Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Two pseudopolymorphs of LiCl trimers with semicubane structures

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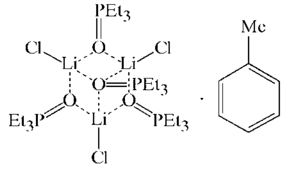
Received 2 August 2007
Accepted 13 November 2007
Online 14 December 2007

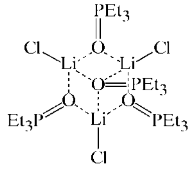
The title compounds, trichlorido(μ_3-triethylphosphine oxide-κ^3O:O:O)tris(μ_2-triethylphosphine oxide-κ^2O:O)trilithium(I) toluene solvate, $[Li_3Cl_3(C_6H_{15}OP)_4]\cdot C_7H_8$, (I), and trichlorido($\mu_3$-triethylphosphine oxide-κ^3O:O:O)tris(μ_2-triethylphosphine oxide-κ^2O:O)trilithium(I), $[Li_3Cl_3(C_6H_{15}OP)_4]$, (II), adopt separated semicubane structures in the solid state which are the first such structures to be reported for LiCl solvates. One triethylphosphine oxide ligand bonds *via* its O atom to the three Li atoms in a μ_3 manner, while the other three triethylphosphine oxide ligands bridge three Li atoms in μ_2 manners. The Cl atoms are in terminal instead of bridging positions, which is rather unusual for lithium chloride solvates.

Comment

The most common feature of the aggregates of lithium chloride is a four-membered ring with Cl atoms in the bridging (μ_2) positions (Bauer *et al.*, 1960). Neutral Lewis bases are able to split the Cl bridges and replace the μ_2-Cl atoms with other donor atoms, mainly O or N. A wide variety of aggregates of LiCl with Lewis bases have been found in the solid state. In monomeric $[LiCl(3,5\text{-}Me_2C_5H_3N)_3]$, the Li atom is tetrahedrally coordinated (Raston *et al.*, 1988), with an Li—Cl distance of 2.320 (9) Å. The more sterically demanding ligand 2-MeC_5H_4N leads to $[Li_2Cl_2(2\text{-}MeC_5H_4N)_4]$, a dimer with an intact Li_2Cl_2 ring. Tetrahydrofuran (THF) is not able to split the Li_2Cl_2 ring and yields $[Li_2Cl_2]\cdot 2THF$ (Hahn & Rupprecht, 1991). Hexamethylphosphoramide (HMPA) does not split the Li_2Cl_2 moiety either, and forms a cluster with a cubane skeleton, $[LiCl\cdot HMPA]_4$ (Barr *et al.*, 1984*a*). The interaction of HMPA with hydrated LiCl leads to the formation of an ionic compound, $[Li(H_2O)_2\cdot HMPA]_2Cl_2$, with an Li_2O_2 ring formed by the participation of the O atoms of HMPA (Barr *et al.*, 1984*b*). Similarly, DMF and H_2O split Li_2Cl_2, yielding $[Li_2Cl_2]\cdot 2DMF\cdot H_2O$, with an Li_2O_2 ring formed by O atoms from the DMF (Rao *et al.*, 1984). The reaction of tetraisopropyl methylenediphosphonate with LiCl, obtained in the reaction of BuLi with BuCl in THF, leads to the formation of $[LiCl\{OP(O^iPr)_2CH_2(^iPrO)_2PO\}]_2$, with a planar Li_2O_2 ring (Henderson *et al.*, 2003).



(I)



(II)

A search of the Cambridge Structural Dateabase (CSD; Version 5.28, May 2007 update; Allen, 2002) reveals 84 structures with an Li_3O_4 semicubane moiety, mainly incorporated in a cubane Li_4O_4 skeleton. Only three of them (Bock *et al.*, 2000; Nassar *et al.*, 2004) can be regarded as fused semicubane Li_3O_4 structures, being not incorporated in cubane Li_4O_4 or MLi_3O_4 structures (M = metal). Moreover, these compounds are lithium alkoxide derivatives but not lithium chloride solvates.

The X-ray analysis of the title compounds, $[(LiCl)_3(Et_3PO)_4]\cdot$toluene, (I), and $[(LiCl)_3(Et_3PO)_4]$, (II), reveals very similar separated semicubane arrangements for both compounds. The molecular structures of (I) and (II) are presented in Figs. 1 and 2, respectively.

These structures can be viewed as cubanes with Cl atoms in the terminal positions, $[Li_4Cl_4(OPEt_3)_4]$, with one LiCl molecule omitted. The absence of a bridging Li atom causes deformation in the cubane structure. It is noteworthy that similar cubane structures have not been known up to now for LiCl solvates.

The scheme shows the molecular arrangement of (I) along the P4—O4 bond. Atom O4 is a μ_3-bridging atom of the $Et_3P{=}O$ group, with an average O4—Li distance of 2.039 (6) Å. The three four-membered rings O4Li$_2$On (n = 1, 2 or 3) are nearly planar, with an average Li—On distance of

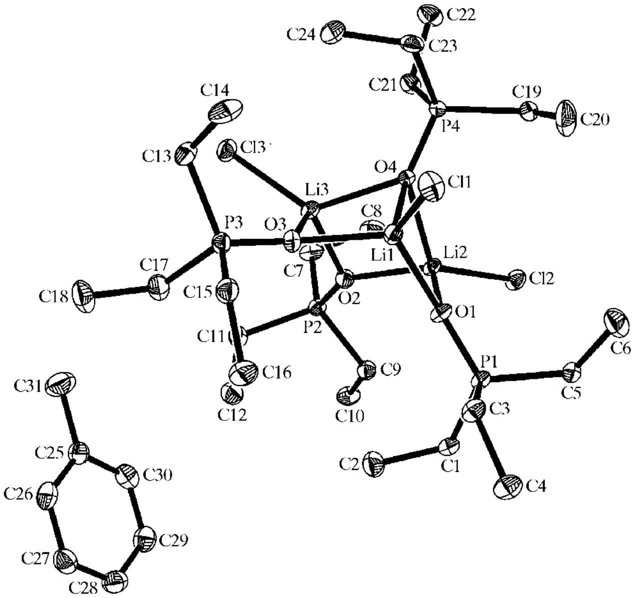


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. All H atoms have been omitted for clarity.

DOI: 10.1107/S0108270107058763

1.947 (6) Å in a μ_2 arrangement. The average $\mathrm{P}n{=}\mathrm{O}n$ (n = 1, 2 or 3) distance is 1.504 (3) Å, slightly shorter than the P4—O4 distance of 1.518 (2) Å. Thus, the μ_3-bridging causes a small but distinct elongation of the Li—O and P—O distances compared with the μ_2-bridging. These distances are very close to the P—O distances reported for complexes incorporating HMPA and tetraisopropyl methylenediphosphonate as Lewis bases. The Li_2O_2 ring in $\{[\mathrm{Li(H_2O)_2{\cdot}HMPA}]_2\}^{2+}$ is formed by the participation of Li^+ ions and the O atoms of HMPA, and shows similar average bond lengths [P═O = 1.496 (1) Å and Li—O = 1.998 (3) Å; Barr *et al.*, 1984*b*].

The average Li–Cl distance in (I) is 2.275 (6) Å, similar to the value of 2.293 (3) Å reported by Henderson for $[\mathrm{LiCl\{OP(O^{\mathit{i}}Pr)_2CH_2(^{\mathit{i}}PrO)_2PO\}}]_2$. This distance is shorter than the reported Li—Cl distances in Li_2Cl_2 rings [2.381 (9) Å; Raston *et al.*, 1988] or for the Li_4Cl_4 cubane [2.357 (10)–2.441 (12) Å; Barr *et al.*, 1984*a*]. It is also shorter than the sum of the covalent radii for Li (1.34 Å) and Cl (0.99 Å) (Purcell & Kotz, 1977) and is significantly shorter than the sum of the ionic radii of Li^+ (0.60 Å) and Cl^- (1.81 Å) (Purcell & Kotz, 1977). It is very close to the value of 2.23 (3) Å reported for the Li—Cl distance for an Li_2Cl_2 dimer in the gas phase (Bauer *et al.*, 1960).

The direct comparison of Et_3PO with $[(^{\mathit{i}}\mathrm{PrO})_2\mathrm{PO}]_2\mathrm{CH}_2$ is not possible because of the chelating properties of the latter compound. The significant difference between HMPA (Barr *et al.*, 1984*b*) or $[\{(^{\mathit{i}}\mathrm{PrO})_2\mathrm{PO}\}_2\mathrm{CH}_2]$ and Et_3PO comes from the presence of additional electronegative atoms, N or O, on the P atoms in the first two compounds. Thus, Et_3PO should possess better donor properties than HMPA or $[(^{\mathit{i}}\mathrm{PrO})_2\mathrm{PO}]_2\mathrm{CH}_2$. Additionally, due to the small Et groups around its P atoms, Et_3PO exhibits a smaller steric effect than HMPA or $(^{\mathit{i}}\mathrm{PrO})_2\mathrm{P(O)CH_2P(O)(O^{\mathit{i}}Pr)_2}$. These two factors probably enable this compound to replace the Li—Cl—Li bridges with Li—O—Li bridges and to push the Cl atoms in to the terminal positions, which HMPA is not capable of doing (Barr *et al.*, 1984*b*).

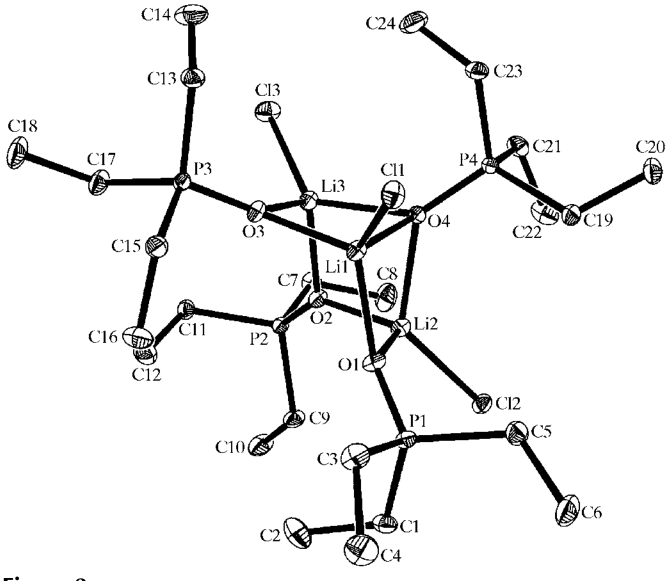


Figure 2
The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. All H atoms have been omitted for clarity.

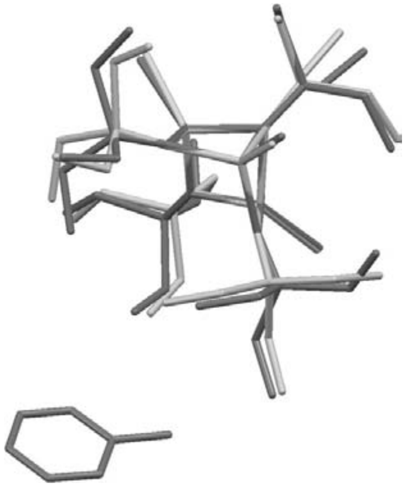


Figure 3
The best overlap of (I), $[(\mathrm{LiCl})_3(\mathrm{Et_3PO})_4]{\cdot}$toluene (dark grey), and (II), $[(\mathrm{LiCl})_3(\mathrm{Et_3PO})_4]$ (light grey).

The similarity of compounds (I) and (II) was examined as follows. The core of (I), O4/Li1/O1/Li2/O2/Li3/O3, was fixed in space and the relevant core of (II) was matched to it in three positions, firstly with O1/O2/O3 from (I) matched with O1/O2/O3 from (II), then with O1/O2/O3 from (I) matched with O2/O3/O1 from (II), and finally with O1/O2/O3 from (I) matched with O3/O1/O2 from (II). This is almost equivalent to rotation of (II) around the P4—O4 bond. The root-mean-square deviations of the core atoms were 0.0899, 0.0532 and 0.0359 Å, respectively. Fig. 3 illustrates the best overlap of molecules of (I) and (II) (the third case). Thus, the two cores are similar. However, the presence of toluene in (I) causes different conformations of the Et groups in the $Et_3P{=}O$ moieties.

Experimental

All experimental manipulations were performed under an argon atmosphere using standard Schlenk techniques. All solvents were carefully dried and deoxidized. In spite of the use of Schlenk techniques, compounds (I) and (II) are probably the oxidation products of the reaction mixtures of $^{t}\mathrm{Bu_2P{-}P(SiMe_3)Li}$ (Fritz *et al.*, 1987) and $[(\mathrm{Et_3P})_2\mathrm{NiCl_2}]$. For the preparation of (I), $^{t}\mathrm{Bu_2P{-}P(SiMe_3)Li}$ (0.266 g, 0.665 mmol) in tetrahydrofuran (THF; 2 ml) was added dropwise slowly *via* syringe to a solution of $[(\mathrm{Et_3P})_2\mathrm{NiCl_2}]$ (0.134 g, 0.366 mmol) in THF (2 ml) at 233 K. The THF was evaporated under vacuum. The residue was dissolved in toluene (3 ml), filtered and evaporated to a volume of 1 ml. After one month at ambient temperature, a small quantity of colourless crystals of (I) was deposited. For the preparation of (II), a solution of $[(\mathrm{Et_3P})_2\mathrm{NiCl_2}]$ (0.147 g, 0.400 mmol) in THF (2 ml) was added dropwise slowly *via* syringe to a solution of $^{t}\mathrm{Bu_2P{-}P(SiMe_3)Li}$ (0.329 g, 0.795 mmol) in THF (3 ml) at ambient temperature. The THF was evaporated under vacuum. The residue was dissolved in THF (1 ml), filtered and left to stand at ambient temperature. After two weeks, a small quantity of colourless crystals of (II) was deposited near the neck of the Schlenk vessel.

Compound (I)

Crystal data

$[Li_3Cl_3(C_6H_{15}OP)_4]\cdot C_7H_8$
M_r = 755.9
Monoclinic, $P2_1/c$
a = 11.3414 (7) Å
b = 32.9899 (19) Å
c = 16.1000 (10) Å
β = 134.162 (3)°
V = 4321.3 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.39 mm^{-1}
T = 120 (2) K
0.3 × 0.2 × 0.1 mm

Data collection

Oxford Diffraction KM-4 CCD diffractometer
29430 measured reflections
7657 independent reflections
5468 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.06

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.06
$wR(F^2)$ = 0.127
S = 1.06
7657 reflections
419 parameters
H-atom parameters constrained
$\Delta\rho_{\rm max}$ = 0.93 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.49 e Å^{-3}

Compound (II)

Crystal data

$[Li_3Cl_3(C_6H_{15}OP)_4]$
M_r = 663.77
Monoclinic, $P2_1/c$
a = 12.0507 (4) Å
b = 12.1447 (3) Å
c = 25.8698 (7) Å
β = 94.564 (2)°
V = 3774.09 (19) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.44 mm^{-1}
T = 120 (2) K
0.44 × 0.39 × 0.26 mm

Data collection

Oxford Diffraction KM-4 CCD diffractometer
19943 measured reflections
6648 independent reflections
6073 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.011

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.092
S = 1.13
6648 reflections
355 parameters
H-atom parameters constrained
$\Delta\rho_{\rm max}$ = 0.52 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.30 e Å^{-3}

All H atoms were refined as riding on their parent atoms, with methyl C—H = 0.98 Å, methylene C—H = 0.99 Å and aromatic C—H = 0.95 Å, and with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) for aromatic and methylene, 1.3$U_{\rm eq}$(C) for CH_2 and 1.5$U_{\rm eq}$(C) for methyl groups.

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3103). Services for accessing these data are described at the back of the journal.

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