An "Open Cube" Lithium Chloride Tetramer Containing Azetidine Ligands

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Introduction

Alkali halide oligomers $(MX)_n$ protected by suitable ligands against aggregation to form the standard ionic lattices have attracted growing interest in the recent literature, because these cation/anion clusters are nanoparticles carved out of the three-dimensional framework of the ligand-free salts.[1] Lithium chloride shows a particularly rich variety of core structures with the $(LiCl)_4$ cube as the basic unit (**A**).[2] Mixed species containing both lithium halides and lithium alkyls or other components based on the same structural principles are also known.[1,3]

The experimental structural work has been complemented by extensive theoretical studies, and various pathways from the cube to clusters of lower symmetry and lower or higher nuclearity have been calculated delineating the energetics of distortions (MNDO)[2] and the entrance to new minimum energy geometries.[1,2]

Among the set of fundamental clusters and their relations considered in recent studies are species with one, two or three edges of the cube elongated to give polycyclic geometries with squares tilted against each other. One of the more common forms is the stair-like arrangement (**B** in Figure 1).[3,4] However, to the best of our knowledge there has been no experimental observation of a species where the cubic box of $(LiCl)_4$ is unfolded by just a slight elongation of two neighboring parallel edges (**A**−**C**).[1,2]

We have now discovered such an example among the reaction products obtained in an attempt to prepare tetrakis(1-azetidino)-methane from the metathesis of carbon tetrachloride or tetrabromide and the corresponding lithium amide.

Results

Treatment of azetidine (in diethyl ether) with *n*-butyllithium (in hexane, azetidine in a large excess 4:1) at −70 to 20 °C affords a reaction mixture that has tentatively and tacitly been assumed to contain the expected lithium *N*-azetidinide. However, when the solution was cooled to −70 °C again and reacted with carbon tetrachloride [molar ratio 4:1, to generate tetrakis(1-azetidino)methane] a colorless crystalline product could be isolated, which contained both unreacted azetidine and *N*-(3-aminopropyl)azetidine. It thus appears that the lithiation reaction
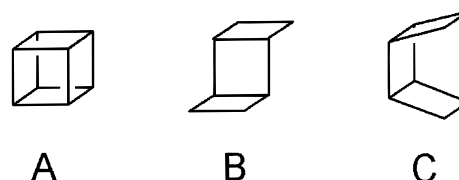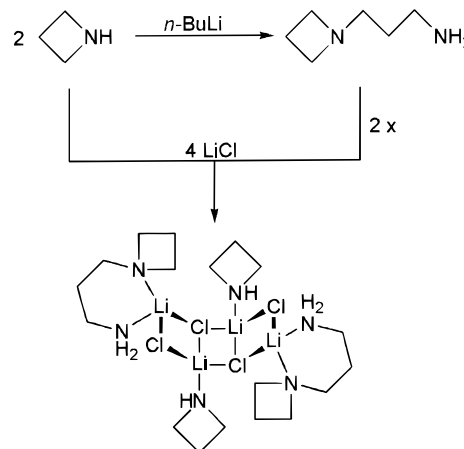

Figure 1. Complexes of $(LiCl)_4$.

is accompanied by partial ring opening of the azetidine via a nucleophilic attack of the lithium azetidinide (eq 1).

The formation of *N*-(3-aminopropyl)azetidine has previously been observed in the catalytic oligomerization of azetidine.[5] There are also several other preparative pathways to this dimer of azetidine.[6]

Azetidine and the γ-aminopropylazetidine are trapping the lithium chloride generated in the carbon tetrachloride amination to give a tetranuclear complex $(LiCl)_4$(azetidine)$_2$[*N*-(3-amino-propyl)azetidine]$_2$, which decomposes at 121 °C without melting (yield ca. 20%). The composition of the compound was confirmed by elemental analysis and NMR spectroscopy (in CDCl$_3$ solution). The connectivity of the nuclei was verified by H,H COSY and HMQC experiments. In the mass spectra (FAB) the γ-aminopropylazetidine ligand and $(LiCl)_2$ dimers and $(LiCl)_3$ trimers have been detected.

Crystals of the title compound (from diethyl ether/hexane at −30 °C) are orthorhombic (space group $Pca2_1$, $Z = 8$) (Table 1). The lattice is composed of neutral tetranuclear units (Figure 2) with no crystallographically imposed symmetry, but the molecular geometry obeys very closely the symmetry requirements of point group C_2, the pseudo-2-fold axis passing through the center of the square Li3−Cl3−Li4−Cl4.

The $(LiCl)_4$ core has the shape of an unfolding cube with the endocyclic angles Li−Cl−Li smaller and Cl−Li−Cl larger than 90°. The coordination sphere of the lithium atoms Li3 and Li4 with their three chlorine neighbors is complemented by one azetidine ligand, while the lithium atoms Li1 and Li2, with only two chlorine neighbors, are chelated by the γ-aminopropyl-

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Table 1. Crystal Data and Structure Refinement

empirical formula	$C_9H_{21}Cl_2Li_2N_3$
fw	256.07
space group	$Pca2_1$
a (Å)	18.2688(8)
b (Å)	7.0112(4)
c (Å)	22.6479(10)
T (°C)	−77
λ (Å)	0.710 73
V (Å^3)	2900.9(4)
ρ_{calcd} (g cm^{-3})	2.332
Z	8
μ (cm^{-1})	4.24
final R indices^a	R1 = 0.0409
	wR2 = 0.1015

^{a} R1 = $\Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; wR2 = $\{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0788$; $b = 0.2736$.
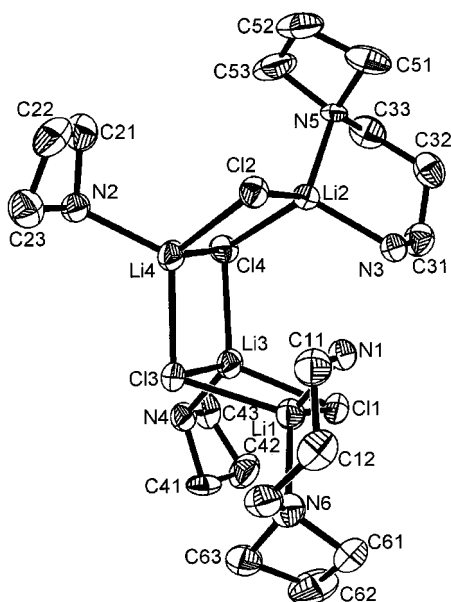
Figure 2. Molecular structure of (LiCl)$_4$(azetidine)$_2$[*N*-(3-aminopropyl)azetidine]$_2$. (ORTEP drawing with 50% probability ellipsoids; hydrogen atoms omitted for clarity.)

Table 2. Bond Lengths (Å) and Angles (deg) for (LiCl)$_4$(azetidine)$_2$[*N*-(3-aminopropyl)azetidine]$_2$

Cl1−Li1	2.321(8)	Cl4−Li2	2.400(6)
Cl1−Li3	2.358(5)	Cl4−Li4	2.430(5)
Cl2−Li2	2.317(7)	Li1−N1	2.011(7)
Cl2−Li4	2.356(5)	Li1−N6	2.016(9)
Cl3−Li1	2.369(6)	Li2−N3	2.003(7)
Cl3−Li4	2.381(5)	Li2−N5	2.061(8)
Cl3−Li3	2.438(5)	Li3−N4	2.051(5)
Cl4−Li3	2.382(5)	Li4−N2	2.046(5)
Li1−Cl1−Li3	78.1(2)	N5−Li2−Cl2	121.5(3)
Li2−Cl2−Li4	78.6(2)	N3−Li2−Cl4	109.7(3)
Li1−Cl3−Li4	109.2(2)	N5−Li2−Cl4	106.4(3)
Li1−Cl3−Li3	75.7(2)	Cl2−Li2−Cl4	103.7(2)
Li4−Cl3−Li3	81.9(2)	N4−Li3−Cl1	109.5(2)
Li3−Cl4−Li2	108.7(2)	N4−Li3−Cl3	110.6(2)
Li3−Cl4−Li4	82.1(2)	N4−Li3−Cl4	118.7(2)
Li2−Cl4−Li4	75.6(2)	Cl1−Li3−Cl3	101.3(2)
N1−Li1−N6	100.8(3)	Cl1−Li3−Cl4	116.6(2)
N1−Li1−Cl1	115.1(3)	Cl4−Li3−Cl3	97.8(2)
N6−Li1−Cl1	117.8(4)	N2−Li4−Cl2	110.1(2)
N1−Li1−Cl3	110.8(4)	N2−Li4−Cl4	110.9(2)
N6−Li1−Cl3	107.8(3)	N2−Li4−Cl3	118.2(2)
Cl1−Li1−Cl3	104.5(3)	Cl2−Li4−Cl3	115.7(2)
N3−Li2−N5	99.3(3)	Cl2−Li4−Cl4	101.7(2)
N3−Li2−Cl2	115.8(3)	Cl3−Li4−Cl4	98.1(2)

Figure 3. Intermolecular hydrogen bridges in (LiCl)$_4$(azetidine)$_2$[*N*-(3-aminopropyl)azetidine]$_2$.

azetidine molecules. The chelation generates two six-membered rings in a strain-free chair conformation. N5 and N6 are spiro-centers for these six-membered rings and the parent azetidine rings. (See Table 2.)
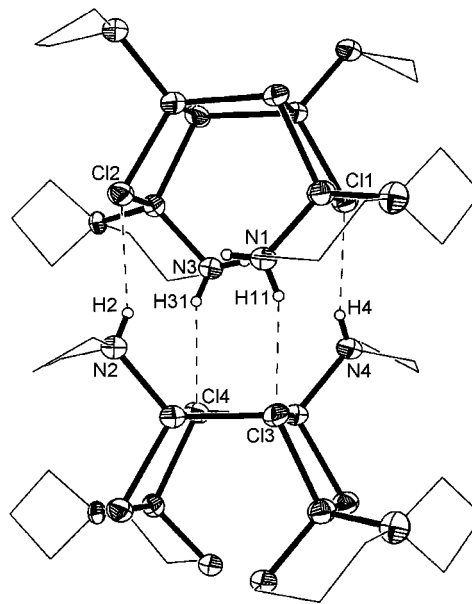
The folding angles of the three Li$_2$Cl$_2$ "squares" are 112.2 and 112.9°, showing that each of the two faces of the Li$_4$Cl$_4$ "cube" involved in the opening has been tilted by 22.5° (average), similar to the parameters of the stair-type array in structures **B** [114.3/126.1, 112.4/110.8].[4]

Folding **C** may be preferred over folding **B** because of the packing of the molecules in the crystal lattice. The molecules are stacked in columns along the z axis in such a way that four hydrogen bonds N−H- - -Cl can be maintained (Figure 3). These hydrogen bonds have H- - -Cl distances in the narrow range between 2.622/2.626 (Cl3, Cl4) and 2.647/2.656 Å (Cl2, Cl1), and angles N−H- - -Cl between 145.5 and 150.3° (with the N−H bond lengths fixed at 0.90 Å).

These weak hydrogen bonds are probably broken in solution, and the molecular units become fluxional on the NMR time scale, as suggested e.g. by the presence of only one ^{13}C signal for the two α-CH$_2$ groups of the spiro-azetidine ring. The results indicate that the Li$_4$Cl$_4$ array of the title compound is trapped in the lattice with a very special set of ligands favoring just

this type of unfolded cube. In solution the compound is probably part of a set of delicate equilibria influenced by many factors such as solvent, temperature and ligand concentration.

Experimental Section

All experiments were routinely carried out in an atmosphere of dry and pure nitrogen. Standard equipment was used throughout. Azetidine was prepared following a literature procedure.[7] All other reagents were commercially available.

Preparation. A 14 mL amount of a 1.7 M solution of *n*-butyllithium (23.8 mmol) in hexane is added over a period of 25 min to a solution of azetidine (5.6 g, 98 mmol) in diethyl ether (50 mL) at −70 °C with stirring. The reaction mixture is allowed to slowly warm to room temperature, and stirring is continued for 1 h at 20 °C. The mixture is cooled again to −70 °C, treated with a solution of tetrachloromethane

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(0.77 g, 5 mmol) in diethyl ether (10 mL), warmed to room temperature, and stirred at 20 °C overnight. A brown precipitate is filtered off, and the volume of the filtrate is reduced to one-third of the original volume in a vacuum. Cooling of this solution to −30 °C gives a crop of colorless crystals (590 mg, 2.3 mmol, 19.4%). The product decomposes upon heating at 121 °C without melting. Anal. Calcd for $C_9H_{21}Cl_2N_3Li_2$: C, 42.21; H, 8.27; Cl, 27.69; N, 16.41. Found: C, 42.35; H, 8.20; Cl, 28.22; N, 16.11. ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C), ppm: δ 1.47 [s, 2H, $J_{H,H}$ = 6.2/6.6 Hz, CH_2(CH$_2$NH$_2$)], 1.65 [br. s, 4H, NH/NH_2, 2.05 [q, 2H, $J_{H,H}$ = 7.0 Hz, CH_2(CH$_2$)$_2$NC], 2.33 [q, 2H, $J_{H,H}$ = 7.3 Hz, CH_2(CH$_2$)$_2$NH], 2.43 [t, 2H, $J_{H,H}$ = 6.2/6.6 Hz, CH_2NC$_2$], 2.72 [t, 2H, $J_{H,H}$ = 6.2 Hz, CH_2NH$_2$], 3.16 [t, 4H, $J_{H,H}$ = 7.0 Hz, (CH_2)$_2$NC], 3.64 [t, 4H, $J_{H,H}$ = 7.3 Hz, (CH_2)$_2$NH]. ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$, 25 °C), ppm: δ 17.6 [CH$_2$(CH$_2$)$_2$NC], 22.0 [CH$_2$(CH$_2$)$_2$NH], 31.3 [CH$_2$-CH$_2$NH$_2$], 40.6 [CH$_2$NH$_2$], 48.1 [CH$_2$(CH$_2$)$_2$NH], 55.3 [CH$_2$(CH$_2$)$_2$NC], 57.8 [CH$_2$N(CH$_2$)$_2$CH$_2$]. ^{14}N{^{1}H} NMR (29 MHz, CDCl$_3$, 25 °C), ppm: δ −355.8 [br. s, rel. MeNO$_2$]. ^{7}Li{^{1}H} NMR (105 MHz, CDCl$_3$, 25 °C), ppm: δ 4.27 [br. s, rel. 70% LiBr (D$_2$O)]. MS (FAB): *m/e* 355, 313, 115.

Crystal Structure Determination. A crystal of suitable quality and size was mounted in a glass capillary on an Enraf-Nonius CAD4 diffractometer (graphite monochromated Mo Kα radiation) and used for measurements of precise cell constants and intensity data collection. During data collection, three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed. 6289 reflections measured, 6289 unique. No absorption correction was applied. The structure was solved by Direct Methods (SHELXS-86)[8] and refined by full-matrix least-squares techniques on F^2 (SHELXL-93).[9] All non-H atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in idealized calculated positions and allowed to ride on their corresponding atoms with fixed isotropic contributions [$U_{iso(fix)}$ = 1.5U_{eq} of the attached atom]. The absolute structure has been confirmed successfully by considering the alternative solution for refinement.

Supporting Information Available: An X-ray crystallographic file, in CIF format, for the structure determination of (LiCl)$_4$(azetidine)$_2$-[N-(3-aminopropyl)azetidine]$_2$ is available free of charge via the Internet at http://pubs.acs.org.

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