH_3)]_4$, $[LiI(NEt_3)]$, and $[LiI(NEt_3)]_4$, which show good agreement with the detailed calculations performed for the lighter lithium halides.[23] The most important results of a population analysis of the optimized minimum geometries are summarized in Table 4.

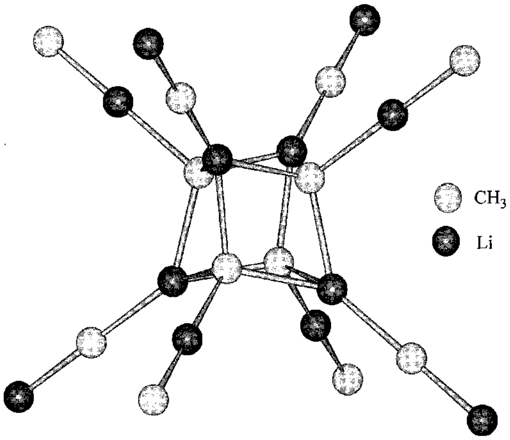

Figure 2. Calculated structure of $[LiCH_3(LiCH_3)_2]_4$ (**4c**). The H atoms are omitted for clarity.

Table 4. SEN(LiI), *Q*(Li), and Selected Distances [pm] of the BP86/SV(P) Minimum Structures of LiI, $[LiI]_4$, $[LiI(NH_3)]$, $[LiI(NH_3)]_4$, $[LiI(NEt_3)]$, and $[LiI(NEt_3)]_4$

compd (symmetry)	SEN(LiI)	*Q*(Li)	*d*(Li−I)	*d*(Li−Li)	*d*(I−I)	*d*(Li−N)
LiI	1.11	+0.37	245.3			
$[LiI]_4$ (T_d)	0.27	+0.31	277.3	324.6	441.9	
$[LiI(NH_3)]$ (C_{3v})	1.07	+0.39	249.3			203.7
$[LiI(NH_3)]_4$ (T_d)	0.22	+0.31	284.7	340.1	449.9	204.3
$[LiI(NEt_3)]$ (C_{3v})	1.04	+0.35	249.1			207.1
$[LiI(NEt_3)]_4$ (T_d)	0.19	+0.31	287.1	364.2	440.5	224.8

The bond distances of the computed structures of $[LiI(NH_3)]_4$ and $[LiI(NEt_3)]_4$ are similar to the experimentally observed distances of **1** (especially Li−Li and I−I contacts). This is an indication of the reliable computational description of these species (at least within similar compounds). To understand the energetic situation of $[LiI]_4$ molecules as intermediates of monomeric LiI and solid LiI, the following computed reaction energies between the gaseous molecules LiI and NR_3 presented in Chart 1 have been obtained from our DFT calculations.[19]

The relative energy diagram shown in Chart 2 results from the calculated reaction energies and the experimentally available sublimation energy[19] of LiI (179 kJ/mol).[24] The sums of the total energies of the gaseous LiI and NR_3 molecules represent the starting point for the subsequent reactions to the various lithium iodide species. The reaction energies given in Chart 2 are normalized to 1 equiv of LiI.

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(21) The SEN provides a reliable measure of the covalent bond strength, and for a better understanding, we list some representative cases. Strong bonds such as C−C or C−H give a SEN of about 1.4. Double bonds such as C═C lead to a SEN of about 2.2. Triple bonds such as C≡C or N≡N have a high SEN of about 3.3. A reduced SEN is found for polar bonds as in NaF (about 0.3), and for weak bonds such as in Cl_2 and in F_2 the SEN is reduced to about 0.6.

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Chart 1. Reaction Energies Obtained from DFT Calculations for Several Reactions of Gaseous [LiI], $[LiI]_4$, and NR_3

		ΔE_R [kJ/mol]			
4 LiI (g)	→ $[LiI]_4$ (g)	–496			
LiI (g) + NR_3 (g)	→ $[LiI(NR_3)]$ (g)	–122	(R = H)	–78	(R = Et)
4 $[LiI(NR_3)]$ (g)	→ $[LiI(NR_3)]_4$ (g)	–389		–340	
$[LiI]_4$ (g) + 4 NR_3 (g)	→ $[LiI(NR_3)]_4$ (g)	–381		–157	

Chart 2. Relative Energy Diagram of the Calculated Reaction Energies (cf. Chart 1) Normalized to 1 equiv of LiI and the Sublimation Energy of LiI

			ΔE [kJ/mol LiI]
LiI (g) + NEt_3 (g)	→ $[LiI(NEt_3)]$ (g)	–78	↑
LiI (g) + NH_3 (g)	→ $[LiI(NH_3)]$ (g)	–122	
LiI (g)	→ ¼ $[LiI]_4$ (g)	–124	
LiI (g) + NEt_3 (g)	→ ¼ $[LiI(NEt_3)]_4$ (g)	–163	
LiI (g)	→ LiI (s)	–179	
LiI (g) + NEt_3 (g)	→ LiI (s) + NEt_3 (l)	–214	
LiI (g) + NH_3 (g)	→ ¼ $[LiI(NH_3)]_4$ (g)	–219	
LiI (g) + NEt_3 (g)	→ ¼ $[LiI(NEt_3)]_4$ (g)	–223	

If the reaction proceeds by formation of liquid NH_3 or NEt_3, all ΔE_R values have to be corrected for the vaporization energies of NH_3/NEt_3 (23/35 kJ/mol). Entropy influences are neglected within this discussion, though it has been shown that they are essential in some special cases.[3,25]

Within this diagram the solvated ions Li^+ and I^- are calculated to be at −242 kJ/mol (H_2O as solvent) and −244 kJ/mol (NH_3 as solvent).[26,27] To the best of our knowledge, the solvation energy of LiI in NEt_3 is not published; however, our experiments showed that solid LiI is nearly insoluble in liquid NEt_3. Consequently, the reaction energy (−214 kJ/mol) of the formation of solid LiI and liquid NEt_3 starting from the gaseous phase is expected to be at the bottom of the thermodynamic ladder. The sublimation enthalpy of **1** has been estimated from the known sublimation enthalpies of CI_4 (ΔH_{Subl} = 81 kJ/mol; M_r = 474 au), TiI_4 (98 kJ/mol; M_r = 555 au), C_{60} (175 kJ/mol; M_r = 721 au), and C_{70} (200 kJ/mol; M_r = 841 au). Plotting the sublimation enthalpies against the formula weights and extrapolating to the formula weight of **1** (M_r = 940 au) lead to a sublimation energy[19] of about 240 kJ/mol (60 kJ/mol after normalization to 1 equiv of LiI). Solid **1** (−223 kJ/mol) and solid LiI in liquid NEt_3 (−214 kJ/mol) are energetically nearly equal; however, solid **1** cannot be obtained from a mixture of LiI and NEt_3 as shown experimentally.

This observation seems reasonable, since the activation energy of the solvation of solid LiI to give monomeric $[LiI(NEt_3)]$ as an intermediate is too high. Therefore, the formation of **1** instead of solid LiI seems to be kinetically controlled by the very special conditions (e.g., type of donor, concentration, and temperature) of the reaction described here, and so it is not surprising that only three examples of this heterocubane arrangement have been characterized so far.

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure of $[LiI(NEt_3)]_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) Furthermore, it is well-known that the position of the equilibrium is drastically shifted if a reinforcement of hydrogen bonding due to entropy changes upon dissolution of ionic species in NH_3 or H_2O occurs. However, in the case of NEt_3 solutions, entropy influences should not loom large.

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