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The Bicyclic Structure of a Novel TMEDA-Solvated Lithium Chloride Tetramer $[(LiCl)_4\cdot3.5TMEDA]_2$: X-ray Structural Analysis and MO Investigations

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Crystals of $[(LiCl)_4\cdot3.5TMEDA]_2$, **1**, were obtained as an unexpected byproduct in two different lithiation reactions. X-ray analysis reveals that **1** forms a pair of TMEDA-bridged tetrameric units (TMEDA = *N,N,N',N'*-tetramethylethylenediamine) each with fused six- and four-membered rings and tetracoordinated lithiums. The tetrameric unit in **1** is unprecedented. *Ab initio* and semiempirical methods (MNDO and PM3) show tetrameric aggregates, $(LiCl)_4$, to be favored over trimers and dimers. Among the tetramers, a distorted cube constitutes the most stable arrangement. MNDO calculations find the potential energy surface for the different TMEDA-solvated tetrameric aggregates to be extremely shallow. In contrast, with the recently developed Li/PM3 parametrization, the solvated tetramers are distinct energetically. The Li NMR shifts computed by the IGLO method for several LiCl oligomers differ only slightly. Hence, ^{7}Li NMR spectroscopy could not detect an equilibrium between different species, if they were present in solution.

Introduction

The structural variety exhibited by lithium compounds seems almost unlimited.[1] Tetramers are a case in point. Not only tetrahedral arrangements[2] but also open eight-membered rings[3] and ladder structures[4] are known. We now describe a new type of tetramer involving a simple salt, lithium chloride. In the presence of the ligand TMEDA, this crystallizes as a bicyclic system with fused six- and four-membered rings. The crystal structure is easy to understand, after the fact.

Complexes of permethylated amines with main group I halides are highly soluble in organic solvents[5] and have been well studied by various techniques in solution.[6] Their potential use as soluble halogenating agents in organic synthesis,[7] as components in ionic conductors and batteries,[8] and as low energy electrolytic source for pure lithium[9] has rejuvenated the investigation of such "inorganic" molecular complexes. Moreover, LiX addition (X = halogen) to organometallic reagents often has a pronounced influence on the regio- and stereoselectivity of alkylation reactions,[10] indicating that the detailed nature of the mixed aggregates is important.[11]

Various crystal structures of a number of simple lithium salts have been reported.[9,12−14] These were usually obtained by deliberate crystallization. Our sample crystallized from two

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different lithiation reactions in the presence of TMEDA. Although an RLi·TMEDA complex was sought in both cases, the LiCl·TMEDA complex is just as likely.

Experimental Section

All manipulations were carried out under an argon atmosphere by using standard Schlenk as well as needle septum techniques. Hexane was freshly distilled from Na/K alloy under argon. TMEDA was dried over CaH_2, distilled, and then kept over Na/Pb alloy.

$[(LiCl)_4 \cdot 3.5TMEDA]_2$, 1. To a stirred suspension of 1.416 g (204 mmol) of Li powder in 120 mL of hexane was added 36.4 mL (242.3 mmol) of TMEDA, followed by slow addition (ca. 1 h) of 10 mL (96.2 mmol) of freshly distilled cyclopentyl chloride. Care should be taken that the temperature does not rise above 30 °C; external cooling may be necessary. The reaction mixture was allowed to stand overnight. The solution was separated from the violet-colored precipitate by filtration. Crystals of X-ray quality formed after 3 days at +4 °C. Yield: 15.6 g (28.1%) first batch. Anal. Calcd for $Li_4Cl_4N_7C_{21}H_{56}$: C, 43.77; H, 9.79; N, 17.01. Found: C, 43.81; H, 9.90; N, 17.08. ^1H NMR (400 MHz, THF-d_8, −91 °C), ppm: TMEDA signals at δ 2.36 (4H, s, N−CH_2) and 2.20 (12H, s, N−CH_3). ^{13}C NMR (100 MHz, THF-d_8, −91 °C), ppm: TMEDA signals at δ 57.59 (CH_2) and 46.64 (CH_3).

The crystals are remarkably moisture sensitive and disintegrate when they are dried!

X-ray Measurements

Crystal data for $C_{21}H_{56}Li_4N_7Cl_4$, **1**: $M = 576.30$, monoclinic, space group $C2/c$; $a = 19.640(3)$ Å, $b = 10.853(2)$ Å, $c = 34.850(11)$ Å, $\beta = 106.20(3)°$, $V = 7133(3)$ Å^3, $D_{calc} = 1.073$ Mg m^{-3}, $Z = 8$; $F(000) = 2488$, $\lambda = 0.710\,73$ Å (graphite-monochromated Mo-Kα radiation), μ(Mo-Kα = 0.352 mm^{-1}, $T = 153$ K. Data were collected with a Siemens Stoe AED on an oil-coated rapidly cooled[15a] crystal of 0.45 × 0.5 × 0.6 mm^3 using the 2θ-ω scan method ($8° \le 2\theta \le 50.0°$). Of a total of 6621 collected reflections, 6260 were unique. The structure was solved by direct methods using SHELXS-86;[15b] 325 parameters were refined using 4962 reflections [$F > 4\sigma(F)$] by full-matrix least squares. Final R values: $R = 4.03\%$ and $R_w = 4.79\%$. Largest peak and hole in the final difference map: 0.81 and −0.33 e Å^{-3}.

All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically in equivalent groups using the riding model.

Results and Discussion

$[(LiCl)_4 \cdot 3.5TMEDA]_2$, **1**, was obtained by treating cyclopentyl chloride with lithium powder in hexane as well as from the reaction of 1-chloro-1-(trichlorovinyl)cyclopropane with *n*-BuLi, both in the presence of TMEDA. The major portion of the LiCl formed was, however, filtered off as an insoluble precipitate. In addition, due to their moisture sensitivity, the crystals were initially expected to be the organolithium compounds, solvated by TMEDA. Instead, no crystalline organolithium compound was present!

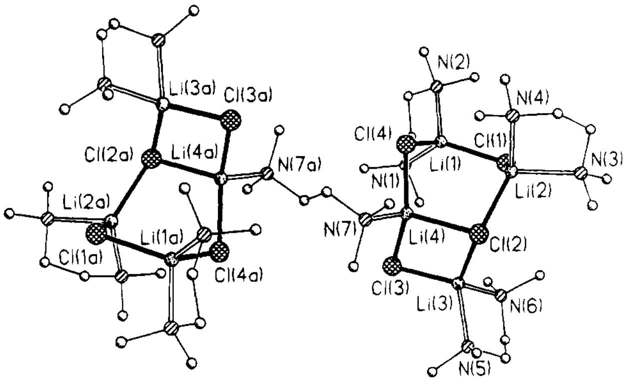

Figure 1. Molecular structure of **1**.

Table 1. Selected Bond Lengths (pm) and Angles (deg) of $[(LiCl)_4 \cdot 3.5TMEDA]_2$, **1**

Cl(1)−Li(1)	232.5(4)	Cl(1)−Li(2)	234.1(4)
Cl(2)−Li(2)	237.8(4)	Cl(2)−Li(3)	234.7(4)
Cl(2)−Li(4)	244.8(4)	Cl(3)−Li(3)	229.3(4)
Cl(3)−Li(4)	237.2(3)	Cl(4)−Li(1)	228.3(4)
Cl(4)−Li(4)	230.8(4)	Li(1)−N(1)	210.7(4)
Li(1)−N(2)	214.1(4)	Li(2)−N(3)	219.3(5)
Li(2)−N(4)	216.3(4)	Li(3)−N(5)	212.1(4)
Li(3)−N(6)	212.0(5)	Li(4)−N(7)	213.5(5)

Li(1)−Cl(1)−Li(2)	95.1(1)	Li(2)−Cl(2)−Li(3)	115.6(1)
Li(2)−Cl(2)−Li(4)	96.0(1)	Li(3)−Cl(2)−Li(4)	76.3(1)
Li(3)−Cl(3)−Li(4)	78.8(1)	Li(1)−Cl(4)−Li(4)	106.8(1)
Cl(1)−Li(1)−Cl(4)	115.3(2)	Cl(1)−Li(2)−Cl(2)	117.6(2)
Cl(2)−Li(3)−Cl(3)	105.1(1)	Cl(2)−Li(4)−Cl(3)	99.7(1)
Cl(3)−Li(4)−Cl(4)	121.2(2)	Cl(2)−Li(4)−Cl(4)	110.1(2)
N(1)−Li(1)−N(2)	86.6(2)	N(3)−Li(2)−N(4)	84.1(2)
N(5)−Li(3)−N(6)	86.1(2)	Cl(3)−Li(4)−N(7)	110.9(2)
Cl(4)−Li(4)−N(7)	106.5(1)		

Two independent X-ray analyses revealed the structure shown in Figure 1. $[(LiCl)_4 \cdot 3.5TMEDA]_2$, **1**, consists of two tetrameric $(LiCl)_4$ subunits which are held together by a single η^1-bound TMEDA ligand (Li−TMEDA−Li).[16] Each subunit consists of a boat-shaped six-membered $(LiCl)_3$ ring fused with a nearly planar four-membered $(LiCl)_2$ ring. With a crystallographic inversion center on the midpoint of the central CC bond of the bridging TMEDA ligand, a dimer of tetramers results overall. The two lithium atoms, Li(4) and Li(4a), associated with the bridging TMEDA are unique in the sense that their coordination spheres are completed by *three* chloride ions each. All the other lithium cations are solvated in a bidentate manner by TMEDA and have only two Cl^- neighbors. Table 1 gives selected geometrical information; Table 2, fractional coordinates and equivalent isotropic displacement coefficients. The Li−Cl distances (Table 1) in the four-membered ring [229.3(4)−244.8(4) Å] and the six-membered ring [228.3(4)−244.0(4) Å] are in the same range and agree with those observed for other LiCl aggregates (see below). The longest distance corresponds to the Li−Cl bond which fuses the six- and the four-membered ring. A closer inspection of one tetrameric $(LiCl)_4$ core (Figure 2a) reveals that this unit resembles a cube which has been elongated along three edges (cf. dotted lines in Figure 2b).

Apparently, **1** is formed under special conditions only, e.g. by first generating monomeric LiCl (as a side product of the reactions mentioned above), which is being solvated and subsequently aggregates. In contrast, treating solid LiCl with an excess of TMEDA yields a solvate with different stoichiometry, $[LiCl \cdot TEMDA]_3$, in nearly quantitative yield.[17] Preliminary X-ray data show a cyclic structure with a puckered $(LiCl)_3$ ring and bidentate TMEDA ligands on each lithium atom. Another LiCl−TMEDA adduct of the composition $[(LiCl)_6 \cdot 4TMEDA]_n$ was obtained deliberately from the reaction of *tert*-butyl chloride with *n*-butyllithium.[13a] Here, the $(LiCl)_6$ core corresponds to a double cubane unit (Figure 3). This aggregate exhibits the same structural features as **1**: fused six- and four-membered rings with similar LiCl distances and similar angle sums within the rings as in **1**. The double cube contains the structural element found in **1** twice (cf. normal and bold lines in Figure 3). Thus, three LiCl−TMEDA adducts of

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Table 2. Atomic Coordinates ($\times 10^{-4}$) and Isotropic Displacement Parameters (pm^2 $\times$ 10^{-1}) of 1

	x	*y*	*z*	*U*(eq)[a]
Cl(1)	9039(1)	4117(1)	3435(1)	36(1)
Cl(2)	8183(1)	988(1)	3722(1)	28(1)
Cl(3)	6726(1)	3056(1)	3776(1)	33(1)
Cl(4)	8728(1)	3691(1)	4483(1)	33(1)
Li(1)	8820(2)	5026(3)	3993(1)	29(1)
Li(2)	9209(2)	2132(4)	3708(1)	35(1)
Li(3)	7099(2)	1811(4)	3343(1)	33(1)
Li(4)	7824(2)	2338(3)	4193(1)	30(1)
N(1)	7986(1)	6316(2)	3879(1)	32(1)
N(2)	9517(1)	6550(2)	4203(1)	28(1)
C(1)	7630(1)	6324(3)	4197(1)	52(1)
C(2)	7463(1)	6084(3)	3495(1)	51(1)
C(3)	8361(1)	7486(2)	3864(1)	39(1)
C(4)	9029(1)	7573(2)	4207(1)	37(1)
C(5)	9930(1)	6780(2)	3920(1)	43(1)
C(6)	10010(1)	6391(2)	4603(1)	41(1)
N(3)	9773(1)	1087(2)	3354(1)	38(1)
N(4)	10141(1)	1761(2)	4197(1)	35(1)
C(7)	9780(2)	1659(4)	2979(1)	87(2)
C(8)	9512(2)	−155(3)	3282(1)	80(2)
C(9)	10512(2)	1113(3)	3615(1)	62(1)
C(10)	10569(1)	892(3)	4035(1)	50(1)
C(11)	9993(1)	1213(2)	4550(1)	45(1)
C(12)	10512(1)	2935(3)	4315(1)	52(1)
N(5)	6375(1)	416(2)	3061(1)	35(1)
N(6)	7049(1)	2421(2)	2758(1)	41(1)
C(13)	6597(2)	−824(3)	3218(1)	65(1)
C(14)	5670(2)	682(3)	3097(1)	68(1)
C(15)	6397(2)	461(3)	2644(1)	49(1)
C(16)	6439(2)	1749(3)	2505(1)	56(1)
C(17)	7711(2)	2077(3)	2672(1)	55(1)
C(18)	6949(2)	3747(3)	2702(1)	74(1)
N(7)	7667(1)	1220(2)	4665(1)	28(1)
C(70)	6974(1)	608(3)	4531(1)	46(1)
C(71)	8223(1)	273(2)	4760(1)	44(1)
C(72)	7738(1)	1945(2)	5033(1)	33(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

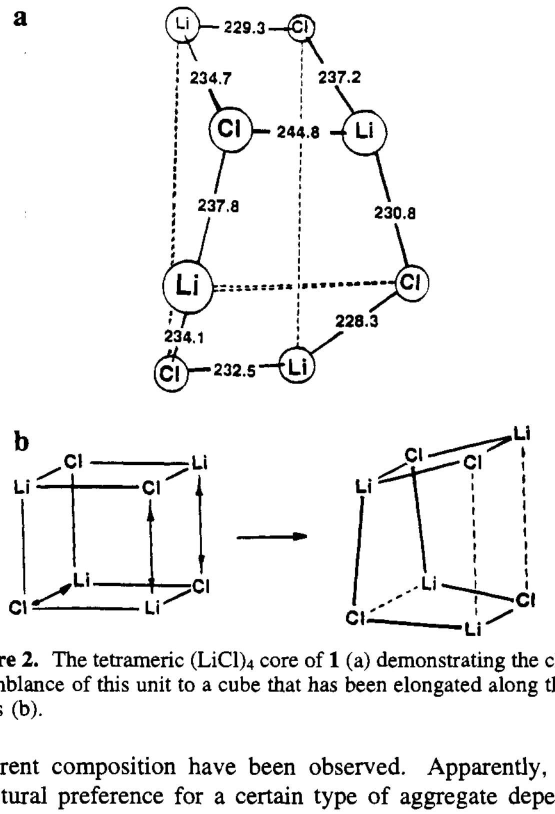

Figure 2. The tetrameric $(LiCl)_4$ core of **1** (a) demonstrating the close resemblance of this unit to a cube that has been elongated along three edges (b).

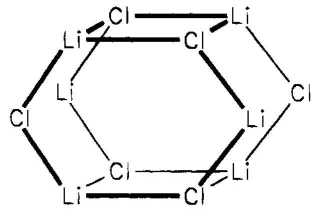

Figure 3. The double cubane unit of $[(LiCl)_6{\cdot}4TMEDA]_n$[13a] containing the structural LiCl elements found in **1** twice (cf. bold lines and normal lines).

different composition have been observed. Apparently, the structural preference for a certain type of aggregate depends on the reaction conditions, but the reasons are not fully understood yet. Various other solvated lithium halides document the unusual coordinations found in these species.[9,12–14] However, four- and six-membered rings seem to be a general feature. A four-membered ring structure was also observed for LiCl at 820 °C by gas-phase electron diffraction.[18] $(LiCl)_4{\cdot}3PMDTA$ (PMDTA = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine) consists of two $(LiCl)_2$ four-membered rings connected via an LiCl bridge.[13d] An $(LiX)_2$ unit also is present in $(LiCl)_2{\cdot}4THF$,[14a] in $(LiBr)_2{\cdot}2PMDTA$,[13c] and in the cationic aggregate $[(Li_4Cl_2){\cdot}10Et_2O]^{2+}$.[19] $(LiCl{\cdot}HMPTA)_4$ (HMPTA = hexamethylphosphortriamide) has a pseudo-cubane structure.[12d] With 4-*tert*-butylpyridine as a ligand, a monomeric complex, LiCl·3L (L = ligand), is favored.[13b] With ethylenediamine as a ligand, a polymer, $(LiCl{\cdot}2NH_2CH_2CH_2NH_2)_n$, with solvent-separated lithium ions results.[14d] Cationic LiX aggregates include $[(PMDTA)Li(\mu_2\text{-}Cl)Li(PMDTA]^+$ with a linear Li−Cl−Li arrangement[20] and $[Li_6Br_4{\cdot}10Et_2O]^{2+}$ with a complex structure composed of fused $(LiBr)_2$ rings.[21] Mixed lithium halogenide/organolithium aggregates are known as well.[2d,22]

In the $(LiCl)_n$ Lewis base contact ion aggregates, all Li−Cl distances range between 228 and 260 pm. This compares to a value of 257 pm within the LiCl lattice[23] and a value of 202.1 pm for LiCl in the gas phase.[24] LiCl separations in charged cationic species[19,20] deviate somewhat from these values.

Interestingly, the ^7Li NMR spectrum of a solution of **1** in toluene-d_8 shows only one line down to −90 °C. Similar observations have been made for several other lithium halide Lewis base adducts, and this has been attributed to fast exchange processes.[6a,13d] Recall that one Li^+ ion in **1** is unique as it is surrounded by three Cl^- ions and should in principle be distinguishable from the other Li^+ ions, which are surrounded by only two Cl^- ions each. However, the Li NMR shift range is usually very small (±2 ppm)[25a] and exceptions have only been noted for $Li^+{-}\pi$-complexed aromatic compounds.[25] We have used the IGLO method (Individual Gauge for Localized Orbitals)[26] to compute the Li NMR shifts in **1** (*vide infra*).

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Computations

MO calculations were performed to help understand why the structure shown in Figure 1 is favored over other alternatives. Several possible aggregates, unsolvated (**2a**−**9a**) and solvated (**2b**−**9b**), were considered (Figure 4, schematic representation). The solvated species are coordinated to TMEDA in a fashion, that each Li$^+$ cation is tetracoordinate. While the unsolvated aggregates **2a**−**9a** are small enough to be studied by *ab initio* methods as well, a computational investigation of the larger TMEDA solvated compounds, **2b**−**9b**, is restricted to semiempirical methods.

Ab initio calculations (for **2a**−**9a**) were performed using the GAUSSIAN 92 program package[27a] and the standard split valence 6-31G* basis set for lithium and chlorine.[27b−d] All geometries were completely optimized at the correlated level [MP2(FC)] within the indicated symmetry constraints using standard gradient optimization techniques. Stationary points were characterized as minima or transition structures by calculating the vibrational frequencies at the SCF level (HF/6-31G*). Total energies were refined by performing single-point calculations [MP2(FC)/6-31+G*//MP2(FC)/6-31G* and MP4SDQ(FC)/6-31+G*//MP2(FC)/6-31G*] on the MP2(FC)/6-31G* geometries. Final energy estimates were obtained by adding the differences in zero-point energies (ΔZPE), scaled by the empirical factor 0.91,[28] to the MP4SDQ(FC)/6-31+G* //MP2(FC)/6-31G* data. Only these energies will be discussed in the text. The *ab initio* data are listed in Tables 3 and 4. The lithium chemical shifts in **2a**−**9a** (Table 8) were computed with the IGLO method (Individual Gauge for Localized Orbitals)[26] using the DZ basis sets[29] and the MP2(FC)/6-31G*//MP2(FC)/6-31G* geometries.

Semiempirical calculations (MNDO[30] and PM3[31,32]) were performed for both unsolvated (**2a**−**9a**, Table 5) and solvated aggregates (**2b**−**9b**, Table 6). Geometries were fully optimized without symmetry constraints. However, in most cases symmetric structures (cf. point groups in Table 5) resulted on optimization. All stationary points were characterized to be minima by calculation of their vibrational frequencies. Heats of formation, ΔH_f, and association enthalpies [$\Delta H_{assn} = \Delta H_f((LiCl)_n) - n\Delta H_f(LiCl)$] of the unsolvated aggregates **2a**−**9a** are presented in Table 5 along with experimental data[33] (where available). With Coulomb's law, the potential energies of the

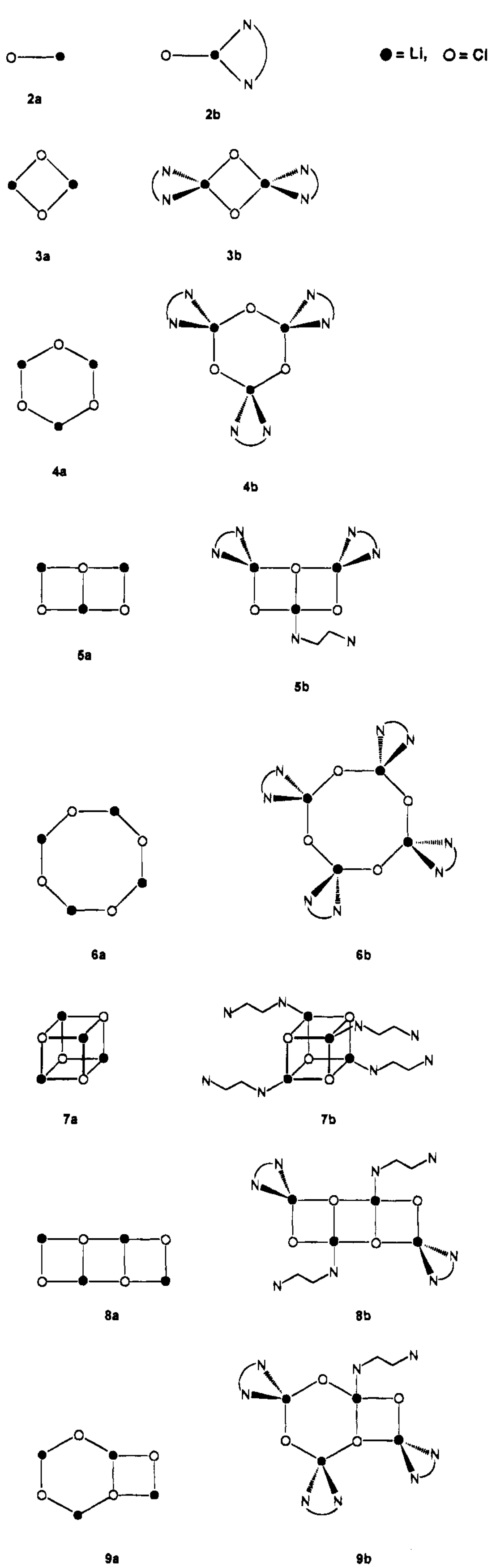

Figure 4. Schematic illustration of unsolvated (**2a**−**9a**) and TMEDA-solvated (**2b**−**9b**) LiCl aggregates, for which MO calculations were performed.

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Table 3. *Ab Initio* Computed Total Energies (au) and ZPE (Zero-Point Energies, kcal/mol) of $(LiCl)_n$ Aggregates at 0 K at Various Levels[a]

	point group	MP2/6-31G*// MP2/6-31G*	MP2/6-31+G*// MP2/6-31G*	MP4SDQ/6-31+G*// MP2/6-31G*	ZPE
2a		−467.14597	−467.14988	−467.16225	0.89
3a	D_{2h}	−934.37974	−934.38539	−934.40994	3.06
4a	D_{3h}	−1401.60177	−1401.61170	−1401.64871	4.72
6a	D_{4h}	−1868.81203 [8.95]	−1868.82622 [15.28]	−1868.87577 [14.28]	6.19
7a	T_d	−1868.84223 [0.0]	−1868.85058 [0.0]	−1868.89853 [0.0]	7.24
8a	C_{2h}	−1868.81227 [18.80]	−1868.82486 [16.14]	−1868.87373 [15.57]	6.42
9a	C_s	−1868.80752 [21.78]	−1868.82081 [18.68]	−1868.87001 [17.90]	6.17

[a] Relative energies of the tetrameric isomers are given in brackets.

aggregates **2a**−**9a** consisting of unit point charges at distance *d* may be determined by simply taking *all* attractive (1, $2n$) and *all* repulsive (1, $2n + 1$) interactions (n = integer number) into account (Table 5). These potential energies may be used as a crude estimate for the stabilization of LiCl aggregates, as the LiCl bond is highly ionic.[34] Hence, the basic structures are determined mainly by electrostatic repulsion and attraction between these point charges.

1. Computational Investigation of 2a−9a. On the basis of the association energy per monomer, both *ab initio* and semiempirical methods find tetramers to be the most stable aggregates. Among the tetrameric isomers, a distorted cubic arrangement is favored (Tables 3−5).

The *ab initio* tetramerization energies [MP4SDQ(FC)/6-31+G*//MP2(FC)/6-31G* + ΔZPE(HF/6-31G*)] range between −136.4 (**9a**) and −153.3 kcal/mol (**7a**) (Table 4). Both electronegativities and ionic radii of the atoms involved influence the oligomerization energies.[35] The energy differences between the eight-membered ring **6a**, the ladder **8a**, and the annulated ring structure **9a** (ca. 3.6 kcal/mol; Table 3) are extremely small. The aggregate **9a**, which corresponds to the planarized $(LiCl)_4$ core of the X-ray structure, is a minimum at our *ab initio* level but rearranges to the ladder **8a** on optimization with MNDO and PM3. MNDO underestimates the association energies for the tetramers by approximately 43 kcal/mol on average, while PM3 overestimates them by ca. 57 kcal/mol (Table 5), on the basis of the *ab initio* results.

The *ab initio* stability order for the tetramers (Table 3) seems puzzling at first sight: the eight-membered ring **6a** is favored over the ladder **8a** and over the annulated ring structure **9a**. If the energies were determined by electrostatic bonding exclusively, the D_{4h} isomer **6a** should be the least stable (cf. Coulomb energies in Table 5, column 1) because of the lower number of attractive Li−Cl interactions compared to those in the other isomers. An explanation for the *ab initio* stability order may be that the gas-phase calculations tend to favor structures with the lowest dipole moment μ. Hence, the D_{4h}, T_d, and C_{2h} tetramers (**6a**, **7a**, **8a**) with $\mu = 0$ D would be favored over the annulated ring system, **9a**, which has a nonzero dipole moment. Only among structures with the same dipole moment (**6a**, **7a**, **8a**), does the number of Li−Cl interactions become important, causing the T_d isomer, **7a**, to be the most stable. According to this model, the D_{4h} isomer should be higher in energy than the C_{2h} ladder. However, *ab initio* finds the reversed order; i.e., the eight-membered ring **6a** is more stable than the ladder **8a** (by only 1.48 kcal/mol, however). This suggests that small covalent contributions to the bonding may be important. Hence, **8a**, which consists of three annulated four-membered rings, might be too "strained". In contrast, the eight-membered ring **6a** has favorable quasi-linear Cl−Li−Cl arrangements.

With MNDO and PM3, the order of stability follows the Coulomb energies for **6a**−**8a**; i.e., the ladder is more stable than the eight-membered ring (Table 5). However, the energetic preference for the ladder is only slight with MNDO (**8a** is stabilized by only 1.4 kcal/mol vs **6a**), whereas PM3 finds the ladder to be stabilized by 14.3 kcal/mol vs the eight-membered ring! The limitations of the Li/PM3 parametrization for small inorganic molecules were pointed out in the original publication.[32] *Ab initio* calculations have demonstrated that tetrahedral arrangements are also preferred for $(LiOH)_4$,[35] $(LiF)_4$,[35] and $(CH_3Li)_4$.[36] In contrast, $(LiNH_2)_4$ favors an eight-membered ring, which has been attributed to the importance of lone pair orientation effects.[35] In the solid state, both eight-membered rings[3] and ladder structures[4] are known for lithium amides. Eight-membered rings are also observed for organocopper and organosilver complexes[37,38] as well as for benzylsodium.[39]

Although the "simple" electrostatic model, applying Coulomb's law, outlined earlier performs reasonably well, this is partly because of the choice of ideal geometries (*vide supra*). With this model, the distance between the point charges (*d*) is assumed to be the same for all structures, and the bond angles are set to the values found in regular geometric figures. The small discrepancies between the predictions of the Coulomb model and the high-level theoretical calculations may in part be due to the deviation of the optimized geometries from those of the regular geometric figures (cube, octagon, etc.) on which the electrostatic model is based.

We have also investigated the dimer **3a** and two possible trimeric aggregates, **4a** and **5a**, for which experimental data are available for comparison. No attempt has been made to correct the *ab initio* data to 298 K since the temperature dependence of the enthalpies is rather small. The dimerization energy computed by *ab initio* (−52.5 kcal/mol, MP4SDQ(FC)/6-31+G*//MP2(FC)/6-31G* + ΔZPE; Table 4) is within the standard deviation of the experimental value (−49.5 kcal/mol; Table 5).[33] Again, MNDO underestimates the oligomerization energy, while PM3 overestimates it.

Among the two possible trimeric aggregates **4a** and **5a**, the ladder **5a** is found to be a minimum only with PM3. However, the optimized PM3 geometry features a rather long bridging Li−Cl distance that may be viewed as a ladder partially opened to a boat-shaped six-membered ring. With both MNDO and *ab initio*, **5a** converges to the D_{3h} six-membered ring **4a** on optimization. Again, **4a** may be favored over **5a**, because the former has no dipole moment. The *ab initio* trimerization energy (−99.6 kcal/mol; MP4SDQ(FC)/6-31+G*//MP2(FC)/6-31G* + ΔZPE) is identical with the experimental value (−99.6 kcal/mol).[33] Note that the *ab initio* oligomerization

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Table 4. *Ab initio* Association Eneriges (kcal/mol) of $(LiCl)_n$ at Various Levels (Oligomerization Energy per Monomer in Parentheses)

	point group	MP2/6-31G*//MP2/6-31G*	MP2/6-31+G*//MP2/6-31G*	MP4SDQ/6-31+G*//MP2/6-31G*	final estimate[a]
3a	D_{2h}	−55.09	−53.73	−53.62	−52.47
4a	D_{3h}	−102.81	−101.69	−101.63	−99.61 (−33.20)
6a	D_{4h}	−143.16	−142.26	−142.31	−139.94 (−34.99)
7a	T_d	−162.11	−157.55	−156.59	−153.28 (−38.32)
8a	C_{2h}	−143.31	−141.41	−141.02	−138.46 (−34.62)
9a	C_s	−140.33	−138.87	−138.69	−136.35 (−34.09)

[a] Final estimates were obtained by adding ΔZPE (scaled by a factor of 0.91)[28e] to the MP4SDQ/6-31+G*//MP2/6-31G* results.

Table 5. Coulomb Energies ϕ_c (au/Monomeric Unit; Point Charges at Distance *d*) of $(LiCl)_n$ **2a**−**9a**; MNDO, PM3, and Experimental Heats of Formation ΔH_f (kcal/mol) (Relative Energies in Brackets); Association enthalpies ΔH_{assn} (kcal/mol) $[\Delta H_f((LiCl)_n) - n\Delta H_f(LiCl)]$, and ΔH_{assn} per Monomer in Parentheses[a]

		ΔH_f $[E_{rel}]$			ΔH_{assn}		
	ϕ_c	MNDO	PM3	exp[a]	MNDO	PM3	exp
			Monomer				
2a	−1/*d*	−38.5	−48.0	−46.8			
			Dimer				
3a	−1.2929/*d*	−116.5	−165.2	−143.1 ± 3	−39.5	−69.3	−49.5
(→D_{2h})					(−19.7)	(−34.7)	(−24.8)
			Trimers				
4a	−1.3453/*d*	−186.5	−273.7	−240.1 ± 5	−70.9	−129.7	−99.6
(→D_{3h})			[0.0]		(−23.6)	(−43.3)	(−33.2)
5a	−1.3553/*d*	−186.5[b]	−277.9			−133.9	
(→C_1)			[4.2]			(−44.7)	
			Tetramers				
6a	−1.3634/*d*	−250.6	−378.4		−96.5	−186.5	
(→D_{4h})		[12.9]	[28.8]		(−24.1)	(−46.6)	
7a	−1.4560/*d*	−263.5	−407.2		−109.4	−215.3	
(→T_d)		[0.0]	[0.0]		(−27.3)	(−53.8)	
8a	−1.3951/*d*	−252.00	−392.7		−97.9	−200.9	
(→C_1)		[11.5]	[14.5]		(−24.5)	−(50.2)	
9a	−1.3605/*d*	−252.00[c]	−392.7[c]				

[a] Experimental heats of formation (kcal/mol) were taken from the literature.[33] The point groups given in column 1 below the compound numbers indicate the symmetries resulting *after* optimization. [b] With MNDO the ladder **5a** converges to the six-membered ring **4a** on optimization. [c] On optimization the annulated ring structure **9a** converges to the ladder **8a**.

energy (MP4SDQ(FC)/6-31+G*//MP2(FC)/6-31G* + ΔZPE) per monomer is very similar for the six-membered ring **4a** (−33.2 kcal/mol) and for the eight-membered ring **6a** (−35.0 kcal/mol). This is in accord with the rather small differences in Coulomb energies for **4a** and **6a** (−1.3453/*d* and −1.3634/*d*, in au/Å; Table 5).

Geometrical features will not be discussed in detail. Both MNDO- and PM3-optimized geometries of **2a**−**9a** deviate significantly from the *ab initio* optimized geometries. While MNDO Li−Cl distances are ca. 24 pm too long on average, the PM3 distances are ca. 15 pm too short on average. The angles in the MNDO-optimized structures are in much better agreement with the *ab initio* values than in the PM3-optimized structures.

2. Solvation Effects: **2b**−**9b**. Solvation with polar ligands is known to influence the stability of Li aggregates dramatically.[36] A previous MNDO and *ab initio* study of the thermodynamics of solvation of lithium compounds has demonstrated that MNDO provides reasonably reliable data and may be used to estimate solvation enthalpies.[40] No experimental data on the solvation energies of $(LiCl)_n$ aggregates are available. The existence of stable 1:1 LiX amine complexes was established by early matrix isolation infrared studies.[41] Lower level *ab initio* calculations (4-31G and STO-3G basis sets) of the interaction of LiCl with amines were provided by Szczesniak et al.[42a] and by Rao et al.[42b] We have employed both MNDO and PM3 to compare the heats of formation of the TMEDA-solvated aggregates **2b**−**9b** and to estimate the solvation enthalpies (Table 6).

We first consider the effect of solvation on the tetramers **6a**−**9a**. Note that the tetrameric isomer **9b**, which comprises the central unit in the X-ray structure of **1**, indeed is a mimimum (Table 6), in contrast with the unsolvated **9a**, which collapsed to the ladder structure **8a** on optimization with both semiempirical methods (Table 5). The MNDO potential energy surface for the tetramers is extremely flat; this is also indicated by the low values of the computed vibrational frequencies. The energy difference between the four solvated tetrameric isomers is less than 5 kcal/mol (Table 6)! While cubic **7b** is the global minimum, the ladder **8b** is only 0.6 kcal/mol less stable. This is followed by the eight-membered ring **6b** and by the annulated ring structure **9b** (only 0.4 kcal/mol less stable than **6b**!). Due

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Table 6. Heats of formation ΔH_f (kcal/mol) of the TMEDA-solvated $(LiCl)_n$ aggregates **2b**–**9b** (Relative Energies in Brackets), Heats of Solvation ΔH_{solv} (kcal/mol) [$\Delta H_{solv} = \Delta H_f((LiCl)_n{\cdot}m\text{TMEDA}) - \Delta H_f((LiCl)_n) - m\Delta H_f(\text{TMEDA})$], and Heats of Solvation per TMEDA in Parentheses

	ΔH_f		ΔH_{solv}	
	MNDO	PM3	MNDO	PM3
		TMEDA		
	+6.7	−13.7		
		Monomer		
2b	−64.6	−80.5	−32.6	−18.9
		Dimer		
3b	−143.5	−216.1	−40.3 (−20.2)	−23.5 (−11.75)
		Trimers		
4b	−209.1 [0.0]	−337.9 [4.8]	−42.6 (−14.2)	−23.2 (−7.7)
5b	−206.5 [2.6]	−342.7 [0.0]	*a*	−23.8 (−7.9)
		Tetramers		
6b	−272.5 [4.4]	−454.3 [37.9]	−48.7 (−12.2)	−21.1 (−5.2)
7b	−276.9 [0.0]	−492.2 [0.0]	−40.2 (−10.05)	−30.2 (−7.55)
8b	−276.3 [0.6]	−471.5 [20.7]	−51.0 (−12.75)	−24.0 (−6.00)
9b	−272.1 [4.8]	−463.5 [28.7]	*b*	*b*

[a] ΔH_{solv} cannot be determined as the unsolvated $(LiCl)_3$ ladder converges to the six-membered ring **4a** on optimization with MNDO. [b] ΔH_{solv} cannot be determined as the unsolvated $(LiCl)_4$ annulated ring structure converges to the ladder structure **8a** on optimization with MNDO and PM3.

Table 7. Solvation Enthalpies (kcal/mol) of the "Model Complexes" LiCl·EDA (Ethylenediamine) and Li_2Cl_2·EDA at Various Levels (Bidentate Coordination of EDA)

	ΔH_{solv}		
	MNDO	PM3	ab initio[a]
LiCl·EDA	−32.5	−29.1	−38.55[b]/−41.08[c]
Li_2Cl_2·EDA	−28.42	−25.61	−34.18[b]/−37.72[c]

[a] Reference 43. [b] MP4SDQ(FC)/6-31+G*//MP2(fu)/6-31+G* + ΔZPE (HF/6-31G*). [c] MP2(fu)/6-31+G*//MP2(fu)/6-31+G* + ΔZPE (HF/6-31G*).

Table 8. IGLO-Calculated Absolute Lithium Shielding Constants (σ, ppm) and Chemical Shifts (δ, ppm Relative to LiCl ≡ 0.0 ppm; IGLO/DZ//MP2(FC)/6-31G*)[26]

	point group	σ	δ
2a	$C_{\infty h}$	99.44	0
3a	D_{2h}	98.91	+0.53
4a	D_{3h}	99.64	−0.2
6a	D_{4h}	99.72	−0.28
7a	T_d	98.50	+0.94
8a	C_{2h}	99.11/98.59	+0.33/+0.85[a]
9a	C_s	98.95/99.63/98.55/98.67	0.48/−0.19/+0.89/+0.77[b]

[a] The Li shifts at +0.33 and +0.85 ppm correspond to the "inner" and "outer" lithium atoms of **8a**, respectively. [b] These shifts correspond to the atoms Li(4), Li(1), Li(2), and Li(3) as numbered in **1**.

to these very small energetic differences—and not taking entropy into account—it might well be possible that an equilibrium between tetramers is present in solution. That **1** crystallizes from the solution may be due to other factors (e.g. solubility and/or crystal packing effects).

In comparison to MNDO, the PM3-optimized tetramers **6b**–**9b** (Table 6) are much more distinct energetically, with the cube **7b** again being the most stable tetramer, followed by the ladder **8b** (E_{rel} = 20.7 kcal/mol), the annulated ring structure **9b** (E_{rel} = 28.7 kcal/mol), and the eight-membered ring **6b** (E_{rel} = 37.9 kcal/mol). Note that both PM3 and MNDO show the tetrahedral arrangement **7b** to be the most stable, although solvation by the *monodentate* TMEDA ligand is *not effective*.

A comparison between the experimental geometrical parameters of **1** and those computed by MNDO and PM3 shows the average MNDO Li–Cl and Li–N distances to be 33 and 17 pm too long, respectively. The PM3-calculated values are on average ca. 17 pm too short for Li–Cl and ca. 10 pm too long for Li–N bonds (in comparison to the X-ray values).

In general, computed solvation enthalpies at MNDO and at PM3 (Table 6) differ dramatically. The solvation enthalpies per TMEDA ligand are given in parentheses (Table 6, columns 3 and 4). These are averaged values for monodentate and bidentate TMEDA coordinations for **5b**, **8b**, and **9b**.

The complexation energies are not affected when amine alkyl groups are present (provided no adverse steric effects are involved). Thus, the complexation enthalpies of LiCl·NH_3 (−25.7 kcal/mol) and LiCl·NMe_3 (−25.7 kcal/mol) are identical at the MP4(FC)/6-31+G*//MP2(fu)/6-31+G* + ΔZPE(HF/6-31G*) level.[43] Similarly, MNDO finds the interaction energy in LiCl·TMEDA (−32.6 kcal/mol, Table 6) to be essentially the same as for LiCl·EDA (−32.5 kcal/mol, Table 7). PM3, however, gives a much lower value for LiCl·TMEDA (−18.9 kcal/mol, Table 6) than for LiCl·EDA (−29.1 kcal/mol, Table 7). Likewise, the PM3 TMEDA-complexation enthalpies for **4b** and **6b** (−7.7 and −5.2 kcal/mol, Table 6) are much lower. The latter results are presumably due to deficiencies in the Li parametrization in PM3, which overestimates the oligomerization energies of the unsolvated aggregates (Table 5). Although MNDO is known to overestimate steric repulsion effects,[44] the relative energies of the complexed tetramers calculated are much more reliable with MNDO than with PM3.

3. Li NMR Shift Calculations with the IGLO Method. As pointed out above, a solution of **1** in toluene-d_8 shows only one ^{7}Li NMR line down to −90 °C, although the lithium nuclei are nonequivalent. Computing the Li NMR shifts by the IGLO method[26] (Table 8) demonstrates that, for **9a**, which constitutes the central LiCl core of **1**, δ(Li) ranges between −0.89 and +0.19 ppm [relative to δ(LiCl) ≡ 0.0 ppm, which was chosen as the computational reference]. The δ(Li)'s of all other aggregates are similar. The overall shift difference for **2a**–**9a** is computed to be only 1.22 ppm according to our calculations! Furthermore, the ^{7}Li nucleus has a rather large quadrupole moment (-3×10^{-30} m^2)[45] and ^{7}Li NMR lines broaden with decreasing temperature due to more efficient quadrupole relaxation.[46] The small Li NMR shift difference of roughly 1 ppm for different lithium chloride aggregates (and within aggregates) would preclude resolution of the observed lithium signal. Hence, neither inter- nor intraaggregate exchange processes could be detected in solution via ^{7}Li NMR spectroscopy. The observation of only one NMR line for other lithium halide aggregates at low temperatures was taken as an indication for fast exchange processes.[6a,13d] Our IGLO calculations demonstrate that this conclusion may be premature, as the Li

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(43) van Eikema Hommes, N. J. R.; Schleyer, P. v. R. Unpublished results.

(44) (a) Stewart, J. J. P. *J. Comput.-Aided Mol. Des.* **1990**, *4*, 1. (b) The MNDO overestimation of steric effects in tetrahedral $(CH_3Li{\cdot}Et_2O)_4$ even results in a positive value for the solvation enthalpy: van Eikema Hommes, N. J. R.; Schleyer, P. v. R. Unpublished results.

(45) Kalinowski, H.-O.; Berger, S.; Braun, S. *^{13}C-NMR-Spektroskopie*; Georg Thieme Verlag: Stuttgart, 1984.

(46) Bauer, W.; Schleyer, P. v. R. In *Advances in Carbanion Chemistry*; Snieckus, V., Ed.; Jai Press: London, 1992; Vol. 1, p 89 and references therein.

NMR shifts may nearly be identical even for nonequivalent lithium nuclei.

Conclusions

Besides $[(LiCl)_4 \cdot 3.5TMEDA]_2$, **1**, which features a novel $(LiCl)_4$ core, two more LiCl−TMEDA adducts are known: a LiCl trimer, $[LiCl \cdot TMEDA]_3$,[17] and a polymer with hexameric subunits, $[(LiCl)_6 \cdot 4TMEDA]_n$,[13a] form, when the reaction conditions are varied. The formation of three different TMEDA-solvated LiCl aggregates in the solid state suggests that the energy differences between the isomers are small and the lattice energies are nearly the same. Indeed, the *ab initio* oligomerization energies per LiCl monomer are very similar for the six-membered ring **4a** and the tetramers **6a**, **8a**, and **9a**. *Ab initio* and MNDO calculations suggest that the potential energy surface of the LiCl tetramers **6a**−**9a** is very flat. For the TMEDA-solvated LiCl aggregates **6b**−**9b**, the MNDO potential energy surface becomes even more shallow. Both MNDO and PM3 reveal that solvation stabilizes isomers which are unstable in the unsolvated form.

Although the Li/PM3 parametrization seems to be superior to the Li/MNDO parametrization in certain respects,[32] it clearly fails to estimate association energies and solvation enthalpies of LiCl aggregates correctly. The strong underestimation of solvation enthalpies with PM3 presumably results from the overestimation of $(LiCl)_n$ oligomerization energies.

Li NMR shift calculations with the IGLO method confirm that the Li NMR shift range for LiCl oligomers apparently is too small to detect equilibria between different aggregates which might be present in solution.

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Supplementary Material Available: Tables of crystallographic experimental data, bond distances, bond angles, hydrogen atomic coordinates, and anisotropic displacement parameters as well as an ORTEP plot for **1** (7 pages). Ordering information is given on any current masthead page. Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, GB-Cambridge CB2 1EW, U.K., by quoting the full journal citation. Optimized geometries of the calculated LiCl isomers are available as "archive entries" from the authors on request.