Organolithium Compounds

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A Dilithium 1,4-Butanediide with a Chlorine-Centered Li_{12} Icosahedral Structure**

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Dedicated to Professor Dirk Walther on the occasion of his 70th birthday

First organolithium compounds were prepared in the middle of the 19th century,[1] and today they continue to play a key role in organometallic chemistry for many reasons such as commercial availability, straightforward preparative procedures, and a broad application spectrum. To understand and tune the properties of organolithium derivatives, their structures have been investigated in the solid state as well as in solution. The structural diversity of organolithium derivatives is a consequence of aggregation often based on triangle-based Li_n polyhedrons and platonic bodies. The triangular faces often are capped by carbanions, thus leading to short Li–Li contacts. Small aggregation degrees can be achieved with bulky substituents and by addition of Lewis bases L such as ethers or amines. Depending on the coligand L and on the bulkiness of R, the following structures are the most common: $Li(L)_nR$ (monomeric molecules), $Li(L)_n^+$ $(R\text{-}Li\text{-}R)^-$ (lithium lithiates), $[Li(L)_2(\mu\text{-}R)]_2$ (with Li_2C_2 rings), $[Li(\mu_3\text{-}R)]_4$ (with Li_4 tetrahedrons), and $[Li(\mu_3\text{-}R)]_6$ (with distorted Li_6 octahedrons).[2] Higher nuclearity and aggregation degrees are rather seldom, and usually similar structural features are observed such as $(LiX)_2$ and $(LiX)_3$ rings that dimerize to cubes or hexagonal prisms or aggregate to ladder-like structures.[2–4]

Whereas in molecular organolithium chemistry larger lithium cages are to date unknown, icosahedral cages that contain an interstitial lithium atom are known for zero-valent lithium. These lithium(0)-centered Li_{13} icosahedra were found in intermetallic phases such as $Li_{18.9}Na_{8.3}Ba_{15.3}$[5] or the subnitride $Li_{80}Ba_{39}N_9$.[6] Interpenetrating lithium icosahedra Li_{19} formed during the crystallization of $Li_{33.3}Ba_{13.1}Ca_3$[5] and of binary $Li_{44}Ba_{19}$.[7] Icosahedra seem to be typical in Li-rich intermetallic compounds. In these lithium(0) clusters, Li–Li separations between 287 and 344 pm were found.

These results suggest that icosahedral cages of lithium(I) cations should also be feasible. To overcome electrostatic repulsion between lithium cations, the lithium cage has to contain an anion X^{n-}, which is surrounded by the Li^+ ions (Figure 1). However, the presence of halide ions in many lithium organometallic compounds does not lead to halide-centered lithium cages, but the halide ion is able to replace alkyl groups which cap Li_3 faces of lithium polyhedrons. This substitution leads to less reactive organolithium compounds, for example $[Li_4Me_{4-n}X_n]$ with a central Li_4 tetrahedron.[8] Therefore, the concept had to be expanded, and as an outer organic clamp a 1,ω-butanediide ion was used.

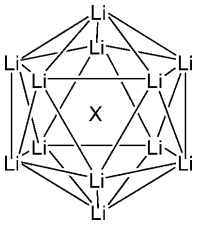

Figure 1. An anion-centered lithium icosahedron.

The reaction of lithium sand with 1,4-dichlorobutane in diethyl ether[9] led to a clear solution which contained several chemically different 1,4-butanediide anions, as determined by ^1H and ^{13}C NMR spectroscopy. Cooling of the reaction mixture led to the precipitation of single crystals. However, a high-quality structure determination failed owing to heavy disordering of the cation. Nevertheless, the structure determination suggested a solvent-separated ion pair $[Li(Et_2O)_4][Li_{12}\{\mu_3,\mu_3\text{-}(CH_2)_4\}_6(@\text{-}X)]$ (**1**), which showed a Li_{12} icosahedron centered around an anion X^-. The nature of X^- was not absolutely clear; the electron density pointed towards a hydride anion (which can be explained by β-H abstraction), but a chloride also seemed to offer a possible solution.

To investigate the stability of these $[Li_{12}\{\mu_3,\mu_3\text{-}(CH_2)_4\}_6(@\text{-}X)]^-$ cages towards Lewis bases and to obtain less soluble compounds that crystallize without disordering, two- and three-dentate Lewis bases were added to the reaction solutions. The addition of the two-dentate Lewis bases 1,2-dimethoxyethane (dme) and 1,2-bis(dimethylamino)ethane (tmeda) only led to ligand exchange reactions at the cation, yielding $[Li(dme)_2][Li_{12}\{\mu_3,\mu_3\text{-}(CH_2)_4\}_6(@\text{-}Cl)]$ (**2**) and $[Li(tmeda)_2][Li_{12}\{\mu_3,\mu_3\text{-}(CH_2)_4\}_6(@\text{-}Cl)]$ (**3**), respectively (Scheme 1). These compounds displayed similar disorder problems as observed in **1**, because both of these complexes crystallized in the same space group $Fd\bar{3}$ with the cations on crystallographic C_3 axes, which leads to severe disordering of the complex cations. To meet the crystallographically specified symmetry, thus resolving the disorder, a cyclic base with C_3 symmetry, 1,3,5-trimethyl-1,3,5-triazinane (tmta), was chosen. In this way, the complex $[Li(tmta)_2][Li_{12}\{\mu_3,\mu_3\text{-}(CH_2)_4\}_6(@\text{-}Cl)]$ (**4**) could be isolated in high yield, and its crystal structure showed no signs of disorder.

The molecular structure of **4** and its numbering scheme is shown in Figure 2. The cation of this solvent-separated ion

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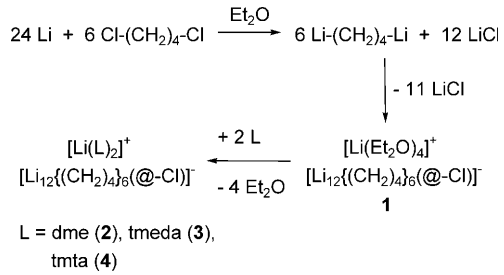

Scheme 1. Synthesis of the solvent-separated ion pairs **2**–**4**.

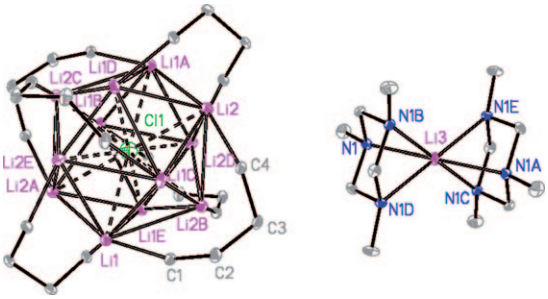

Figure 2. Molecular structure of solvent-separated ion pair **4**. The ellipsoids represent a probability of 40%, H atoms are omitted. Only black lines represent two-electron two-center bonds. The following symmetry operations complete the structural model: A: $-x+y, -x, z$; B: $y, -x+y, -z$; C: $-x, -y, -z$; D: $-y, x-y, z$; E: $x-y, x, -z$; F: $-x, -y, -z+1$; G: $x-y, x, -z+1$; H: $y, -x+y, -z+1$. Selected bond lengths not given in the text [pm]: Li1–C1 215.5(6), Li1–C1E 221.2(6), Li1–C4E 221.6(6), Li2–C4 214.8(6), Li2–C4D 218.3(6), Li2–C1D 222.3(6), C1–C2 154.7(4), C2–C3 153.8(4), C3–C4 154.8(4).

pair shows a hexacoordinate lithium atom in a distorted octahedral environment with Li–N bond lengths of 219.1(2) pm. The chlorine-centered Li_{12} icosahedron of the anion shows Li–Cl bond lengths of 257.2(5) and 259.3(5) pm, leading to Li–-Li distances of 244.8(7) and 274.9(9)–281.4(7) pm. The small value belongs to the Li1–Li2 edge between two carbanion-capped faces, whereas the larger values describe Li–Li edges between capped and uncapped triangular faces. The lithium cations of the anion form an icosahedron; twelve of the twenty faces are capped by a carbanion. The centers of the eight uncapped faces form a cube. Every lithium cation shows a distorted tetrahedral environment and is bound to the central anion and to three carbanions. The high symmetry of this polyhedron is represented by the rather small asymmetric unit containing two Li atoms, the halide center, and only one butanediide substituent.

The 1,4-butanediide groups cover the surface of the Li_{12} icosahedron. In this way they clamp the lithium cations and also shield the metal cluster from further aggregation, dissociation, and attack of Lewis bases such as amines and ethers. To clarify this situation, a ball-and-stick representation is shown in Figure 3 including the hydrogen atoms. This picture shows that the coordination spheres of the lithium atoms are saturated by short contacts to α- and β-CH fragments, leading to small Li–H distances (Li1–C3

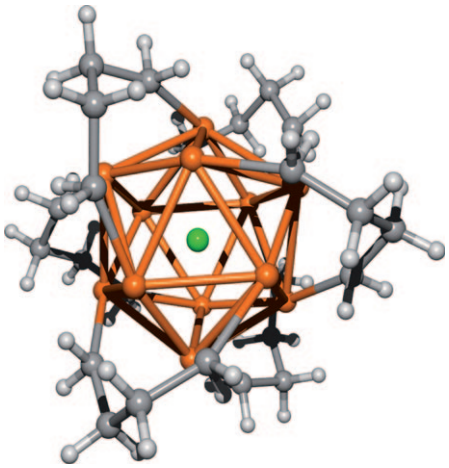

Figure 3. Ball-and-stick model of the core-shell anion of **4** (Li orange, Cl green, C gray, H light gray). The orange lines represent the Li_{12} icosahedron.

240.0(6), Li1–H1A 218(5), Li1–H3A 225(4), Li2–C2 247.1(6), Li2–H4B 224(5), and Li2–H2A 230(5) pm). These agostic interactions are possible because the butanediide groups bend towards the uncapped triangular Li_3 faces.

To deduce the importance of the size of the inner anion, these experiments were repeated in the presence of bromide. Thus, lithium sand was used to reduce 1,4-dibromobutane in diethyl ether.[10] Owing to the high solubility of $Li_2(CH_2)_4$ in ether, we were only able to crystallize $[Li(Et_2O)(\mu_3\text{-}Br)]_4$.[11] Addition of dme led to precipitation of $[Li(dme)_2Br]$.[4,12] The organolithium compound was highly soluble in these organic donor solvents, and we were unable to isolate similar anions with cage structures.

Anion-centered lithium polyhedrons have also been reported for oxide-centered lithium cages containing Li_6O moieties.[3,13] Incorporation of LiCl into molecular structures is rather common. In these complexes, the above-mentioned structural principle of stacking and ladder formation of $(LiX)_n$ rings ($n=2$ or 3) is maintained, as in $[Li_8Cl_7]^+$ with two corner-sharing $(LiCl)_4$ heterocubane cages[14] or in an Li_4O_3Cl cubane cage.[15] In $Li[\{MeAl(PPh)_3Li_4(thf)_3\}_4(\mu_4\text{-}Cl)]$ the central chloride anion shows small separations from four lithium atoms, whereas the other twelve lithium atoms coordinate to THF molecules.[16] Solvent-separated $[Li(L)_2][Li_{12}\{\mu_3,\mu_3\text{-}(CH_2)_4\}_6(@\text{-}Cl)]$ (**2**–**4**) are unique examples of alkyl lithium compounds with a chloride-centered cage structure which, however, also needs to be stabilized by 1,ω-alkanediide clamps. The repulsive forces between the lithium cations of the icosahedral anion are overcome by the carbanions of the butanediide ligands, which cap twelve faces. The importance of having 1,ω-alkanediide substituents is evident, because similar structures are unknown in the chemistry of alkyl lithium compounds prepared from chloro- or bromoalkanes. It is somewhat surprising that this icosahedral cage structure is maintained even in the presence of strong chelating Lewis bases such as dme (in **2**), tmeda (in **3**), and tmta (in **4**), whereas the lithium countercation immediately binds to these bases. The stability of the cage structure of the $[Li_{12}\{\mu_3,\mu_3\text{-}(CH_2)_4\}_6(@\text{-}Cl)]$ anion is a consequence of syner-

getic effects: internal templating by the Cl^- anion and external clamping by 1,4-butanediides.

Experimental Section

All manipulations were performed in an argon atmosphere. The compounds are pyrophoric and therefore elemental analyses did not give reliable results. Lithium sand was prepared from molten lithium in paraffin oil by vigorous stirring as described elsewhere.[17]

Dilithium 1,4-butanediide (from Cl-$(CH_2)_4$-Cl): An excess of lithium sand (4.5 g) was suspended at room temperature in Et_2O (160 mL). 1,4-Dichlorobutane in Et_2O (20 mL) was added dropwise over 6 h. After complete addition, the reaction mixture was heated under reflux for 0.5 h. Then all solids (LiCl, excess lithium) were removed by filtration. The molarity of the solution was determined by titration of an aliquot with sulfuric acid (phenolphthalein indicator). Yield: 78%. NMR spectroscopic investigation showed the presence of three chemically different butanediide anions. ^{1}H NMR (400.2 MHz, C_6D_6/OEt_2): $\delta = -0.91$ (2.33 H, br t, Li-CH_2), −0.79 (0.53 H, br, Li-CH_2), −0.71 (1.14 H, br t, Li-CH_2), 1.78 (1.6 H, br, $J \approx 3.6$ Hz, CH_2), 1.84 (CH_2), 1.86 ppm (2.38 H, br, CH_2). ^{13}C{1H} NMR (100.6 MHz, C_6D_6/OEt_2): $\delta = 5.6$ (br, Li-CH_2), 9.2 (Li-CH_2), 31.7 (CH_2), 33.4 ppm (CH_2). This solution was used for ligand exchange reactions. Dilithium 1,4-butanediide is insoluble in pentane; addition of toluene led to formation of a biphasic system.

4: In a Schlenk flask, a solution of dilithium 1,4-butanediide in diethyl ether (1M; 8 mL, 8.0 mmol) was cooled to 0 °C. This solution was layered with diethyl ether (40 mL), and this layer again was covered with a layer of TMTA (2.58 g, 20.0 mmol) in diethyl ether (7 mL). Storage at 0 °C led to formation of small crystals at the phase border. Larger colorless crystals precipitated thereafter. These crystals were collected, washed with diethyl ether, and dried in vacuum. Yield: 77%. ^{1}H NMR (200.1 MHz, [D_8]THF): $\delta = -1.06$ (24 H, s, Li-CH_2), 1.72 (24 H, s, CH_2), 2.17 (18 H, s, N-CH_3), 3.06 ppm (12 H, br, N-CH_2-N). ^{13}C{^{1}H} NMR (50.3 MHz, [D_8]THF): $\delta = 8.0$ (Li-CH_2), 34.2 (CH_2), 40.5 (N-CH_3), 78.1 ppm (N-CH_2-N). Crystal structure determination: The intensity data were collected on a Nonius KappaCCD diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation. Data were corrected for Lorentz and polarization effects, but not for absorption.[18,19] The structure was solved by direct methods (SHELXS[20]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97[21]). All hydrogen atoms for the molecule were located by difference Fourier synthesis and refined isotropically.[21] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations. Crystal data for **4**: $C_{36}H_{78}ClLi_{13}N_6$, $M = 720.71$ g mol^{-1}, colorless prism, size $0.05 \times 0.05 \times 0.04$ mm^3, rhombohedral, space group $R\bar{3}$, $a = 14.8791(7)$, $b = 14.8791(7)$, $c = 18.1178(9)$ Å, $V = 3473.7(3)$ Å^3, $T = -140$ °C, $Z = 3$, $\rho_{calcd} = 1.034$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 1.11$ cm^{-1}, $F(000) = 1176$, 8245 reflections in $h(-17/19)$, $k(-19/17)$, $l(-23/19)$, measured in the range $2.74° \le \Theta \le 27.49°$, completeness $\Theta_{max} = 99.8\%$, 1785 independent reflections, $R_{int} = 0.0489$, 1431 reflections with $F_o > 4\sigma(F_o)$, 138 parameters, 0 restraints, $R1_{obs} = 0.0974$, $wR^2_{obs} = 0.2928$, $R1_{all} = 0.1159$, $wR^2_{all} = 0.3081$, GOOF = 1.076, largest difference peak and hole: 0.566/−2.398 e Å^{-3}. CCDC-744679 (**4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Dilithium 1,4-butanediide (from Br-$(CH_2)_4$-Br): Lithium sand (2.3 g, 331 mmol) was suspended in diethyl ether (50 mL) at 0 °C. A mixture of 1,4-dibromobutane (12.5 g, 59.5 mmol) and diethyl ether (20 mL) was added until the reaction started. Then the stirred reaction mixture was cooled to −10 °C and the rest of the 1,4-dibromobutane/ether mixture was added dropwise over 2 h. Thereafter the reaction solution was warmed to 10 °C and stirred for additional 30 min. Then all solids were removed at 0 °C, and a yield of 61% was determined by titration with sulfuric acid with phenolphthalein indicator. ^{1}H NMR (200.1 MHz, C_6D_6-OEt_2): $\delta = -0.84$ (4 H, br, Li-CH_2), 1.95 ppm (4 H, br CH_2). ^{13}C{^{1}H} NMR (50.3 MHz, C_6D_6/OEt_2): $\delta = 9.9$ (Li-CH_2), 31.2 ppm (CH_2).

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