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Bis[μ-*P*,*P*′-methylenebis(diisopropyl phosphonate)-κ^3*O*,*O*′:*O*]bis[chlorolithium(I)]: a centrosymmetric dimer of lithium chloride with terminal chloride anions

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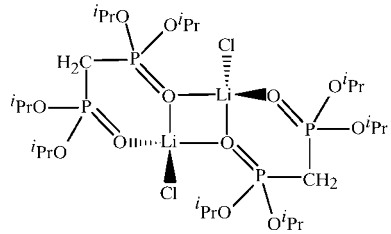
The molecule of the title dimeric compound, $[Li_2Cl_2(C_{13}H_{30}O_6P_2)_2]$ or $[LiCl\{[(^iPrO)_2P(O)]_2CH_2\}]_2$, lies about an inversion center and features tetrahedrally coordinated Li atoms. The neutral ligands each chelate to one metal center and bridge to the other center through P═O units. Unusually for lithium chloride complexes, the Cl^- ions are in terminal rather than bridging positions. Principal dimensions include Li—O(four-membered ring) = 1.959 (3) and 2.056 (3) Å, Li—O(phosphonate ring) = 1.929 (3) Å, and Li—Cl = 2.293 (3) Å.

Comment

Neutral Lewis base complexes of lithium chloride display a surprisingly wide variety of aggregated forms in the solid state (Chivers *et al.*, 2001). These include monomers (Raston *et al.*, 1988), dimers (Hahn & Rupprecht, 1991), tetramers (Barr *et al.*, 1984*a*), polymers (Kopp & Neumuller, 1999) and charge-separated compounds (Barr *et al.*, 1984*b*), with the extent and nature of the aggregation being dependent on the donor ligand. Monomers and charge-separated complexes are generally found when polydentate ligands, such as crowns, are used or when sufficient quantities of strong Lewis bases are present. A common feature of the remaining aggregated forms of lithium chloride is the use of Cl^- bridges to link the metals. This may either be in a μ_2 fashion, as seen in the simple dimer $[LiCl(THF)_2]_2$ (THF is tetrahydrofuran; Hahn & Rupprecht, 1991), or alternatively in a μ_3 mode, as found in the tetrameric cubane $[LiCl(HMPA)]_4$ (HMPA is hexamethylphosphoramide; Barr *et al.*, 1984*a*). We now add to this collection the structure of the title compound, (I), which, although dimeric, unusually displays terminal Cl^- units.

X-ray analysis of (I) revealed a centrosymmetric dimer, with the metal atoms bridged by a pair of P═O units, one from each of the attached phosphonate ligands. The remaining P═O unit of each phosphonate ligand chelates to an Li center, to give an overall framework composed of a centrosymmetric four-membered Li_2O_2 ring sandwiched between two six-membered LiOPCPO rings in a step-like configuration (Fig. 1). Tetracoordination of the metal atoms is completed by the terminal Cl^- anions. Principal dimensions are given in Table 1.



(I)

The closest analogue of (I) is the complex $[\{LiCl(DMF)\}_2{\cdot}H_2O]_n$ (DMF is dimethylformamide; Rao *et al.*, 1984), which also contains solvent-bridged Li_2O_2 units. However, in this instance, the attached Cl^- anions bridge between dimeric units, as well as binding to water molecules, to form a network assembly. Interestingly, when the closely related monodentate phosphoryl ligand HMPA is used as a Lewis base for LiCl, the tetrameric cubane $[LiCl(HMPA)]_4$ (Barr *et al.*, 1984*a*), with μ_3-bridging Cl^- anions and terminal donor ligands, is formed. Inclusion of water into this system results in the formation of the charge-separated complex

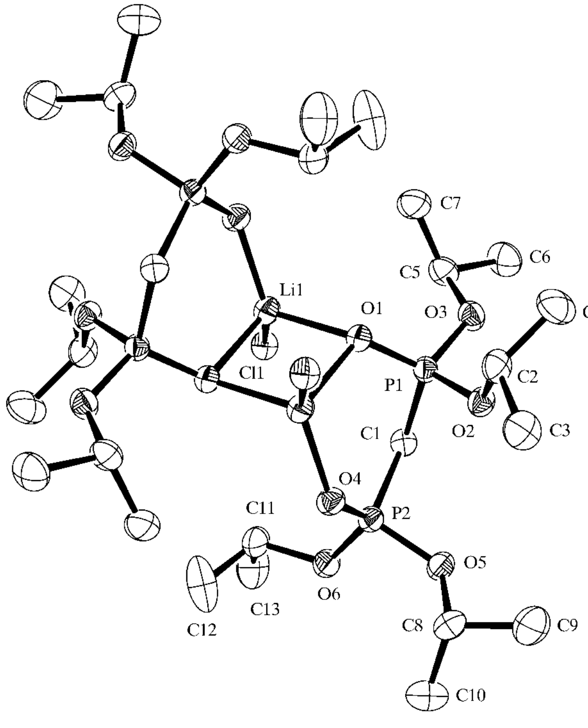


Figure 1
The molecular structure of (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids. The minor-occupancy methyl atoms C12*A* and C13*A*, and all H atoms, have been omitted for clarity.

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$[\{Li(H_2O)_2(HMPA)_2\}^{2+}\cdot 2Cl^-]$ (Barr *et al.*, 1984*b*), incorporating P═O-bridged dimeric units, as found in (I). Therefore, the formation of (I) can be rationalized by the bidentate phosphonate ligand enabling the preferential bridging of the P═O units, while maintaining tetracoordination at the metal centers.

Rather than considering complex (I) as a traditional dimer, which normally bridge through their anionic groups, it may be better viewed as an associated pair of monomers. This is demonstrated by the short Li—Cl bond length of 2.293 (3) Å in (I), which compares favourably with the value of 2.290 (4) Å found in the monomeric complex [LiCl(12-crown-4)] (Gingl *et al.*, 1991). Finally, the Li—O bond distances within the Li_2O_2 dimer are highly asymmetrical, with a value of 1.959 (3) Å for Li1—O1 and 2.056 (3) Å for Li1—O1^i [symmetry code: (i) $-x$, $-y$, $2 - z$]. This is an unusual feature compared with similarly P═O-bridged complexes of Li, such as $[(RO)_2P(O)CHCNLi\cdot THF]_n$ (*R* is Et or ^{i}Pr; Henderson *et al.*, 2000), and may be a consequence of chelation of the ligand, resulting in a stronger interaction with one metal than the other.

Experimental

All experimental manipulations were performed either under a purified argon atmosphere using standard Schlenk techniques or in an argon-filled glove-box. All solvents were distilled from sodium benzophenone ketyl prior to use. Tetraisopropyl methylenediphosphonate was purchased from Lancaster, distilled from CaH_2 and stored over 4A molecular sieve before use. *n*-Butyllithium was purchased from Aldrich and standardized before use. *n*-Butyl chloride was purchased from Aldrich, distilled from CaH_2 and stored over 4A molecular sieve prior to use. The NMR spectroscopy data were recorded on a Bruker DPX 400 spectrometer at 298 K. The elemental analysis was carried out on a Perkin–Elmer 2400 elemental analyzer. For the synthesis of (I), *n*-BuLi (5 mmol as a 1.6 *M* solution in hexane) was added to a solution of *n*-BuCl (5 mmol, 0.52 ml) in tetrahydrofuran (THF, 5 ml). The resulting solution was stirred for 2 h before the addition of one equivalent of $[(^iPrO)_2P(O)]_2CH_2$ (5 mmol, 1.6 ml). After formation of a white precipitate, the THF was removed *in vacuo* and replaced by toluene (10 ml). Complete dissolution was achieved on strong heating of the mixture. X-ray quality crystals of (I) were produced on slowly cooling the hot solution to 277 K over a period of several hours (yield 0.4 g, 20.1%). Elemental analysis, expected: C 40.38, H 7.82%; found: C 40.62, H 7.87%. ^{1}H NMR (d_5-pyridine, δ): 1.34 (*d*, 12H, ^{i}Pr CH$_3$, ^3J = 6.2 Hz), 1.36 (*d*, 12H, ^{i}Pr CH$_3$, ^3J = 6.2 Hz), 3.09 (*t*, 2H, P$_2$CH$_2$, $^2J_{PH}$ = 21.2 Hz), 5.04 (*sext*, 4H, ^{i}Pr CH, ^3J = 6.2 Hz); ^{13}C NMR (d_5-pyridine, δ): 24.55 (^{i}Pr CH$_3$), 24.94 (^{i}Pr CH$_3$), 28.10 (*t*, CH$_2$, $^1J_{PC}$ = 135.2 Hz), 72.03 (^{i}Pr CH).

Crystal data

$[Li_2Cl_2(C_{13}H_{30}O_6P_2)_2]$
$M_r = 773.40$
Triclinic, $P\overline{1}$
$a = 10.2172$ (2) Å
$b = 10.3740$ (3) Å
$c = 10.8197$ (3) Å
$\alpha = 84.2355$ (12)°
$\beta = 68.9131$ (12)°
$\gamma = 76.9692$ (10)°
$V = 1042.23$ (5) Å^3
$Z = 1$
$D_x = 1.232$ Mg m^{-3}
Mo *K*α radiation
Cell parameters from 23 647 reflections
$\theta = 2.9$–$30.5°$
$\mu = 0.36$ mm^{-1}
$T = 150$ (2) K
Prism, colorless
0.25 × 0.25 × 0.20 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ and ω scans
17 790 measured reflections
5337 independent reflections
4538 reflections with $I > 2\sigma(I)$
$R_{int} = 0.043$
$\theta_{max} = 30.3°$
$h = -13 \rightarrow 13$
$k = -12 \rightarrow 13$
$l = -14 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.116$
$S = 1.06$
5337 reflections
228 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0536P)^2 + 0.6511P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.60$ e Å^{-3}
$\Delta\rho_{min} = -0.51$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.033 (4)

Table 1
Selected geometric parameters (Å, °).

Li1—Cl1	2.293 (3)	P1—O2	1.5584 (12)
Li1—O1	1.959 (3)	P1—O3	1.5626 (13)
Li1—O1^i	2.056 (3)	P2—O4	1.4756 (13)
Li1—O4^i	1.928 (3)	P2—O5	1.5623 (13)
P1—O1	1.4840 (12)	P2—O6	1.5741 (13)
P1—O1—Li1	132.30 (11)	O1^i—Li1—Cl1	112.10 (14)
Li1—O1—Li1^i	87.55 (13)	O4^i—Li1—O1	109.16 (15)
O1—Li1—Cl1	110.93 (14)	O4^i—Li1—O1^i	100.19 (14)

Symmetry code: (i) $-x$, $-y$, $2 - z$.

The methyl groups bonded to C11 were each modeled as disordered over two positions, and the occupancies refined to 0.832 (14):0.168 (14). The minor component was treated isotropically, whilst the major component and all other non-H atoms were treated anisotropically. All H atoms were treated as riding, with C—H distances in the range 0.98–1.00 Å.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1675). Services for accessing these data are described at the back of the journal.

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