

## The Structure of Lithiumiodide 3-Tetrahydrofuran

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Z. Naturforsch. **53b**, 1525–1530 (1998);  
received August 31, 1998

Lithiumiodide THF Solvate, X-Ray Data

$\text{LiI} \cdot 3\text{THF}$  was obtained from the reaction of  $\text{tmp}_2\text{AlI}$  ( $\text{tmp}$  = tetramethylpiperidino) with  $\text{LiAsHPh}$  in toluene/THF. It is more, conveniently prepared from  $\text{LiH}$  and iodine in THF. It forms molecule in the lattice, the  $\text{Li}$  ion being tetracoordinated in a slightly distorted tetrahedral fashion.

We have recently described the preparation of bis(tetramethylpiperidino)phenylarsino alane [1] as one of the still rare examples of monomeric arsinolanes. The question arose whether analogous monomeric phenylarsino or even arsinolanes of type  $\text{tmp}_2\text{Al-AsHR}$  or  $\text{tmp}_2\text{Al-AsH}_2$  might be also accessible.

For this reason  $\text{tmp}_2\text{AlI}$  was allowed to react with  $\text{LiAsHPh}$  in hexane solution in a 1:1 ratio. Surprisingly, no precipitate formed and no crystalline product separated on concentration of the solution. However, after addition of THF to the reaction mixture colorless prismatic crystals separated. These proved not to be  $\text{tmp}_2\text{Al-AsHPh}$  but  $\text{LiI} \cdot 3\text{THF}$ .  $\text{LiI}$  itself is insoluble in hexane. Therefore, we assume that the reaction of  $\text{tmp}_2\text{AlI}$  with  $\text{LiAsHPh}$  leads to the hexane soluble complex  $[\text{Li}(\text{tmp}_2\text{Al}(\text{I})\text{AsHPh})]_n$  which on addition of THF yields  $\text{LiI} \cdot 3\text{THF}$  and  $\text{tmp}_2\text{Al-AsHPh}$ . The latter compound could not be isolated. While this is no preparative route, the compound can readily be obtained by the reaction of a slurry of  $\text{LiH}$  in THF by adding  $\text{I}_2$ .

### Molecular Structure of $\text{LiI} \cdot 3\text{THF}$

The crystals which had separated were found to be  $\text{LiI} \cdot 3\text{THF}$  by X-ray structure analysis. Figure 1 depicts its molecular structure.

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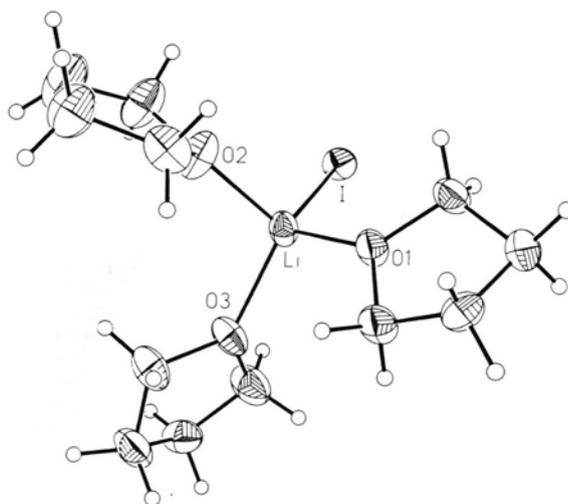


Fig. 1. Molecular structure of  $\text{LiI} \cdot 3\text{THF}$  in the lattice. Thermal ellipsoids represent a 25% probability. Atom distances (in Å):  $\text{Li-I}$  2.741(7),  $\text{Li-O1}$  1.927(7),  $\text{Li-O2}$  1.915(8),  $\text{Li-O3}$  1.947(7). Bond angles (in °):  $\text{O1-Li-I}$  114.5(3),  $\text{O2-Li-I}$  111.2(3),  $\text{O3-Li-I}$  113.2(3),  $\text{O1-Li-O2}$  105.0(4),  $\text{O1-Li-O3}$  105.6(3),  $\text{O2-Li-O3}$  106.7(3). Sum of bond angles at  $\text{O1}$  = 359.6°, at  $\text{O2}$  = 359.4° and at  $\text{O3}$  = 357.2°.

The  $\text{Li}$  ion of  $\text{LiI} \cdot 3\text{THF}$  resides in a slightly distorted tetrahedral environment with  $\text{O-Li-I}$  bond angles ranging from 111.2 to 114.5(3)°. Consequently the  $\text{O-Li-O}$  bond angles are smaller than expected for a tetrahedron. Within estimated standards of deviations the  $\text{Li-O}$  distances can be considered as being equal with an average value of 1.925 Å.

The sum of bond angles at the oxygen atom of the THF molecules are very close to 360°. Although this implies  $\text{sp}^2$  hybridization at the  $\text{O}$  atoms, it is more likely that this is the result of an ion-dipole interaction between the  $\text{Li}^+$  center and the oxygen atoms of THF molecules.  $\text{C-O}$  and  $\text{C-C}$  bond lengths lie in the expected ranges.

Finally, it should be noted that the  $\text{Li-I}$  atom distance is comparatively short, and that there are no  $\text{I} \cdots \text{I}$  contacts in the lattice (closest distance: 7.636 Å).

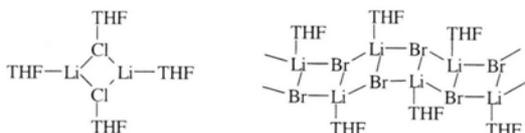
### Discussion

Lithium iodide readily forms solvates with ethers. It is soluble in diethylether, however, no solvates  $\text{LiI} \cdot n\text{OEt}_2$  are described. The only characterized product seems to be the the dioxanate



$\text{LiI} \cdot 2\text{O}_2\text{C}_4\text{H}_8$  [2], which so far has not been structurally characterized. Amongst THF solvates,  $\text{LiI} \cdot 3\text{THF}$  structurally resembles  $\text{LiI} \cdot 2\text{DME}$  [3] and  $\text{LiBr} \cdot 2\text{DME}$  [4]; both solvates containing, however, pentacoordinated Li centers, the former with a Li-I distance of 2.878(2) Å which is considerably longer than the 2.741(7) Å in  $\text{LiI} \cdot 3\text{THF}$  reflecting the higher coordination number in  $\text{LiI} \cdot 2\text{DME}$ . These ether solvates differ structurally from amine solvates of LiI [5] which are either typically ionic  $(\text{LiL}_n)\text{I}^-$  (L = TMEDA, en, or HMPT [6]) or form aggregates with bridging iodides (L = 2-methylpiperidine, 2,6-dimethylpiperidine) [5]. In these cases Li-I distances ranging from 2.77 to 2.93 Å are found in harmony with the well known fact that M-I-M bridging bonds are generally by 0.1 to 0.2 Å longer than single bond Li-I interactions.

In contrast to the comparatively stable  $\text{LiI} \cdot 3\text{THF}$ , the LiCl solvate  $\text{LiCl} \cdot 2\text{THF}$  [7] is readily desolvated. It is a chloride bridged dimer containing tetracoordinated Li centers.



The most stable THF solvate of LiBr is  $\text{LiBr} \cdot \text{THF}$  [8]. Its structure in the solid state shows a ladder where four-membered  $\text{Li}_2\text{Br}_2$  units form an infinite chain by anellation *via* tricoordinated Br ions while all Li centers are tetracoordinated by three bromide ions and one oxygen atom of a THF molecule. Thus for the series of  $\text{LiX} \cdot n(\text{THF})$  solvates with  $n = 1, 2$  and 3 are structurally realized with tetracoordinated Li centers as a common feature.  $\text{LiI} \cdot 3\text{THF}$  is the least associated species. It is likely that a low temperature species  $\text{LiI} \cdot 4\text{THF}$  exists as  $[\text{Li}(\text{THF})_4]\text{I}$ . This type of compounds, *e.g.*  $[\text{Li}(\text{HMPA})_4]\text{Br}$ , is known with tri(dimethylamino)phosphine oxide [HMPA] as a ligand [9]. Association of the lithium halide species decreases from  $[\text{LiCl} \cdot \text{HMPA}]_4$ , which shows a cubane structure [10], *via*  $(2\text{LiBr}) \cdot 3\text{HMPA}$  [11], where the oxygen atoms of HMPA bridge the lithium centers of two LiBr units, to  $\text{LiI} \cdot 4\text{HMPA}$  which is an ion separated species  $[\text{Li}(\text{HMPA})_n]\text{I}$  [6]. It appears that LiI is the best candidate for tetrasolvation and ion separation due to the lowest lattice energy in the series of lithium halides.

## Experimental

Phenylarsane was prepared by a literature procedure [12] and PhAsHLi obtained by allowing this hydride to react with LiBu in hexane in a 1:1 ratio.  $\text{tmp}_2\text{AlI}$  was available [13].

*Lithiumiodide-3-tetrahydrofuran:* a) Equimolar amounts of LiHAsPh and  $\text{tmp}_2\text{AlI}$  (2.5 mmol each) dissolved in 20 ml of toluene, were mixed at  $-78^\circ\text{C}$  and allowed to warm to ambient temperature. No precipitate formed. The solvent was removed to a volume of approximately 4 ml. Then 5 ml of THF was added and the solution cooled to  $-40^\circ\text{C}$ . Within 6 d crystals separated which were isolated and subjected to a X-ray structure investigation. The yield was not determined. – b) A slurry of LiH (795 mg, 100 mmol) in THF (30 ml) was vigorously stirred and a solution of iodine (2.54 g, 10 mmol) in 40 ml of THF was added. Decoloration and gas evolution set in rapidly. After the gas evolution ceased the excess of solid material was removed by filtration (G3 glass frit) and the solution reduced to a volume of approximately 15 ml in a vacuum. Cooling of the remaining solution to  $-40^\circ\text{C}$  caused the formation of crystals, from which the supernatant liquid was removed *via* a syringe. Passing a stream of dinitrogen over the crystals led to rapid deterioration; yield 4.3 g (~50%).

$\text{LiI} \cdot 3\text{C}_4\text{H}_8\text{O}$  (350.15)  
 Calcd I 36.24%,  
 Found I 33.4%.

*X-ray structure determination of LiI·3THF:* A single crystal was selected under cold ( $-30^\circ\text{C}$ ) perfluoroether oil and mounted on a glass fiber. The unit cell dimensions were obtained from the reflexions collected by a CCD area detector fitted to a Siemens P4 diffractometer from a total of 60 frames at four different setting angles using graphite monochromated  $\text{MoK}_\alpha$  radiation. Data collection was performed at 193 K with 10s exposures per frame by changing the  $\psi$  setting by  $0.3^\circ$  per frame. Reflexions collected on a total of 1265 frames were reduced by the program SAINT [14] and a semiempirical absorption correction was applied (SADABS). The structure was solved by the heavy atom method followed by difference Fourier calculations. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and included in the refinement by applying a riding model (SHELXTL [15]).

$\text{C}_{12}\text{H}_{24}\text{LiO}_3$ , mol. weight 350.15; colorless prism, crystal dimensions: 0.45 x 0.35 x 0.25 mm;

unit cell dimension:  $a = 9.030(6)$ ,  $b = 13.306(1)$ ,  $c = 13.251(1)$  Å,  $\beta = 95.73(2)^\circ$ ,  $V = 1584(2)$  Å<sup>3</sup>,  $Z = 4$ , space group  $P2_1/n$ ,  $d_{\text{calc.}} = 1.468$  g/cm<sup>3</sup>,  $F(000) = 704$ ,  $\mu = 2.051$  mm,  $2\theta$  range:  $4.3$  to  $54.6^\circ$  ( $-10 \geq h \geq 10$ ,  $-17 \geq k \geq 17$ ,  $-17 \geq l \geq 16$ ) 8037 data collected, 2825 independent reflexions, 1576 observed [ $F \geq 4\sigma(F)$ ]; 154 variables. GOF = 1.136,  $R_1 = 0.0355$ ,  $wR_2 = 0.0731$ ; weighting factor:  $w^{-1} = \sigma^2 F_o^2 + (0.0266P)^2 + 2.5851P$ ,  $P = (F_o^2 + 2F_c^2)/3$ . Largest difference peak:  $0.698e/\text{Å}^3$ .

Further details of the structure determination are deposited at the Cambridge Crystallographic

Data Center and can be obtained from the Director, CCDC, 12 Union Road GB-Cambridge CB2 1EZ by quoting the deposition number 102812, the name of the authors and the literature citation.

#### Acknowledgements

We thank Dr. I. Krossing for the data collection and preliminary calculations of LiI·3THF, and Chemetall GmbH, Frankfurt for continuous support, as well as Mr. M. Warchold for experimental help.

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