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Structural chemistry of new lithium bis(oxalato)borate solvates

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Recently lithium bis(oxalato)borate, $LiB(C_2O_4)_2$, has been proposed as an alternative lithium salt for the electrolyte in rechargeable batteries that do not contain explosive perchlorate, reactive fluoride or toxic arsenic. This lithium salt crystallizes in the form of solvates from such solvents as water, acetonitrile, acetone, dimethoxyethane, 1,3-dioxolane and ethylene carbonate. Their crystal structures were determined in order to explore the crystal chemistry of this lithium salt. It was found that most of the solvents consist of a lithium bis(oxalato)borate dimer in which the ligand acts as both a chelating and a bridging agent. Lithium has octahedral coordination that typically includes one or, less commonly, two solvent molecules. An exception to this rule is the ethylene carbonate solvate where the lithium is tetrahedrally surrounded exclusively by the solvent and bis(oxalato)borate plays the role of counter-ion only. The ethylene carbonate solvates were also studied for $LiPF_6$ and $LiAsF_6$ salts and they have similar structures to the bis(oxalato)borate tetrahedral complexes.

1. Introduction

Rechargeable Li-ion batteries are the state-of-art portable power sources for small electronic devices such as mobile phones, laptop computers and digital cameras. The successful operation of the electrochemical cell imposes several requirements for the electrolyte salt such as:

(i) a high ionic conductivity in organic solvent even at low temperature (Mashiko *et al.*, 1991; Ozawa, 1994);

(ii) the ability to form a stable solid electrolyte interface on the graphite anode;

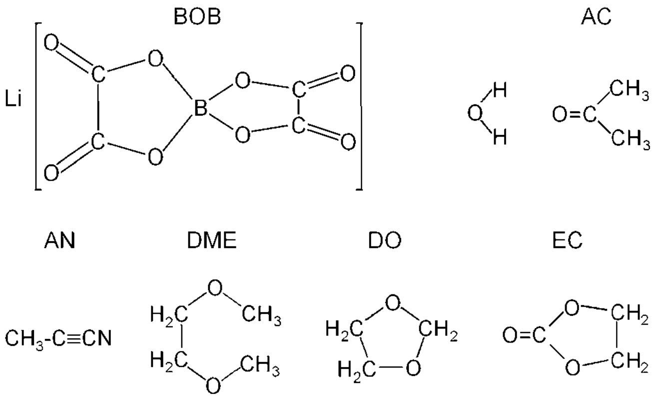
(iii) the capability of passivating the Al cathode current collector at high operating voltage;

(iv) stability in the presence of lithium and at potentials of 5 V oxidizing relative to lithium;

(v) stability over a wide range of temperatures and in the presence of traces of moisture.

For example, $LiPF_6$-based electrolyte solutions meet the first four requirements, but decompose at elevated temperature and are very hygroscopic, forming HF which can solubilize cathodic species such as Mn^{2+} (Aurbach *et al.*, 1987; Sloop *et al.*, 2001). In addition, this salt is expensive and toxic. Two other commonly used salts, $LiAsF_6$ and $LiClO_4$, are also toxic or explosive. To address these problems, the usability of several other salts is being explored. One of these is the bis(oxalato)borate (BOB) salt $LiB(C_2O_4)_2$ that has received much attention due to its low toxicity, stability and easy preparation method (Webber, 1991; Sylla *et al.*, 1992; Krause *et* *al.*, 1997; Xu & Angell, 2001). It has been patented as a conducting salt for lithium-ion batteries (Wietelmann *et al.*, 1999, 2003). However, the crystal chemistry of LiBOB and its interaction with a range of solvents is presently not known, except for the recent structural study of the unsolvated Li, Na and K salts (Zavalij *et al.*, 2003).

Here the crystal structures of the LiBOB salt solvated with water, acetonitrile (AN), acetone (AC), 1,2-dimethoxyethane (DME), 1,3-dioxolane (DO) and ethylene carbonate (EC) are reported and the crystal chemistry of these solvates is discussed. For comparison, the structures of the ethylene carbonate solvates of the $LiPF_6$ and $LiAsF_6$ salts were also determined.



(I)

2. Experimental

2.1. Preparation

The anhydrous LiBOB salt was prepared as described by Xu & Angel (2001; see also Zavalij *et al.*, 2003). The crystals of solvated salts were grown from a solution of 50 mg LiBOB in the corresponding solvents. The beaker with the solution was covered by parafilm$^{\text{TM}}$ with a tiny hole and put in a desiccator under reduced pressure. The colorless single crystals were obtained from the following solvents: water, AN, AC, DME, DO and EC. The first compound, the hydrate, was obtained from the AN solution when excess air was introduced; the last EC compound was obtained from the EC/DMC solution (DMC: dimethyl carbonate, CH_3O-CO-OCH_3, a common electrolyte solvent). Other solvents, such as thf, 1,4-dioxane, pure DMC and propylene carbonate, were also tested but always gave a sticky paste or poorly crystalline material and therefore they were not pursued further.

2.2. Crystal structure determination

The anhydrous LiBOB salt was prepared only in the form of a fine powder and therefore its crystal structure along with the structure of the anhydrous Na and K salts were solved from powder diffraction data and reported previously (Zavalij *et al.*, 2003). However, when crystallized from most of the solvents listed, LiBOB forms solvated crystals large enough for single-crystal diffraction studies. Thus, the crystals of the six LiBOB solvates were obtained and their crystal structures determined using single-crystal data collected on a Bruker Smart Apex CCD diffractometer. These are: LiBOB·H_2O (I), 2LiBOB·5AN (II), LiBOB·4/3AC (III), LiBOB·DME (IV), 2LiBOB·3DO·H_2O (V) and $Li(EC)_4BOB$ (VI). All these solvates are quite unstable; in the open air they lose the solvent over several minutes and therefore all the diffraction experiments were conducted at the low temperature of 110 K. One exception is the hydrate, which only loses water at *ca* 383 K. The diffraction data were collected at room temperature. The corresponding crystal data, collection and refinement details are provided in Table 1.[1] Table 2 contains the bond lengths and selected bond angles, while Table 3 provides the standard geometry information about the hydrogen bonds in the two compounds that contain water (LiBOB·H_2O and 2LiBOB·3DO·H_2O).

The crystal data and full structure details for the two other Li salts $Li(EC)_4PF_6$ and $Li(EC)_4AsF_6$, which are highly disordered and only mentioned in this manuscript, are available from the CSD database as entries CCDC 244695 and CCDC 244694, respectively (Zavalij *et al.*, 2004*a*,*b*).

3. Crystal structures of the LiBOB solvates

The crystal chemistry of lithium–oxygen coordination and bonding was discussed by Wenger & Armbruster (1991). According to this review, the most typical Li coordination is tetrahedral (134 polyhedra from 94 compounds) with 32 Li octahedra in the second place and only seven cases of five-coordinated Li (four square pyramids and three trigonal bipyramids). It was shown that Li octahedra are sometimes distorted in a 5 + 1 (five relatively short Li—O distances and one longer), 4 + 2 or even 3 + 3 way. This section describes the individual structures of the LiBOB solvates that are compared and discussed in the following section.

3.1. Hydrate – LiBOB·H_2O

In LiBOB·H_2O hydrate the Li has octahedral coordination consisting of two symmetrically equivalent water molecules and four O atoms from oxalate groups (Table 2). The water molecule links the Li ions along the *c* axis to form an infinite —Li—H_2O— chain, as shown in Fig. 1(*a*). Two of the four terminal O atoms of the BOB ion (O2 and O6) coordinate two Li ions each to form additional bridges along the chain. Thus, the Li ions are linked by three O atoms that can be represented as face sharing of Li octahedra and yield a short Li—Li distance of 2.801 (1) Å. Two of the other terminal O atoms (O4 and O8) do not coordinate Li, but form weak hydrogen bonds with the water molecule (Table 3). The four inner O atoms from both oxalate groups are bonded only to the B atom, except for the O3 atom that forms an additional weak hydrogen bond with the water molecule. The BOB ions bridge

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA5011). Services for accessing these data are described at the back of the journal.

Table 1
Crystal data and experimental details for LiBOB solvates.

	(I)	(II)	(III)
Crystal data			
Chemical formula	$C_4H_2BLiO_9$	$C_{12}H_6B_2Li_2N_2O_{16}\cdot 3C_2H_3N$	$C_7H_6BLiO_9\cdot 0.33C_3H_6O$
M_r	211.81	592.85	271.21
Cell setting, space group	Orthorhombic, *Pbca*	Monoclinic, $P2_1/n$	Monoclinic, *C*2/*m*
a, *b*, *c* (Å)	16.075 (3), 15.880 (3), 5.6008 (9)	7.6346 (8), 22.631 (2), 14.9338 (16)	16.3987 (16), 7.6308 (7), 10.9904 (11)
β (°)	90.00	91.879 (2)	121.201 (2)
V (Å^3)	1429.7 (4)	2578.9 (5)	1176.4 (2)
Z	8	4	4
D_x (Mg m^{-3})	1.968	1.527	1.531
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	3095	2595	2604
θ range (°)	2.5–30.5	3.0–28.1	2.6–31.1
μ (mm^{-1})	0.20	0.13	0.14
Temperature (K)	294 (2)	110 (2)	110 (2)
Crystal form, color	Plate, colorless	Prism, colorless	Needle, colorless
Crystal size (mm)	0.38 × 0.09 × 0.02	0.48 × 0.36 × 0.30	0.50 × 0.16 × 0.11
Data collection			
Diffractometer	Three-circle	Three-circle	Three-circle
Data collection method	ω scans	ω scans	ω scans
Absorption correction	Multi-scan (based on symmetry-related measurements)	Multi-scan (based on symmetry-related measurements)	Multi-scan (based on symmetry-related measurements)
$T_{\min}$	0.873	0.873	0.914
$T_{\max}$	0.996	0.961	0.985
No. of measured, independent and observed reflections	9124, 1440, 1044	14 456, 4542, 3039	4923, 1437, 1116
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R_{\rm int}$	0.082	0.039	0.041
$\theta_{\max}$ (°)	26.4	25.0	27.5
Range of *h*, *k*, *l*	$-19 \Rightarrow h \Rightarrow 20$ $-19 \Rightarrow k \Rightarrow 19$ $-7 \Rightarrow l \Rightarrow 6$	$-8 \Rightarrow h \Rightarrow 9$ $-25 \Rightarrow k \Rightarrow 26$ $-17 \Rightarrow l \Rightarrow 17$	$-20 \Rightarrow h \Rightarrow 19$ $-9 \Rightarrow k \Rightarrow 9$ $-14 \Rightarrow l \Rightarrow 14$
Intensity decay (%)	0.34	−0.02	−0.30
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.060, 0.089, 1.00	0.042, 0.090, 1.00	0.047, 0.129, 1.00
No. of reflections	1440	4542	1437
No. of parameters	144	393	134
H-atom treatment	Constrained to parent site	Constrained to parent site	Constrained to parent site
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.001P)^2 + 2.51P]$, $P = [\max(F_o^2,0) + 2F_c^2]/3$	$w = 1/[\sigma^2(F_o^2) + (0.0299P)^2]$, $P = [\max(F_o^2,0) + 2F_c^2]/3$	$w = 1/[\sigma^2(F_o^2) + (0.07P)^2 + 0.94P]$, $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{\max}$	<0.0001	0.001	<0.0001
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.23, −0.30	0.21, −0.26	0.40, −0.32
Extinction method	None	None	None

	(IV)	(V)	(VI)
Crystal data			
Chemical formula	$C_8H_{10}BLiO_{10}$	$C_{17}H_{20}B_2Li_2O_{23}$	$C_{12}H_{16}LiO_{12}\cdot C_4BO_8$
M_r	283.91	627.83	546.04
Cell setting, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Tetragonal, $I\bar{4}$
a, *b*, *c* (Å)	8.6690 (7), 8.8519 (7), 9.3328 (8)	9.1327 (14), 9.6378 (15), 14.812 (2)	10.2343 (5), 10.2343 (5), 10.8245 (7)
α, β, γ (°)	114.159 (2), 94.764 (2), 106.412 (2)	80.640 (3), 79.414 (3), 70.642 (3)	90.00, 90.00, 90.00
V (Å^3)	610.45 (9)	1201.8 (3)	1133.77 (11)
Z	2	2	2
D_x (Mg m^{-3})	1.545	1.735	1.599
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	2770	2243	3376
θ range (°)	2.7–31.1	2.5–27.5	2.7–31.5
μ (mm^{-1})	0.14	0.16	0.15
Temperature (K)	110 (2)	110 (2)	110 (2)
Crystal form, color	Prism, colorless	Prism, colorles	Prism, colorless
Crystal size (mm)	0.51 × 0.36 × 0.26	0.27 × 0.14 × 0.08	0.51 × 0.46 × 0.38
Data collection			
Diffractometer	Three-circle	Three-circle	Three-circle
Data collection method	ω scans	ω scans	ω scans
Absorption correction	Multi-scan (based on symmetry-related measurements)	Multi-scan (based on symmetry-related measurements)	Multi-scan (based on symmetry-related measurements)

Table 1 (continued)

	(IV)	(V)	(VI)
$T_{\min}$	0.841	0.881	0.905
$T_{\max}$	0.964	0.987	0.945
No. of measured, independent and observed reflections	7526, 3509, 3051	9591, 4074, 2144	7169, 876, 871
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R_{\rm int}$	0.021	0.098	0.020
$\theta_{\max}$ (°)	30.0	24.7	30.0
Range of h, k, l	$-12 \Rightarrow h \Rightarrow 12$	$-10 \Rightarrow h \Rightarrow 10$	$-13 \Rightarrow h \Rightarrow 14$
	$-12 \Rightarrow k \Rightarrow 12$	$-11 \Rightarrow k \Rightarrow 11$	$-10 \Rightarrow k \Rightarrow 14$
	$-13 \Rightarrow l \Rightarrow 13$	$-17 \Rightarrow l \Rightarrow 17$	$-15 \Rightarrow l \Rightarrow 15$
Intensity decay (%)	−0.54	0.34	0.79
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.096, 1.00	0.058, 0.110, 0.89	0.024, 0.050, 1.00
No. of reflections	3509	4074	876
No. of parameters	221	398	103
H-atom treatment	Constrained to parent site	Constrained to parent site	Constrained to parent site
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0661P)^2]$, $P = [\max(F_o^2,0) + 2F_c^2]/3$	$w = 1/[\sigma^2(F_o^2) + (0.005P)^2]$, $P = [\max(F_o^2,0) + 2F_c^2]/3$	$w = 1/[\sigma^2(F_o^2) + (0.01P)^2 + 0.921P]$, $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{\max}$	<0.0001	<0.0001	<0.0001
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.53, −0.22	0.38, −0.35	0.29, −0.15
Extinction method	None	*SHELXL*	*SHELXL*
Extinction coefficient	–	0.0130 (17)	0.0190 (12)

† Computer programs used: *SMART* and *SAINT* (Bruker, 1999), *SADABS* (Sheldrick, 1996), *SHELXS*97 (Sheldrick, 1990), *SHELXL*97 (Sheldrick, 1997), Materials Studio (2001), *ATOMS* (Dowty, 1999).

—Li—H_2O— chains into a layer perpendicular to the *a* axis, while hydrogen bonds bind these wave-like layers into a three-dimensional framework (Fig. 2*a*).

3.2. Acetonitrile solvate – 2LiBOB(AN)·3AN

This structure contains two symmetrically independent Li ions, two BOB ions and five molecules of acetonitrile. The two Li ions have very similar octahedral environments consisting of five terminal O atoms from four BOB ions and one N atom from the solvent (Table 2). Each BOB ion chelates one Li ion with the two terminal O atoms of one oxalate group (Li1 with O3 and O4; Li2 with O7 and O8). One of the O atoms (O4) from the chelating group is bridging and coordinates additionally a second Li ion to form a dimeric complex (Fig. 1*b*) with a Li1—Li2 distance of 3.299 (6) Å. This dimer occupies a general position and has the lowest symmetry, 1. Despite that, both BOB ions and Li ions are perfectly aligned and the dimer would have at least local 2/*m* symmetry if not for the different orientations of the AN ligands. This dimer is practically flat, except for the second non-chelating oxalate group, which is perpendicular to the first group. The two terminal O atoms of this group coordinate Li ions from another dimer to form the layer shown in Fig. 2(*b*). Thus, each BOB ion forms five Li—O bonds and links four Li ions.

While two acetonitrile molecules (N11 and N21) are coordinated to the Li, the other three (N31, N41 and N51) simply separate the layers holding them together through very weak C—H···O and C—H···N hydrogen bonds. Interestingly, N31 and N41 atoms form short contacts with both C atoms from the oxalate groups [N31···C5 2.893 (3), N51···C6 3.031 (3) and N41···C7 2.858 (3), N41···C8 2.843 (3)]. The oxalate groups that are involved in this bonding lie parallel to the 2LiBOB(AN) layer and have slightly elongated C—C distances [C5—C6 1.535 (3) and C7—C8 1.538 (3) Å], while the oxalate groups that are perpendicular to the layers do not form the short contacts with acetonitrile [C1—C2 1.511 (3) and C3—C4 1.511 (3) Å].

3.3. Acetone solvate – LiBOB(AC)·1/3AC

The structure of the acetone solvate very much resembles the structure of the solvate with acetonitrile. The Li ion has octahedral coordination consisting of five terminal O atoms from the BOB ion and one O atom from acetone (Table 2). The BOB ion performs essentially the same binding function as in the AN compound, yielding an almost identical dimeric complex (*cf.* Figs. 1*b* and *c*). The dimer in the AC solvate has the highest possible crystallographic symmetry 2/*m*, unlike the lowest symmetry found above for the AN dimer. The Li—Li distance of 3.468 (9) Å is slightly greater than in the AN compound. Again two terminal O atoms from the second oxalate group of the BOB ion link the dimers into a layer, as shown in Fig. 2(*c*). However, the configuration of the layer as well as the orientation of the acetone is quite different from that in the AN structure: the orientation of all the dimers is the same in the AC structure (Fig. 2*c*), but their orientation alternates in the AN compound (Fig. 2*b*). An acetone molecule that coordinates the Li is disordered across the mirror plane, while another AC molecule that resides in the interlayer space has an occupancy factor of 33.4 (4)%, probably because of the high volatility of acetone.

Table 2
Selected bond lengths (Å), and bond and inter-planar angles (°) for LiBOB solvates.

(I): LiBOB·H$_2$O		(II): 2LiBOB·5AN				(III): LiBOB·1.33AC	
Li1—O1*w*†	2.024 (6)	Li1—O7	2.038 (4)	Li2—O4$^{\rm i}$	2.061 (4)	Li1—O7†	1.951 (5)
Li1—O1*w*$^{\rm ii}$†	2.050 (6)	Li1—N11†	2.072 (4)	Li2—N21†	2.085 (4)	Li1—O4	1.993 (5)
Li1—O6$^{\rm iii}$	2.108 (7)	Li1—O3$^{\rm i}$	2.130 (4)	Li2—O7	2.169 (4)	Li1—O6$^{\rm iv}$	2.087 (5)
Li1—O2$^{\rm v}$	2.154 (6)	Li1—O4$^{\rm i}$	2.225 (4)	Li2—O8	2.222 (4)	Li1—O2$^{\rm vi}$	2.3554 (17)
Li1—O6$^{\rm vii}$	2.165 (7)	Li1—O16$^{\rm i}$	2.265 (5)	Li2—O11$^{\rm viii}$	2.287 (5)	Li1—O2$^{\rm ix}$	2.3554 (17)
Li1—O2	2.216 (7)	Li1—O15$^{\rm x}$	2.443 (5)	Li2—O12	2.415 (5)	Li1—O4$^{\rm iv}$	2.493 (5)
B1—O7	1.463 (4)	B1—O10	1.465 (3)	B2—O13	1.462 (3)	B1—O1	1.465 (2)
B1—O1	1.469 (4)	B1—O9	1.465 (3)	B2—O6	1.470 (3)	B1—O1$^{\rm xi}$	1.465 (2)
B1—O5	1.473 (4)	B1—O1	1.474 (3)	B2—O14	1.471 (3)	B1—O5	1.475 (3)
B1—O3	1.468 (4)	B1—O2	1.478 (3)	B2—O5	1.480 (3)	B1—O3	1.485 (3)
C1—C2	1.534 (4)	C1—C2	1.511 (3)	C3—C4	1.511 (3)	C1—C1$^{\rm xi}$	1.544 (4)
C1—O2	1.198 (3)	C1—O3	1.207 (2)	C3—O7	1.203 (2)	C1—O2	1.197 (2)
C2—O4	1.196 (4)	C2—O4	1.210 (2)	C4—O8	1.201 (2)		
C1—O1	1.312 (4)	C1—O1	1.314 (2)	C3—O5	1.315 (2)	C1—O1	1.331 (2)
C2—O3	1.319 (4)	C2—O2	1.310 (2)	C4—O6	1.321 (3)		
C3—C4	1.528 (4)	C5—C6	1.535 (3)	C7—C8	1.538 (3)	C2—C3	1.527 (4)
C3—O6	1.203 (3)	C5—O11	1.195 (2)	C7—O15	1.197 (2)	C2—O4	1.208 (3)
C4—O8	1.199 (4)	C6—O12	1.199 (2)	C8—O16	1.202 (2)	C3—O6	1.200 (3)
C3—O5	1.314 (4)	C5—O9	1.332 (2)	C7—O13	1.328 (2)	C2—O3	1.309 (3)
C4—O7	1.320 (3)	C6—O10	1.334 (2)	C8—O14	1.327 (3)	C3—O5	1.314 (3)
Li1—Li1$^{\rm ii}$	2.801 (1)	Li1—Li2	3.299 (6)			Li1—Li1$^{\rm iv}$	3.468 (9)
O1*w*$^{\rm ii}$†—Li1—O2$^{\rm v}$	176.2 (4)	O7—Li1—O3$^{\rm i}$	159.1 (2)	N21†—Li2—O7	170.8 (2)	O4—Li1—O6$^{\rm iv}$	156.8 (3)
O6$^{\rm iii}$—Li1—O6$^{\rm vii}$	173.3 (3)	N11†—Li1—O4$^{\rm i}$	171.0 (2)	O4$^{\rm i}$—Li2—O8	159.1 (2)	O2$^{\rm vi}$—Li1—O2$^{\rm ix}$	163.6 (2)
O1*w*†—Li1—O2	176.0 (3)	O16$^{\rm i}$—Li1—O15$^{\rm x}$	169.5 (2)	O11$^{\rm viii}$—Li2—O12	169.7 (2)	O7†—Li1—O4$^{\rm iv}$	176.2 (3)
C1—C2/C3—C4‡	88.69 (7)	C1—C2/C5—C6‡	88.93 (4)	C3—C4/C7—C8‡	89.17 (5)	C1—C1$^{\rm xi}$/C2—C3‡	90

(IV): LiBOB·DME		(V): 2LiBOB·3DO·H$_2$O				(VI): Li(EC)$_4$BOB	
Li1—O10†	2.0059 (17)	Li1—O21†	2.006 (8)	Li2—O17†	2.057 (8)	Li1—O3$^{\rm xii}$†	1.9222 (11)
Li1—O2	2.0574 (17)	Li1—O14$^{\rm xiii}$	2.055 (9)	Li2—O1*w*†	2.104 (8)	Li1—O3$^{\rm xiv}$†	1.9222 (11)
Li1—O8$^{\rm xv}$	2.0949 (17)	Li1—O2	2.068 (9)	Li2—O12$^{\rm vi}$	2.110 (8)	Li1—O3†	1.9222 (11)
Li1—O9†	2.1112 (17)	Li1—O8$^{\rm xv}$	2.158 (9)	Li2—O1*w*$^{\rm vi}$ †	2.113 (8)	Li1—O3$^{\rm xvi}$†	1.9222 (11)
Li1—O8$^{\rm iv}$	2.2229 (17)	Li1—O4$^{\rm xvii}$	2.223 (9)	Li2—O19†	2.141 (8)		
Li1—O6$^{\rm iv}$	2.4232 (18)	Li1—O2$^{\rm xvii}$	2.443 (8)	Li2—O10	2.214 (8)		
B1—O3	1.4611 (11)	B1—O3	1.444 (6)	B2—O9	1.443 (5)	B1—O4$^{\rm xviii}$	1.4707 (10)
B1—O1	1.4751 (11)	B1—O7	1.458 (6)	B2—O15	1.474 (6)	B1—O4$^{\rm xix}$	1.4707 (10)
B1—O5	1.4765 (11)	B1—O5	1.486 (6)	B2—O13	1.476 (6)	B1—O4	1.4707 (10)
B1—O7	1.4870 (11)	B1—O1	1.497 (6)	B2—O11	1.489 (6)	B1—O4$^{\rm xx}$	1.4707 (10)
C1—C2	1.5444 (12)	C1—C2	1.519 (6)	C5—C6	1.522 (6)	C4—C4$^{\rm xx}$	1.536 (3)
C1—O2	1.2009 (10)	C1—O2	1.224 (5)	C5—O10	1.198 (5)	C4—O5	1.1908 (17)
C1—O1	1.3277 (10)	C1—O1	1.295 (5)	C5—O9	1.322 (5)	C4—O4	1.3320 (17)
C2—O4	1.1978 (10)	C2—O4	1.201 (5)	C6—O12	1.208 (5)		
C2—O3	1.3311 (10)	C2—O3	1.333 (5)	C6—O11	1.329 (5)		
C3—C4	1.5294 (12)	C3—C4	1.525 (6)	C7—C8	1.543 (6)		
C3—O6	1.2001 (11)	C3—O6	1.207 (5)	C7—O14	1.199 (5)		
C3—O5	1.3252 (10)	C3—O5	1.331 (5)	C7—O13	1.321 (5)		
C4—O8	1.2081 (10)	C4—O8	1.201 (5)	C8—O16	1.203 (5)		
C4—O7	1.3081 (10)	C4—O7	1.325 (5)	C8—O15	1.323 (5)		
Li1—Li1$^{\rm xxi}$	3.366 (3)	Li1—Li1$^{\rm xvii}$	3.534 (16)	Li2—Li2$^{\rm vi}$	3.091 (15)		
O2—Li1—O9†	175.18 (9)	O14$^{\rm xiii}$—Li1—O8$^{\rm xv}$	175.9 (5)	O17†—Li2—O1*w*$^{\rm vi}$†	173.6 (4)	O3$^{\rm xiv}$—Li1—O3	105.49 (4)
O10†—Li1—O8$^{\rm iv}$	172.64 (9)	O2—Li1—O4$^{\rm xvii}$	153.4 (4)	O1*w*†—Li2—O19†	179.9 (4)	O3$^{\rm xii}$—Li1—O3	117.76 (8)
O8$^{\rm xv}$—Li1—O6$^{\rm iv}$	152.52 (8)	O21†—Li1—O2$^{\rm xvii}$	168.0 (5)	O12$^{\rm vi}$ —Li2—O10	176.4 (4)		
C1—C2/C3—C4‡	88.23 (2)	C1—C2/C3—C4‡	87.10 (8)	C5—C6/C7—C8‡	87.62 (9)	C4—C4$^{\rm xx}$/C4$^{\rm xviii}$—C4$^{\rm xix}$	90

Symmetry codes: (i) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (iii) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (iv) $-x+1, -y+1, -z+1$; (v) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (vi) $x+\frac{1}{2}, y+\frac{1}{2}, z$; (vii) $-x+1, -y+1, -z+2$; (viii) $x-1, y, z$; (ix) $x+\frac{1}{2}, -y+\frac{1}{2}, z$; (x) $x+\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (xi) $x, -y+1, z$; (xii) $-x+1, -y+1, z$; (xiii) $-x+1, -y+2, -z$; (xiv) $-y+1, x, -z$; (xv) $x+1, y, z$; (xvi) $y, -z+1, -z$; (xvii) $-x+2, -y+2, -z$; (xviii) $-y+\frac{1}{2}, x-\frac{1}{2}, -z+\frac{1}{2}$; (xix) $y+\frac{1}{2}, -x+\frac{1}{2}, -2+\frac{1}{2}$; (xx) $-x+1, -y, z$; (xxi) $-x+2, -y+1, -z+1$. † Atom from the solvent. ‡ Angle between two oxalate groups of BOB.

Table 3
Geometry of hydrogen bonds (Å, °) for LiBOB·H_2O (I) and 2LiBOB·3DO·H_2O (V).

D—H···A	d(D—H)	d(H···A)	d(D···A)	∠(DHA)
(I)				
O1w—H1···O4^{i}	0.87 (4)	2.09 (4)	2.960 (3)	174 (4)
O1w—H2···O8^{ii}	0.84 (4)	2.11 (4)	2.910 (3)	159 (4)
O1w—H2···O3^{iii}	0.84 (4)	2.57 (4)	3.039 (3)	117 (3)
(V)				
O1w—H1w···O6	0.99†	1.93†	2.880 (4)	160.3
O1w—H2w···O16^{iv}	0.99†	1.88†	2.865 (4)	176.0

Symmetry codes: (i) $x+\frac{1}{2}, y, -z+\frac{3}{2}$; (ii) $-x+1, y-\frac{1}{2}, -z+\frac{5}{2}$; (iii) $x+\frac{1}{2}, -y+\frac{1}{2}, -z+2$; (iv) $x+1, y-1, z$. † Refined as a rigid body.

3.4. Dimethoxyethane solvate – LiBOB(DME)

In contrast to the previous two structures, in the dimethoxyethane solvate the Li octahedron includes not one but two O atoms from a chelating solvent molecule, while the other four are terminal O atoms from BOB ions (Table 2). Nevertheless, the same dimer but with crystallographic symmetry $\bar{1}$ is formed where one oxalate group of the BOB ion chelates the Li ion by the two atoms O6 and O8, one of which (O8) also bridges to the second Li ion (Fig. 1*d*). The Li—Li distance in this dimer is 3.366 (3) Å. Only one atom of the second oxalate group of BOB (O2) coordinates the Li ion from another dimer. This difference in connectivity between the dimers in this structure and those in the previous two is due to the presence of the bidentate chelating DME solvent *versus* the single coordinating acetonitrile and acetone molecules. This leaves only one free corner (O2) in each of the LiO_6 octahedra for links between the dimers and therefore only a chain can be formed (Fig. 2*d*).

3.5. 1,3-Dioxolane solvate – $(LiBOB)_2(DO)_3(H_2O)$

This structure contains two types of solvent (1,3-dioxolane and water) and therefore two independent Li ions that form two different dimers with the compositions LiBOB(DO) and $LiBOB(DO)_2(H_2O)$. Both Li ions still have octahedral coordination (Table 2). In the first dimer the Li1 atom is coordinated by one O atom from the dioxolane and five O atoms from four BOB ions, as depicted in Fig. 1(*e*) (top). This dimer is the same as that found in the previous three structures, except for the noticeably greater Li1—Li1 distance of 3.534 (16) Å. Also similar is the chelating oxalate group (O2 and O4) with the O4 atom bridged to the second Li ion and an O21 atom from the DO forming a square base around Li1. The two apical corners are occupied by the O atoms of the BOB ion from other dimers. The environment of the Li ion in this dimer is essentially the same as in the AN and AC solvates, but interestingly the symmetry and conformation of the dimer are the same as in the DME structure. The LiBOB(DO) dimer is centrosymmetric and similar to the LiBOB(DME) dimer with both chelating oxalate groups being far from co-planar with each other and with both Li ions.

In the second dimer, $LiBOB(DO)_2(H_2O)$, the Li2 atoms are linked into a pair by two bridging water molecules and two BOB ions (B2). The latter coordinates the two Li ions in the pair by two terminal O atoms from one oxalate group, as shown in Fig. 1(*e*) (bottom). The Li2—Li2 distance of 3.091 (15) Å is much shorter than in the other dimer of this solvate. Two adjacent dioxolane solvent molecules complete the octahedral coordination of the Li2 atom.

The two independent BOB ions play a substantially different role in the structure formation. The first, B1, coordinates only the Li1 atoms, first linking them into dimers and then connecting these dimers into a chain along the *a* axis (Fig. 2*e*, top). The second ion, B2, forms Li2—Li2 dimers (Fig. 2*e*, middle) and links them with the Li1 chains resulting in a complex layer in the (011) plane (Fig. 2*e*, bottom). The water molecules form hydrogen bonds both between the Li2 dimers yielding chains along [$\bar{1}$10] and between the Li2 dimer and the Li1 chain yielding three-dimensional connectivity.

3.6. Ethylene carbonate complex – $[Li(EC)_4]$BOB

This structure differs considerably from all of the previous ones in that the Li ion is tetrahedrally coordinated by four ethylene carbonate molecules, giving the cation $Li(EC)_4^+$ (Fig. 1*f*). The charge of this complex cation is balanced by an isolated BOB^- anion. This happens probably because of the much stronger interaction of the Li ion with the terminal oxygen from the EC than from the BOB. In this compound the symmetry of the $Li(EC)_4{}^+$ cation as well as of the BOB^- anion is $\bar{4}$, resulting in a highly symmetric packing of the ions (Fig. 2*f*).

As might be expected, the Li—O distances are much shorter in the tetrahedral environment than in the octahedral coordination. Thus, they are 1.922 (1) Å in the tetrahedral $Li(EC)_4^+$ complex and range from 1.91 to 1.99 Å in lithium ethylene glycolate, $LiOCH_2CH_2OH$ (Mamak *et al.*, 1998), which also has tetrahedrally coordinated lithium. In all the other compounds discussed here the Li is in an octahedral environment and the Li—O distances are greater than 2.0 Å [except for the one short distance of 1.951 (5) Å to the AC solvate].

The structures of the EC solvates of the $LiPF_6$ and $LiAsF_6$ salts were also determined (Zavalij *et al.*, 2004*a*,*b*) in order to study the effect of the anion and to compare them with the LiBOB solvate. Both compounds are isostructural and consist of the $Li(EC)_4^+$ complex and the corresponding anion. Two of the three independent cationic complexes have conformational disorder that appears as several possible orientations of the EC wings, and two of the three anions show orientational disorder that is quite typical for the hexafluoride ions. The Li—O distances lie in the 1.91–1.94 Å range, the same as for the unsolvated LiBOB salt and other compounds with tetrahedrally coordinated Li.

4. Discussion

The geometry of the rigid BOB ion [see (I) and Table 2] is to a great extent the same in all the compounds: two oxalate groups are mutually perpendicular (within a deviation of less than 3°) and their four single-bonded O atoms form an inner tetrahedral enclosure around the central B atom. The O—B—O angles deviate from those in an ideal tetrahedron by not more than 5°. The other four O atoms are terminal and therefore are those responsible for chemical interactions and the structure formation. Thus, in the Li complexes only the outer O atoms form bonds with the Li, while the interactions of the inner atoms with other molecules is limited to weak interactions such as van der Waals or hydrogen bonding or sometimes weak bonding with the alkali metal, as found in the Na and K salts (Zavalij *et al.*, 2003). The highest observed symmetry of the BOB ion ($\bar{4}$) was found in the EC complex; the highest possible symmetry ($\bar{4}m2$) has yet to be discovered. All the LiBOB solvates studied to date with octahedrally coordinated lithium and without water contain dimeric units (Figs. 1*b*–*e*). In such dimers, typically Li(BOB)X_2Y, each Li ion is coordinated by the two terminal O atoms from the chelating oxalate group of the BOB ion. One of these O atoms is also bridging both Li ions. Three other positions in the LiO_6 octahedra are occupied by the two apical O atoms from external BOB^- ions (X) and the solvent molecule (Y). An exception is the LiBOB(DME) dimer that has the Li(BOB)X_1Y_2 configuration where Y_2 is the chelating DME molecule. The presence of these dimers in various solvates suggests that these or similar dimers are quite stable and may exist in the electrolyte solution with both X and Y being solvent molecules. In the unsolvated LiBOB (Zavalij *et al.*, 2003) the BOB ion behaves in a similar way, but forms a Li(BOB)X_2 chain instead

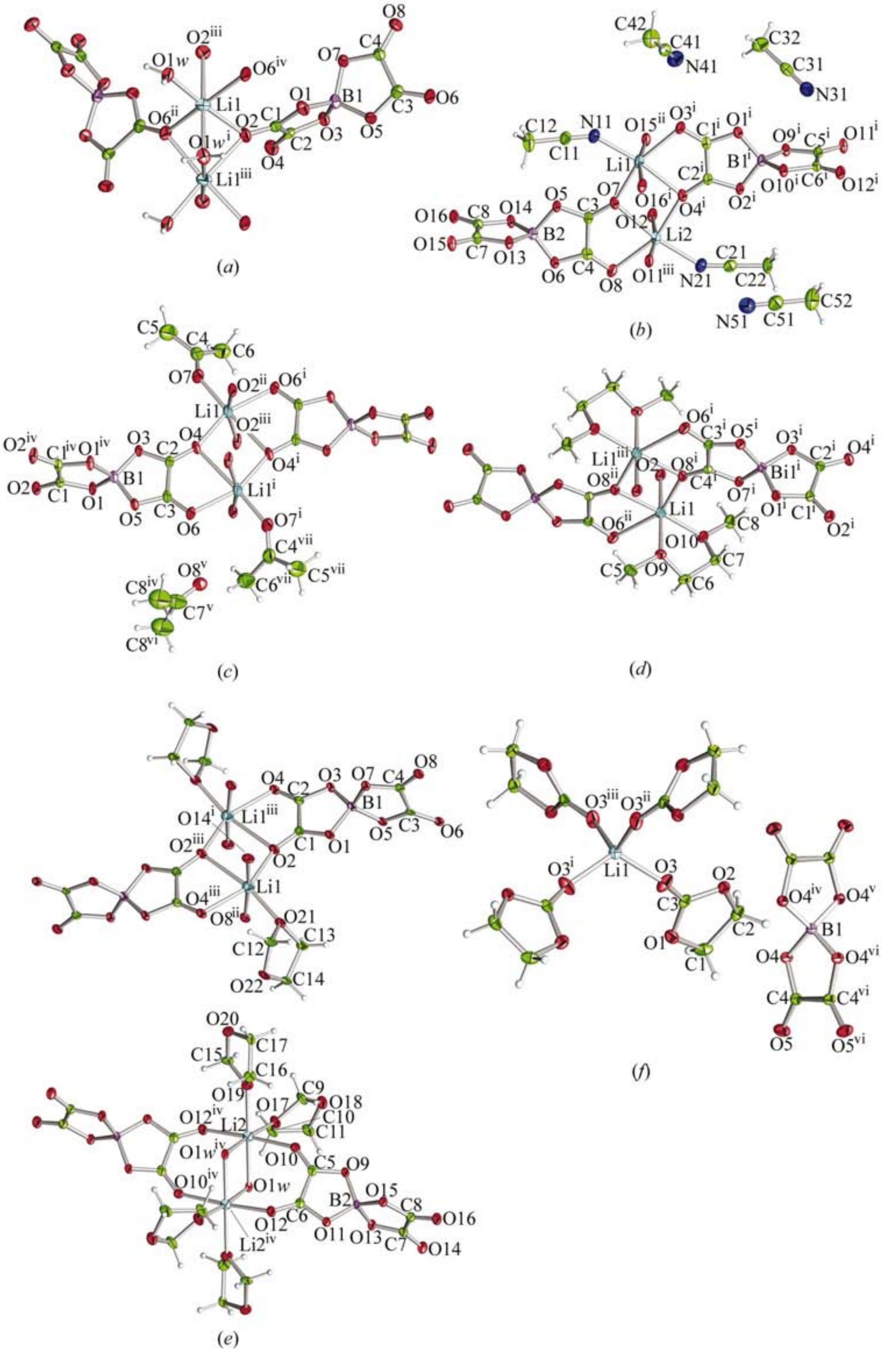

Figure 1
Dimer units in LiBOB solvates with atomic displacement ellipsoids drawn at the 50% probability level: (*a*) LiBOB·H_2O, (*b*) 2LiBOB·5AN, (*c*) LiBOB·4/3AC, (*d*) LiBOB·DME, (*e*) 2LiBOB·3DO·H_2O (top Li1, bottom Li2) and (*f*) Li(EC)$_4$BOB. H atoms are displayed with an arbitrarily small radius. Atom labelling coresponds to that in Table 2. Drawings performed using *ATOMS* (Dowty, 1999).

of the dimers and has five-coordinated Li.

Analysis of the known structures indicates that the Li in its BOB salts has a strong tendency to form octahedral coordination, which in the solvates is achieved by including at least one solvent molecule. It is highly likely that in the absence of any solvent, the octahedral environment of the Li cannot be realised geometrically due to the rigid configuration of the BOB ion. This can be observed in pure LiBOB, where the Li ion has a square-pyramidal environment with Li—O distances in the range 1.94 (3)–2.315 (6) Å (Zavalij *et al.*, 2003). The sixth O atom is far away at 3.01 (4) Å, which corresponds to a very weak interaction. Substantial distortion is observed in all the Li octahedra that do not contain coordinated water with one ligand being closer to Li [1.951 (5)–2.061 (4) Å] and one being much further away [2.415 (2)–2.493 (5) Å] than the others [1.993 (5)–2.355 (2) Å]. In contrast, the hydrated Li octahedra are far less distorted with Li—O distances ranging from 2.024 (6) to 2.216 (7) Å. The average Li—O distances are 2.12 Å in the presence and 2.18 Å in the absence of water in the Li octahedra. The average Li—O distance for all the octahedra is 2.15 Å, which is essentially the same as the average Li—O bond length deduced by Wenger & Armbruster (1991). Their review on Li—O coordination demonstrates that the majority of the structures have Li in tetrahedra. Quite the opposite is found in the LiBOB solvates, which have Li in an octahedral coordination. Interestingly, the anhydrous Li solvates have 5 + 1 distorted octahedra; however, the presence of

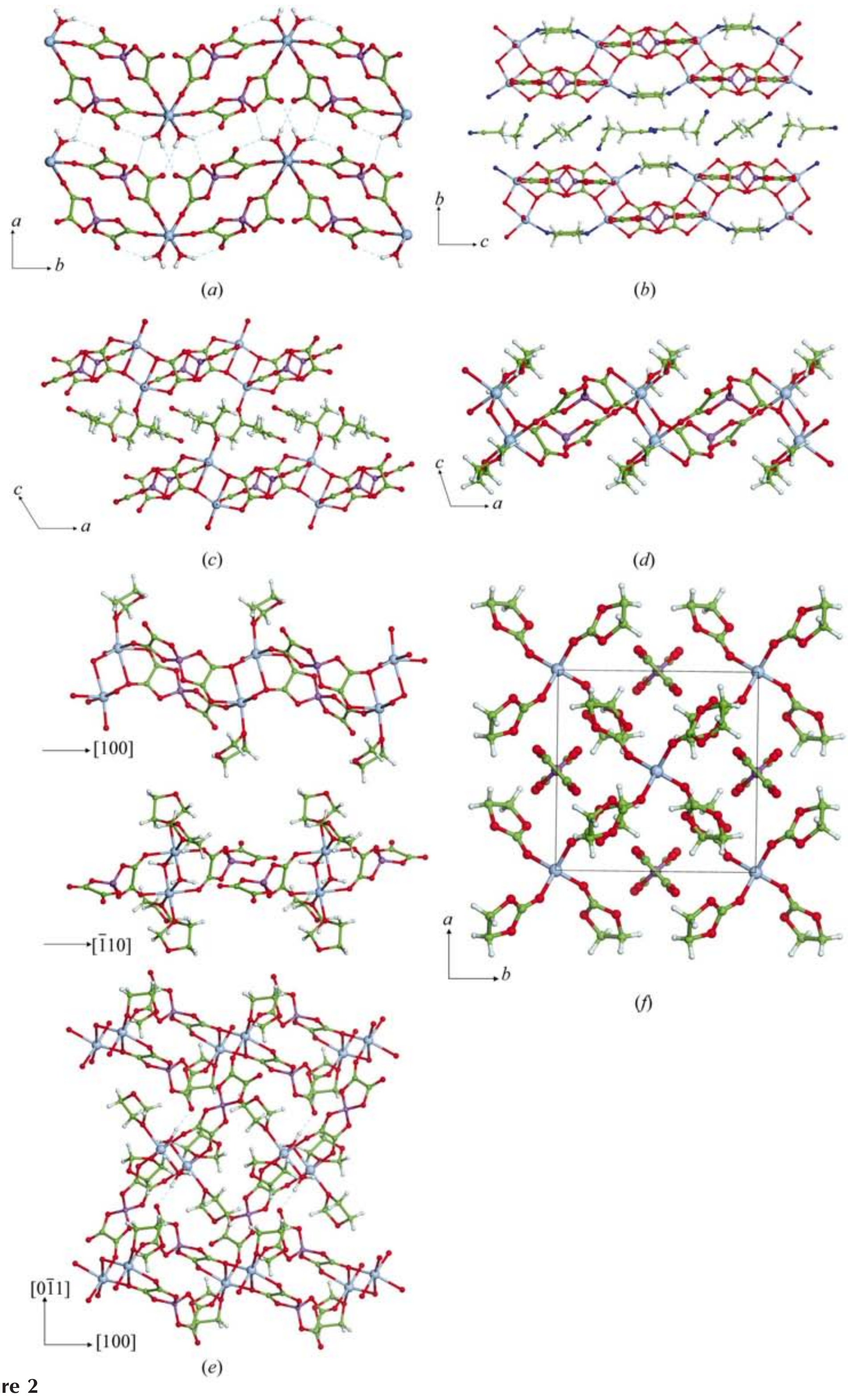

Figure 2
Packing in the LiBOB solvates (Li is shown as a large-sized ball, B as a medium-sized ball): (*a*) LiBOB·H_2O, (*b*) 2LiBOB·5AN, (*c*) LiBOB·4/3AC, (*d*) LiBOB·DME and (*e*) 2LiBOB·3DO·H_2O (top layer: middle Li1 chain; bottom: hydrogen-bonded Li2 dimers). Atom labelling corresponds to that in Table 2. Drawings were performed using Materials Studio (2001).

water in the Li coordination sphere leads to regular octahedra.

However, an exception to this tendency of the Li ion to have octahedral coordination in its BOB salts is the EC compound, Li(EC)$_4$BOB, where Li is tetrahedrally coordinated by four O atoms from the C=O group of four solvent molecules. This complex cation $[Li(EC)_4]^+$ may also exist in the EC/DMC solution, perhaps along with a DMC complex, which could explain why a EC/DMC mixture is so commonly used in commercial lithium batteries. The general tendency to octahedral coordination can also explain why unsolvated LiBOB is highly hygroscopic, the water filling the sixth coordination site, and why it can be obtained only in the form of a fine powder, by decomposition of a well crystalline solvated salt.

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References

Aurbach, D., Daroux, M. L., Faguy, P. W. & Yeager, E. (1987). *J. Electrochem. Soc.* **134**, 1611–1619.

Bruker (1999). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Dowty, E. (1999). *ATOMS* for Windows and Macintosh. Version 5. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.

Krause, L. J., Lamanna, W., Summerfield, J., Engle, M., Korba, G., Loch R. & Atanasoski, R. (1997). *J. Power Sources*, **68**, 320–325.

Mamak, M., Zavalij, P. Y. & Whittingham, M. S. (1998). *Acta Cryst.* C**54**, 937–939.

Mashiko, E., Yokokawa, M. & Nagaura, T. (1991). *Proc. of 32nd Battery Symposium.* Kyoto, Vol. 1B2, p. 31.

Materials Studio (2001). Accelrys Inc., San Diego, CA.

Ozawa, K. (1994). *Solid State Ion.* **69**, 212–221.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Sloop, S. E., Pugh, J. K., Wang, S., Kerr, J. B. & Kinoshita, K. (2001). *Electrochem. Solid State Lett.* **4**, A42–A44.

Sylla, S., Sanchez, J.-Y. & Armand, M. (1992). *Electrochim. Acta*, **37**, 1699–1701.

Webber, A. (1991). *J. Electrochem. Soc.* **138**, 2586–2589.

Wenger, M. & Armbruster, T. (1991). *Eur. J. Mineral.* **3**, 387–399.

Wietelmann, U., Lischka, U. & Wegner, M. (1999). German Patent DE 19829030 C1.

Wietelmann, U., Lischka, U. & Wegner, M. (2003). United States Patent 6,506,516.

Xu, W. & Angell, C. A. (2001). *Electrochem. Solid State Lett.* **4**, E1–E4.

Zavalij, P. Y., Yang, S. & Whittingham, M. S. (2003). *Acta Cryst.* B**59**, 753–759.

Zavalij, P. Y., Yang, S. & Whittingham, M. S. (2004*a*). Private Communication, CCDC 244695.

Zavalij, P. Y., Yang, S. & Whittingham, M. S. (2004*b*). Private Communication, CCDC 244694.