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Key indicators

Single-crystal X-ray study

T = 100 K

Mean $\sigma(\text{C}-\text{C}) = 0.001 \text{ \AA}$

R factor = 0.017

wR factor = 0.045

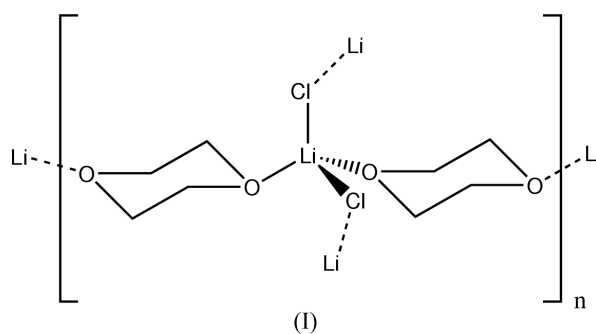
Data-to-parameter ratio = 41.0

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.**A redetermination of lithium chloride
dioxane**

The crystal structure of the title compound, poly[μ_2 -chloro- μ_2 -dioxane- $\kappa^2\text{O}:\text{O}'$ -lithium(I)], $[\text{LiCl}(\text{C}_4\text{H}_8\text{O}_2)]_n$, displays a three-dimensional diamondoid network composed of Li—Cl and Li—O interactions. Each metal centre is similarly surrounded by two dioxane molecules and two chlorine atoms. The Li—O coordination is propagated along the *c* axis, forming a one-dimensional chain, and the three-dimensional structure is completed by Li—Cl interactions parallel to the *ab* plane. Principal dimensions include Li—Cl distances of 2.3115 (10) and 2.3270 (11) Å and Li—O distances of 1.9574 (10) and 1.9981 (11) Å.

Comment

In an effort to synthesize lithium trichlorophenoxide dioxane, we crystallized the title compound lithium chloride dioxane, (I), which was first reported in 1966 by Durant *et al.* (1966). We describe here a more precise low-temperature redetermination of this crystal structure, where $R = 0.017$ in this work *versus* $R = 0.148$ in the previous report, and discuss the structure in the context of supramolecular chemistry. The Li—Cl interaction is also of particular interest due to the wide range of aggregated forms that have been discovered for this apparently simple combination. Previously characterized Li—Cl complexes with neutral Lewis bases include monomers, dimers, tetramers, polymers, three-dimensional arrays and ion pairs (Chivers *et al.*, 2001).



X-ray analysis of (I) revealed a three-dimensional diamondoid network, where lithium acts as a tetrahedral node that is bridged by the 'linear' linkers chloride and dioxane. Fig. 1 presents the asymmetric unit and Fig. 2 shows the extended structure. Variations from the ideal tetrahedral angles around the lithium center give rise to the distorted diamondoid topology. In particular, the Cl—Li—Cl angle is highly distorted at 119.99 (4)°, whereas O—Li—O is 109.56 (5)° and the four independent O—Li—Cl angles lie in the narrow range 105.79 (4) to 108.97 (4)° (mean = 106.75°).

Received 12 January 2005

Accepted 18 January 2005

Online 22 January 2005

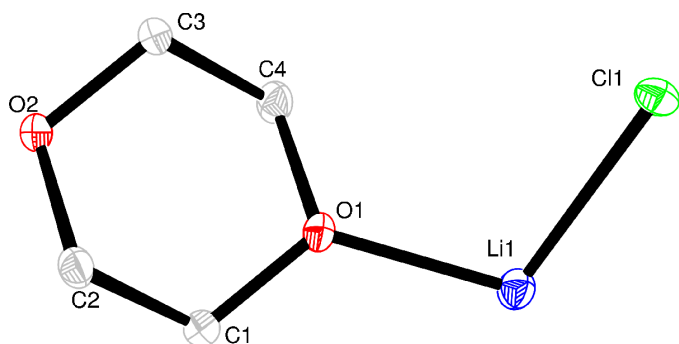


Figure 1
The asymmetric unit of (I), showing 50% probability displacement ellipsoids. H atoms have been omitted.

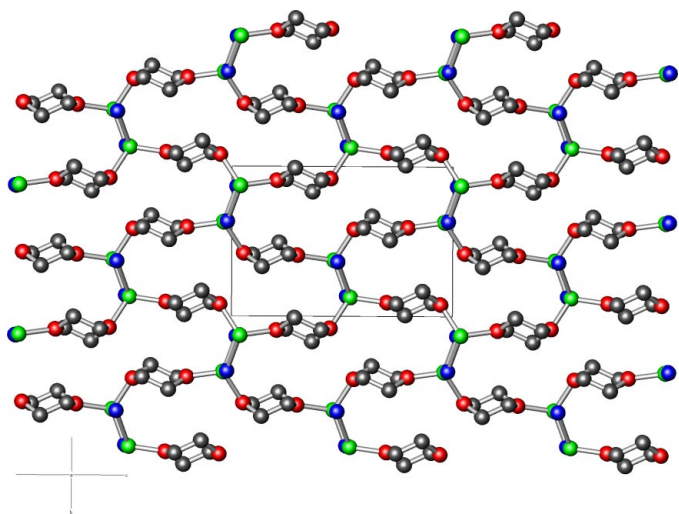


Figure 2
A view along the *a* axis, showing the hexagonal channels. Green spheres are lithium, blue are chlorine, black are carbon and red are oxygen. H atoms have been omitted for clarity.

The two Li—Cl distances are 2.3115 (10) and 2.3270 (11) Å, and the two Li—O distances are 1.9574 (10) and 1.9981 (11) Å, which are all similar to those in related compounds.

The structure of (I) is of current relevance as our group is presently studying the use of *s*-block complexes to rationally direct the self-assembly of network architectures (MacDougall *et al.*, 2005). In this case, the combination of lithium as a tetrahedral node and bridging linear linkers gives the most likely supramolecular arrangement of a diamondoid network.

Experimental

All experimental manipulations were performed under a purified nitrogen atmosphere using standard Schlenk techniques. Dioxane was purchased from Lancaster, distilled from CaH₂ and stored over 4 Å molecular sieve before use. *n*-Butyllithium (1.6 M solution in hexane) was purchased from Aldrich and standardized prior to use. 2,4,6-Trichlorophenol was purchased from Alfa Aesar and dried by recrystallization prior to use. The NMR spectroscopic data were recorded on a Varian Unity Plus 300 spectrometer at 298 K. For the synthesis of (I), *n*-BuLi (5 mmol of a 1.6 M solution in hexane) was

added to a solution of trichlorophenol (5 mmol) in dioxane (6.5 ml). Upon stirring, a white precipitate formed, which was redissolved by heating the solution to reflux. Instead of the expected deprotonation reaction, the dehalogenation reaction occurred to give X-ray quality crystals of (I) that were produced on slow cooling of the solution in a hot water bath. ¹H NMR (300 MHz, DMSO-*d*₆, 298 K): δ 3.56 (s, OCH₂, dioxane). ¹³C NMR (75 MHz, DMSO-*d*₆, 298 K): δ 66.46 (OCH₂, dioxane).

Crystal data

[LiCl(C₆H₈O₂)]
M_r = 130.49
Orthorhombic, *P*2₁2₁2₁
a = 7.1227 (1) Å
b = 7.7284 (1) Å
c = 11.4138 (1) Å
V = 628.296 (13) Å³
Z = 4
D_x = 1.380 Mg m⁻³

Mo *K*α radiation
Cell parameters from 7757 reflections
θ = 3.2–38.3°
μ = 0.51 mm⁻¹
T = 100 (2) K
Block, colourless
0.35 × 0.21 × 0.16 mm

Data collection

Bruker SMART APEX
diffractometer
ω scans
Absorption correction: multi-scan
(SADABS; Sheldrick, 2004)
*T*_{min} = 0.841, *T*_{max} = 0.922
30357 measured reflections

3031 independent reflections
2941 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.023
*θ*_{max} = 36.3°
h = -11 → 11
k = -12 → 12
l = -19 → 18

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.017
wR(*F*²) = 0.045
S = 1.08
3031 reflections
74 parameters
H-atom parameters constrained

w = 1/[σ²(*F*_o²) + (0.0324*P*)² + 0.007*P*]
where *P* = (*F*_o² + 2*F*_c²)/3
(Δ/σ)_{max} = 0.001
Δρ_{max} = 0.38 e Å⁻³
Δρ_{min} = -0.12 e Å⁻³
Absolute structure: Flack (1983),
1285 Friedel pairs
Flack parameter = 0.01 (2)

Table 1

Selected geometric parameters (Å, °).

Li1—O1	1.9574 (10)	Li1—Cl1 ⁱⁱ	2.3115 (10)
Li1—O2 ⁱ	1.9981 (11)	Li1—Cl1	2.3270 (11)
O1—Li1—O2 ⁱ	109.56 (5)	O2 ^j —Li1—Cl1	108.97 (4)
O1—Li1—Cl1 ⁱⁱ	105.79 (4)	Cl1 ⁱⁱ —Li1—Cl1	119.99 (4)
O2 ⁱ —Li1—Cl1 ⁱⁱ	106.16 (4)	Li1 ⁱⁱⁱ —Cl1—Li1	125.22 (3)
O1—Li1—Cl1	106.08 (4)		

Symmetry codes: (i) $\frac{1}{2} - x, -y, z - \frac{1}{2}$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, -z$; (iii) $x - \frac{1}{2}, \frac{1}{2} - y, -z$.

H atoms were placed in calculated positions, with C—H distances of 0.99 Å, and included in the refinement in riding-model approximation, with *U*_{iso} = 1.2*U*_{eq}(C).

Data collection: APEX2 (Bruker, 2004); cell refinement: APEX2 and SAINT (Bruker, 2004); data reduction: SAINT and XPREP (Sheldrick, 2003); program(s) used to solve structure: SHELXLTL (Sheldrick, 2001); program(s) used to refine structure: SHELXLTL; molecular graphics: SHELXLTL; software used to prepare material for publication: SHELXLTL.

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