

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

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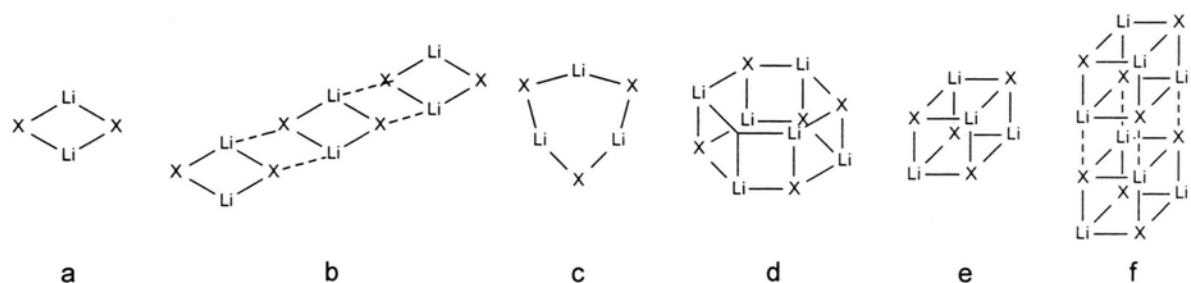
The thermally highly unstable diethyl ether solvate of lithium chloride was crystallised and its crystal structure determined. It consists of a cubic cluster of the composition Li_4Cl_4 with each of the four Li atoms coordinated to a molecule of diethyl ether.

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 complexes 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 $[(\text{THF})\text{LiCl}]_2$ [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 $[\text{LiCl}]_2$ [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 Li_4Cl_4 cube with the lithium centres coordinated to the oxygen atom of $\text{O}=\text{P}(\text{NMe}_2)_3$ molecules. Another solvate of LiCl was observed with TMEDA [6], which adopts a bicyclic structure of the composition $(\text{LiCl})_4\text{tmdea}_{3.5}$, consisting of a six-membered LiCl trimer 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 $(\text{LiBr})_4$ coordinated by four Et_2O units [7].

We got hold of a crystal of $\text{Li}_4\text{Cl}_4 \cdot 4\text{Et}_2\text{O}$ during our attempts to synthesise ethers α -metallated with group 13 metals from the thermally unstable carbenoid LiCH_2OMe . 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 $\text{Li}_4\text{Cl}_4 \cdot 4\text{Et}_2\text{O}$ are present as monomers in the orthorhombic crystal structure (space group $P2_12_12_1$). 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 $\text{Li}_4\text{Cl}_4 \cdot 4\text{Et}_2\text{O}$ and its bromine analogue $\text{Li}_4\text{Br}_4 \cdot 4\text{Et}_2\text{O}$ behave differently. The latter crystallises in the monoclinic space group $C2/c$ and the molecules obey crystallographic C_2 symmetry [7]. This makes the skeleton of $\text{Li}_4\text{Br}_4 \cdot 4\text{Et}_2\text{O}$ more regular than that of $\text{Li}_4\text{Cl}_4 \cdot 4\text{Et}_2\text{O}$.



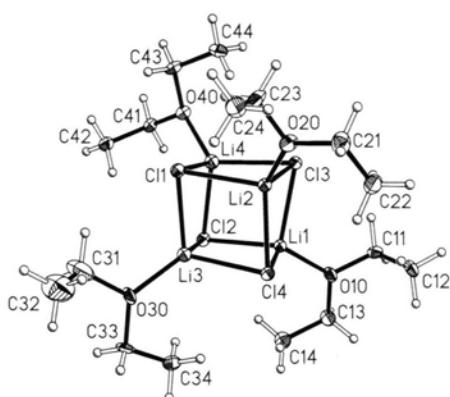


Fig. 1 Crystal structure of $[Et_2O \cdot LiCl]_4$ (ellipsoids are at 30% probability level). Key dimensions of the aggregate are: Li–Cl 2.35(1)–2.40(1), Li–O 1.90(1)–1.93(1), Li–Li 3.00(2)–3.08(1), C–O 1.42(9)–1.50(1), Li–Cl–Li 77.3(3)–81.5(4), Cl–Li–Cl 97.5(4)–102.0(4), Cl–Li–O 108.7(5)–128.8(5).

The lithium atoms in $Li_4Cl_4 \cdot 4Et_2O$ 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 O–Li–Cl angles [108.7(5)–128.8(5) $^\circ$], while the Cl–Li–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 $[LiCl]_2$ where the Cl–Li–Cl angles are 108(4) $^\circ$ [4].

The geometry at the chlorine atoms is steeply pyramidal, with Li–Cl–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 Li–Cl distances [2.346(11)–2.395(11)] are similar to those of the $Li_4Cl_4 \cdot 4HMPA$ adduct [2.375(10)–2.441(12) Å]. However, the Li–Cl distance in crystalline solvent-free lithium chloride (2.182 Å) [8] and that in the gas-phase dimer (2.14 Å) [4] are considerably shorter than in our $Li_4Cl_4 \cdot 4Et_2O$. Therefore this cube should not be regarded as a solvated fragment of the LiCl crystal structure.

Experimental

Preparation of $Li_4Cl_4 \cdot 4Et_2O$

Methylolithium (9.8 ml, 1.6 M solution in diethyl ether, 15.7 mmol) was slowly added to a solution of Me_3SnCH_2OMe (3.13 g, 15 mmol) in diethyl ether (80 ml) at –78 °C. The reaction mixture was stirred for 45 minutes at this temperature. The unstable $LiCH_2OMe$ [9] is formed via tin-lithium transmetallation. A pre-cooled (–50 °C) solution of dimethylaluminium chloride (1.1 g, 12 mmol) in diethylether/hexane (15/10 ml) was slowly added. The reaction mixture was kept at –78 °C for a further 3 h after which a clear solution was obtained. After storage at –78 °C for one week, a colourless precipitate was formed and in addition colourless crystals of $Li_4Cl_4 \cdot 4Et_2O$. Tetramethyltin could be detected in the solution by ^{119}Sn NMR spectroscopy.

Crystal structure determination of $Li_4Cl_4 \cdot 4Et_2O$

Scattering data collection of a single crystal of $Li_4Cl_4 \cdot 4Et_2O$ was performed on a Nonius Turbo CAD4 diffractometer. $C_8H_{20}Li_2Cl_2O_2 M_r = 233.02$, crystal system orthorhombic, space group $P2_12_12_1$, $Z = 8$, $a = 9.994(3)$, $b = 10.496(2)$, $c = 25.571(4)$ Å, $V = 2682(1)$ Å 3 at 133(2) K, $\mu = 0.456$ mm $^{-1}$. $2\theta_{max} = 50^\circ$, 6868 scattering intensities collected, 4698 independent reflections ($R_{int} = 0.0925$). 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).

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