metal-organic compounds

Bromido(12-crown-4)lithium

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The Br and Li ions of the title compound, bromido(1,4,7,10-tetraoxacyclododecane-$\kappa^4 O$)lithium(I), [LiBr(C$_8$H$_{16}$O$_4$)], are located on special positions of site symmetry 4mm. The crown ether ring is disordered over two positions with one C atom located on a mirror plane.

Related literature

For [Li(12-crown-4)Cl], see Gingl *et al.* (1991).
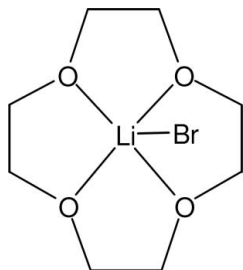
Experimental

Crystal data

[LiBr(C$_8$H$_{16}$O$_4$)]
M_r = 263.06
Tetragonal, $P4/nmm$
a = 8.4895 (10) Å
c = 7.7355 (9) Å
V = 557.51 (11) Å^3

Z = 2
Mo $K\alpha$ radiation
μ = 3.67 mm^{-1}
T = 173 (2) K
$0.29 \times 0.21 \times 0.17$ mm

Data collection

Stoe IPDSII two-circle diffractometer
Absorption correction: multi-scan (*MULABS*; Spek, 2003; Blessing, 1995)

T_{min} = 0.416, T_{max} = 0.574 (expected range = 0.388–0.536)
2624 measured reflections
330 independent reflections
316 reflections with $I > 2\sigma(I)$
R_{int} = 0.051

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.159
S = 1.29
330 reflections

31 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.83 e Å^{-3}

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2293).

References

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supplementary materials

Bromido(12-crown-4)lithium

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Comment

Generally, LiBr is nearly insoluble in organic solvents. However, coordination of Li cation with organic ligands such as 12-crown-4 increases the solubility of LiBr therein. Therefore, we were able to obtain single crystals of the complex LiBr.12-crown-4 in a hexane–tetraydrofuran solution.

The Br and Li ions of the title compound are located on a special position of site symmetry 4 mm. The crown ether ring is disordered over two positions with one C atom located on a mirror plane.

Experimental

Crystallization by slow diffusion of hexane to a tetrahydrofuran (10 ml) solution of 1,4-phenylene-bridged Li scorpionate $Li_2[C_6H_4(Bpz_3)_2]$ (0.09 mmol) in the presence of LiBr and 12-crown-4 (32 mg; 0.2 mmol) gave colourless X-ray quality crystals of LiBr.12-crown-4.

Refinement

H atoms were refined with fixed individual displacement parameters [$U_{iso}(H) = 1.2U_{eq}(C)$] using a riding model with C—H = 0.99 Å. One C and the O atom are disordered over two sites with occupation factors of 0.5 each.
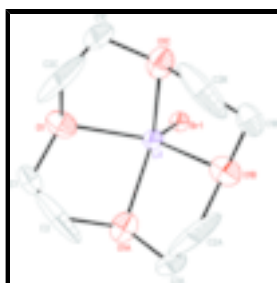
Figures

Fig. 1. Perspective view of the title compound with the atom numbering scheme; displacement ellipsoids are at the 50% probability level; H atoms are drawn as small spheres of arbitrary radii. Only one site of the disordered atoms is shown. Symmetry operators for generating equivalent atoms: (A) $1/2 − y, x, z$; (B) $1/2 − x, y, z$; (C) $y, 1/2 − x, z$.
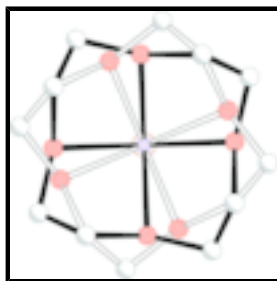

Fig. 2. Perspective view of the title compound showing the disorder of the crown ether ring. H atoms omitted for clarity. Colour codes: C: black, Br: brown, Li: magenta, O: red.

supplementary materials

bromido(1,4,7,10-tetraoxacyclododecane-κ^{4}O)lithium(I)

Crystal data

[LiBr(C$_8$H$_{16}$O$_4$)]	$Z = 2$
$M_r = 263.06$	$F_{000} = 268$
Tetragonal, *P*4/*nmm*	$D_x = 1.567$ Mg m^{-3}
Hall symbol: -P 4a 2a	Mo *K*α radiation $\lambda = 0.71073$ Å
$a = 8.4895$ (10) Å	Cell parameters from 2066 reflections
$b = 8.4895$ (10) Å	$\theta = 3.6–24.9º$
$c = 7.7355$ (9) Å	$\mu = 3.67$ mm^{-1}
$\alpha = 90º$	$T = 173$ (2) K
$\beta = 90º$	Block, colourless
$\gamma = 90º$	$0.29 \times 0.21 \times 0.17$ mm
$V = 557.51$ (11) Å^3	

Data collection

Stoe IPDSII two-circle diffractometer	330 independent reflections
Radiation source: fine-focus sealed tube	316 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.051$
$T = 173(2)$ K	$\theta_{max} = 25.5º$
ω scans	$\theta_{min} = 3.4º$
Absorption correction: multi-scan (MULABS; Spek, 2003; Blessing, 1995)	$h = -10 \rightarrow 9$
$T_{min} = 0.416$, $T_{max} = 0.574$	$k = -10 \rightarrow 9$
2624 measured reflections	$l = -9 \rightarrow 7$

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0565P)^2 + 4.7442P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.057$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.159$	$\Delta\rho_{max} = 1.25$ e Å^{-3}
$S = 1.29$	$\Delta\rho_{min} = -0.83$ e Å^{-3}
330 reflections	Extinction correction: none
31 parameters	
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	
Hydrogen site location: inferred from neighbouring sites	

Special details

Experimental. ;

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Br1	0.2500	0.2500	0.2282 (2)	0.0251 (6)	
Li1	0.2500	0.2500	0.544 (4)	0.029 (6)	
O1	0.2093 (10)	0.0249 (13)	0.6619 (10)	0.040 (3)	0.50
C1	0.3586 (16)	−0.0390 (16)	0.7244 (18)	0.038 (3)	0.50
H1A	0.4217	−0.0809	0.6272	0.046*	0.50
H1B	0.3391	−0.1257	0.8073	0.046*	0.50
C2	0.4316 (9)	0.0684 (9)	0.7956 (14)	0.091 (6)	
H2A	0.3661	0.1115	0.8901	0.109*	0.25
H2B	0.5297	0.0259	0.8472	0.109*	0.25
H2C	0.4544	−0.0638	0.8153	0.109*	0.25
H2D	0.4671	0.2250	0.8457	0.109*	0.25

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0250 (7)	0.0250 (7)	0.0252 (9)	0.000	0.000	0.000
Li1	0.020 (8)	0.020 (8)	0.045 (17)	0.000	0.000	0.000
O1	0.039 (9)	0.051 (5)	0.029 (4)	0.008 (4)	−0.004 (4)	−0.004 (4)
C1	0.044 (8)	0.033 (7)	0.037 (7)	0.015 (6)	−0.004 (6)	0.005 (6)
C2	0.117 (11)	0.117 (11)	0.037 (6)	0.100 (12)	−0.006 (3)	0.006 (3)

Geometric parameters (Å, °)

Br1—Li1	2.44 (3)	Li1—O1^{vii}	2.145 (17)
Li1—O1^{i}	2.145 (17)	O1—C1	1.460 (15)
Li1—O1^{ii}	2.145 (17)	O1—C2^{v}	1.624 (11)
Li1—O1^{iii}	2.145 (17)	C1—H1A	0.9900
Li1—O1	2.145 (17)	C1—H1B	0.9900
Li1—O1^{iv}	2.145 (17)	C2—C1^{ii}	1.232 (14)
Li1—O1^{v}	2.145 (17)	C2—H2A	0.9890

Li1—O1^{vi}	2.145 (17)	C2—H2B	0.9909
O1^{ii}—Li1—O1	96.1 (9)	O1—C1—H1A	110.6
O1^{iii}—Li1—O1	79.6 (6)	C2—C1—H1B	110.2
O1^{ii}—Li1—O1^{iv}	129.8 (15)	O1—C1—H1B	110.2
O1—Li1—Br1	115.1 (7)	H1A—C1—H1B	108.3
C1—O1—C2^{v}	120.8 (8)	C1—C2—O1^{iii}	112.0 (10)
C1—O1—Li1	109.4 (7)	H2A—C2—H2B	108.0
O1^{i}—C1—C2	96.5 (14)	H2C—C2—H2D	108.0
C2—C1—O1	108.1 (11)	C1^{ii}—C2—H2C	115.3
C2—C1—H1A	109.4	O1^{i}—C2—H2D	123.0
Br1—Li1—O1—C1	102.9 (7)	C2^{v}—O1—C1—C2	−72.9 (14)
Br1—Li1—O1—C2^{v}	−128.8 (5)	O1—C1—C2—O1^{iii}	−62.7 (13)

Symmetry codes: (i) $-x+1/2, y, z$; (ii) $-y+1/2, -x+1/2, z$; (iii) $-y+1/2, x, z$; (iv) y, x, z; (v) $y, -x+1/2, z$; (vi) $-x+1/2, -y+1/2, z$; (vii) $x, -y+1/2, z$.
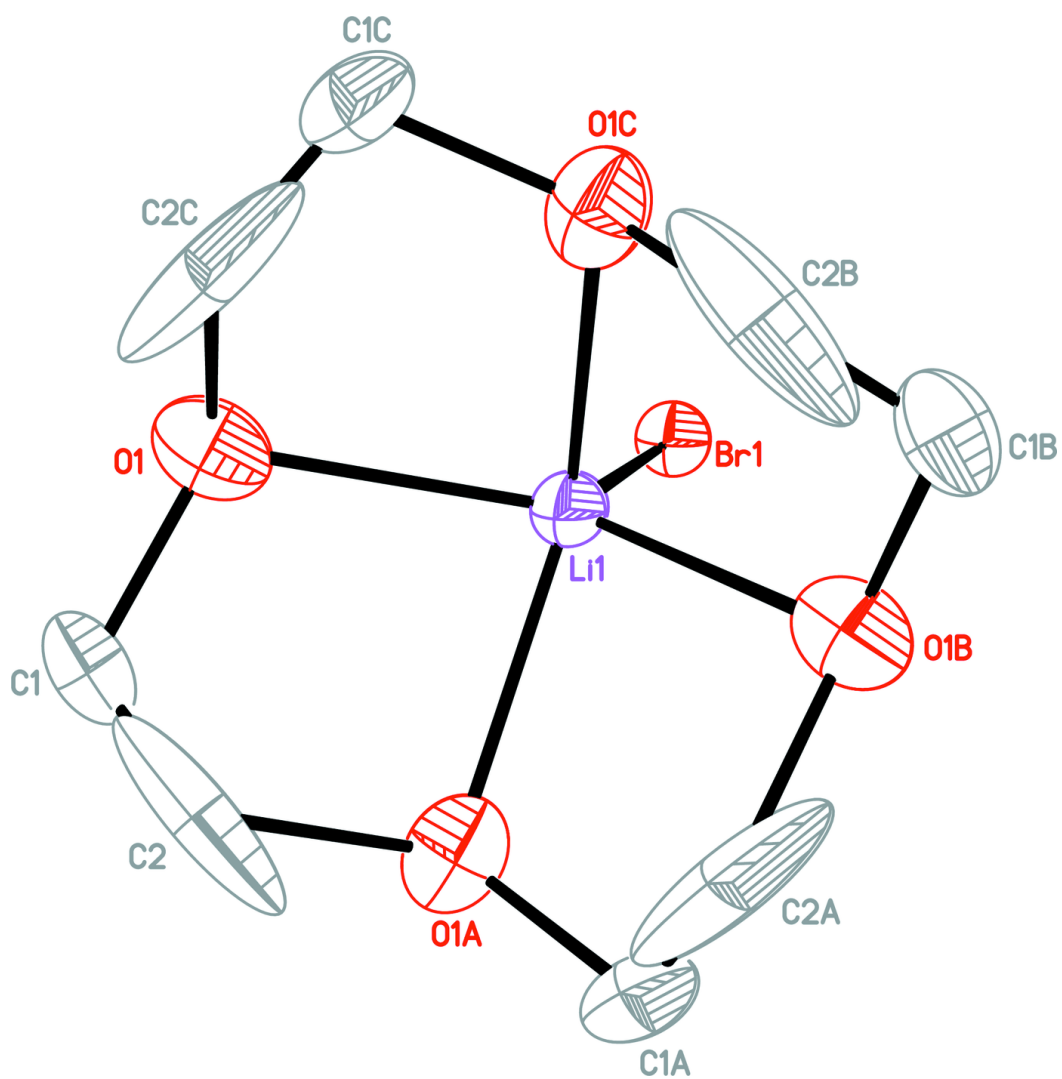
Fig. 1

Fig. 2