Crystal Structure of a Lithium Chloride Cubane Cluster Solvated by Diethyl Ether

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Z. Naturforsch. 56h, 443–445 (2001);

Lithium Chloride, Aggregation, Crystal Structure

Lithium chloride is frequently a by-product of reactions where organolithium compounds or other reagents prepared by deprotonation with butyl-lithium are employed in syntheses. Extensive investigations in the structural chemistry of complexxes of lithium salts were carried out and the results have recently been compiled in a review by Snaith and Wright [1]. The structures adopted by aggregates of ion pairs Li⁺X⁻ (scheme 1) include rhombic dimers (a), ladder-like polymers (b) as in [[(THF)LiCl]2] [2], cyclic trimers (c), drum-like hexamers (d) and cubic tetramers (e), which can further aggregate into polymers (f). All of these structural motifs are verified with various donor molecules bonded to the lithium centres. Fragments of the polymeric structure (b) have been stabilised by azetidine based ligands [3]. Structure (a) without donor stabilisation is also present in the vapour phase of [LiCl]2 [4].

Among all lithium halides and donor solvent molecules, the combination of lithium chloride and diethyl ether is probably the most relevant with regard to preparative chemistry and thus the knowledge of the structure of a lithium chloride diethyl ether solvate is desirable. Earlier investigations have established the structure of a lithium chloride solvate with HMPA [5], which consists of a Li₄Cl₄ cube with the lithium centres coordinated to the oxygen atom of O=P(NMe₂)₃ molecules. Another solvate of LiCl was observed with TMEDA [6], which adopts a bicyclic structure of the composition (LiCl)₄tmedₐ₃, consisting of a six-membered LiCl trimmer fused to a four-membered ring which adds another LiCl unit. A diethyl ether solvate of lithium bromide is also known, which is again a cube of (LiBr)₄ coordinated by four Et₂O units [7].

We got hold of a crystal of Li₄Cl₄·4Et₂O during our attempts to synthesise ethers α-metallated with group 13 metals from the thermally unstable carbenoid LiCH₂OMe. The preparation required continuous manipulation at low temperature and afforded a crystalline material, which itself turned out to be unstable and visibly decomposed with gas evolution at temperatures higher than −30 °C. We managed to transfer such a crystal to the diffractometer under permanent cooling and were thus able to determine its structure.

Molecules of Li₄Cl₄·4Et₂O are present as monomers in the orthorhombic crystal structure (space group P2₁2₁2₁). The structure is shown in Fig. 1, the figure caption gives ranges of bond lengths and angles. No crystallographic symmetry is imposed on the heterocubane structure. In this respect Li₄Cl₄·4Et₂O and its bromine analogue Li₄Br₄·4Et₂O behave differently. The latter crystallises in the monoclinic space group C2/c and the molecules obey crystallographic C2 symmetry [7]. This makes the skeleton of Li₄Br₄·4Et₂O more regular than that of Li₄Cl₄·4Et₂O.
Fig. 1 Crystal structure of \([\text{Et}_2\text{O} \cdot \text{LiCl}]_4\) (ellipsoids are at 30% probability level). Key dimensions of the aggregate are: \(\text{Li} - \text{Cl} = 2.35(1) - 2.40(1), \text{Li} - \text{O} = 1.90(1) - 1.93(1), \text{Li} - \text{Li} = 3.00(2) - 3.08(1), \text{C} - \text{O} = 1.42(9) - 1.50(1), \text{Cl} - \text{Li} - \text{Cl} = 77.3(3) - 81.5(4), \text{Cl} - \text{Li} - \text{O} = 97.5(4) - 102.0(4), \text{Cl} - \text{Li} - \text{O} = 108.7(5) - 128.8(5)\).

The lithium atoms in \(\text{Li}_4\text{Cl}_4 \cdot 4\text{Et}_2\text{O}\) are tetra-coordinate by three chlorine centres and the oxygen atom of an ether molecule. The coordination geometry is very distorted as is illustrated by the extrema of the values for the \(\text{O} - \text{Li} - \text{Cl}\) angles \([108.7(5) - 128.8(5)\^\circ]\), while the \(\text{Cl} - \text{Li} - \text{Cl}\) angles fall over a narrower range of \(97.5(4) - 102.0(4)\^\circ\). These values are generally smaller than in the gas-phase dimer \([\text{LiCl}]_2\) where the \(\text{Cl} - \text{Li} - \text{Cl}\) angles are 108(4)\(^\circ\) [4].

The geometry at the chlorine atoms is steeply pyramidal, with \(\text{Li} - \text{Cl} - \text{Li}\) angles between 77.3(3) and 81.5(4)\(^\circ\). The position of both the Li and the Cl centres fulfil the expectations based on the VSEPR model despite the clearly ionic character of the components. The \(\text{Li} - \text{Cl}\) distances \([2.346(11) - 2.395(11)\text{ Å}]\) are similar to those of the \(\text{Li}_4\text{Cl}_4 \cdot 4\text{HMPA}\) adduct \([2.375(10) - 2.441(12)\text{ Å}]\). However, the \(\text{Li} - \text{Cl}\) distance in crystalline solvent-free lithium chloride \(2.182\text{ Å}\) [8] and that in the gas-phase dimer \(2.14\text{ Å}\) [4] are considerably shorter than in our \(\text{Li}_4\text{Cl}_4 \cdot 4\text{Et}_2\text{O}\). Therefore this cube should not be regarded as a solvated fragment of the LiCl crystal structure.

**Experimental**

**Preparation of \(\text{Li}_4\text{Cl}_4 \cdot 4\text{Et}_2\text{O}\)**

Methyllithium \((9.8 \text{ ml}, 1.6 \text{ m solution in diethyl ether, 15.7 mmol})\) was slowly added to a solution of \(\text{Me}_2\text{SnCH}_2\text{OME}\) \((3.13 \text{ g}, 15 \text{ mmol})\) in diethyl ether \((80 \text{ ml})\) at \(-78\^\circ\text{C}\). The reaction mixture was stirred for 45 minutes at this temperature. The unstable \(\text{LiCH}_2\text{OME}\) [9] is formed via tin-lithium transmetallation. A pre-cooled \((-50\^\circ\text{C})\) solution of dimethylaluminium chloride \((1.1 \text{ g, 12 mmol})\) in diethylether/hexane \((15 / 10 \text{ ml})\) was slowly added. The reaction mixture was kept at \(-78\^\circ\text{C}\) for a further 3 h after which a clear solution was obtained. After storage at \(-78\^\circ\text{C}\) for one week, a colourless precipitate was formed and in addition colourless crystals of \(\text{Li}_4\text{Cl}_4 \cdot 4\text{Et}_2\text{O}\). Tetramethyltin could be detected in the solution by \(^{119}\text{Sn}\) NMR spectroscopy.

**Crystal structure determination of \(\text{Li}_4\text{Cl}_4 \cdot 4\text{Et}_2\text{O}\)**

Scattering data collection of a single crystal of \(\text{Li}_4\text{Cl}_4 \cdot 4\text{Et}_2\text{O}\) was performed on a Nonius Turbo CAD4 diffractometer. \(\text{C}_8\text{H}_{20}\text{Li}_2\text{Cl}_2\text{O}_2\ M_r = 233.02,\) crystal system orthorhombic, space group \(P2_12_12_1, Z = 8, a = 9.994(3), b = 10.496(2), c = 25.571(4)\text{ Å}, V = 2682(1)\text{ Å}^3\) at 133(2)\(^\circ\) at 133(2)\(^\circ\) K, \(\mu = 0.456\text{ mm}^{-1}\), \(2\theta_{\text{max}} = 50^\circ\), 6868 scattering intensities collected, 4698 independent reflections \((R_{\text{int}} = 0.0925)\). 233 parameters, \(R_1 = 0.070\) for 2756 scattering intensities with \(F_o > 4\sigma(F_o)\) and \(wR_2 = 0.164\) for all data. The absolute structure parameter adopts a value of \(-0.04(15)\). Solution by direct methods and refinement of the structure was undertaken with the program SHELXTL 5.01 [8]. Hydrogen and lithium atoms were refined with isotropic displacement parameters while all other atoms were refined anisotropically. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-159334. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).


    b) U. Schöllkopf Annalen 704, 120 (1967).