Inorg. Chem. **1995**, *34*, 6553−6555 **6553**

Crystal Structure of [LiBr·Et$_2$O]$_4$: First Example of a Diethyl Ether-Solvated LiBr Lattice Fragment

Frank Neumann, Frank Hampel, and
Paul v. Ragué Schleyer*

Institut für Organische Chemie,
Friedrich-Alexander-Universität Erlangen-Nürnberg,
Henkestrasse 42, D-91054 Erlangen, Germany

Received April 21, 1995

Introduction

Since organic halides are often used as precursors, lithium halides are frequently formed as byproducts in metalation reactions. We report here the crystal structure of [LiBr·Et$_2$O]$_4$ (**1**), a new example of this type of complex (Figure 1). It was obtained fortuitously as a byproduct of the reaction of bromomesitylene and lithium metal.

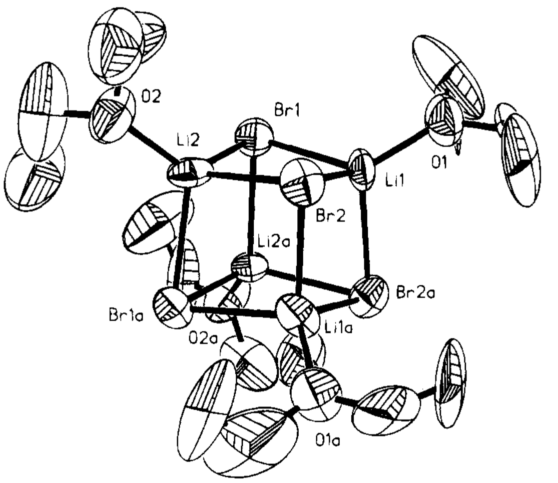

Figure 1. ORTEP diagram of [LiBr·Et$_2$O]$_4$ showing 50% probability ellipsoids.

The various crystal structures of lithium halides solvated by Lewis bases exhibit remarkable structural diversity.[1] Solvent-separated ion pairs,[4,6−8,11,13,15−17,20] monomers,[5,14,18,19,22−25,28] dimers,[2,9,12,17,19−21,25,27] tetramers,[10,18,21,25] larger oligomers[17,30] and polymers[3,26,29] are known. Pyridines (pyridine,[3,5,25] 4-*tert*-butylpyridine,[14] quinoline,[14,15,25] 2,6-dimethylpyridine,[21] 3,5-dimethylpyridine,[19] 2-methylpyridine,[19] 1,10-phenanthroline,[23] 2,2′-bipyridine,[24] collidine,[25] quinaldine[25]) and chelating amines (ethylenediamine,[6,8] TMEDA = *N,N,N′,N′*-tetramethylethylenediamine,[17,30] PMDETA = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine[9,18]) usually serve as ligands. Complexes with Lewis bases containing oxygen (triphenylphosphine oxide,[4] water,[5,11,15,16] urea,[7] HMPTA = hexamethylphosphoric triamide,[10,11,22] acetone,[12] methanol,[13] 2-propanol,[24] sulfolane[26]) are less common. Those with ether solvents are rare: [(LiCl)$_2$·(1,4-dioxane)$_2$]$_\infty$,[2] [LiCl·2THF]$_2$[27] (THF = tetrahydrofuran), [Li(12-crown-4)]Cl,[28] and [LiBr·THF]$_\infty$.[29] Since Et$_2$O is such a commonly used solvent in organolithium chemistry, it is surprising that diethyl ether-solvated complexes have not been reported before. However, such species tend to desolvate rapidly when removed from solution.

Experimental Section

All reactions were carried out under an argon atmosphere using standard Schlenk as well as needle septum techniques. Diethyl ether was freshly distilled from Na under argon. Bromomesitylene was prepared according to the literature procedure.[31]

Preparation of [LiBr·Et$_2$O]$_4$ (1) To a suspension of Li powder (0.73 g, 105 mmol) in diethyl ether (60 mL) was added bromomesitylene (7.7 mL, 50 mmol) in one portion. The resulting mixture was exposed to ultrasound at room temperature for 1 h until virtually all the Li powder had vanished and a white precipitate had been formed. The reaction mixture was allowed to stand overnight. The slightly yellow solution was separated from the precipitate via syringe and stored at −20 °C. **1** formed large colorless crystals of X-ray quality after 2 days. The crystals were found to be stable only in their mother liquor, as they desolvate rapidly when dried. Crystallographic data and selected atomic coordinates are given in Tables 1 and 2, respectively.

X-ray Crystallography. Data were collected with a Nicolet R3mV diffractometer on a crystal with the dimensions 0.5 × 0.4 × 0.4 mm using the ω-scan method (4.0° < 2θ < 54.0°). Of a total of 4892

---

(1) Snaith, R.; Wright, D. S. In *Lithium Chemistry: A Theoretical and Experimental Overview*; Sapse, A.-M., Schleyer, P. v. R., Eds.; Wiley: New York, 1995; p 227.

(2) Durant, F.; Gobillon, Y.; Piret, P.; van Meerssche, M. *Bull. Soc. Chim. Belg.* **1966**, *75*, 52.

(3) Durant, F.; Verbist, J.; van Meerssche, M. *Bull. Soc. Chim. Belg.* **1966**, *75*, 806.

(4) Yasin, Y. M. G.; Hodder, O. J. R., Powell, H. M. *J. Chem. Soc., Chem. Commun.* **1966**, 705.

(5) Durant, F.; Piret, P.; van Meerssche, M. *Acta Crystallogr.* **1967**, *22*, 52.

(6) Durant, F.; Piret, P.; van Meerssche, M. *Acta Crystallogr.* **1967**, *23*, 780.

(7) Verbist, J.; Meulemans, R.; Piret, P.; van Meerssche, M. *Bull. Chim. Soc. Belg.* **1970**, *79*, 391.

(8) Gillier-Pandraud, H.; Jamet-Delcroix, S. *Acta Crystallogr. Sect. B* **1971**, *B27*, 2476.

(9) Hall, S. R.; Raston, C. L.; Skelton, B. W.; White, A. H. *Inorg. Chem.* **1983**, *22*, 4070.

(10) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1984**, 79.

(11) Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1984**, 974.

(12) Amstutz, R.; Dunitz, J. D.; Laube, T.; Schweizer, B.; Seebach, D. *Chem. Ber.* **1986**, *119*, 434.

(13) Weppner, W.; Welzel, W.; Kniep, R.; Rabenau, A. *Angew. Chem.* **1986**, *98*, 1105; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1087.

(14) Raston, C. L.; Skelton, B. W.; Whitaker, C. R.; White, A. H. *Aust. J. Chem.* **1988**, *41*, 341.

(15) Raston, C. L.; Skelton, B. W.; Whitaker, C. R.; White, A. H. *Aust. J. Chem.* **1988**, *41*, 409.

(16) Raston, C. L.; Whitaker, C. R.; White, A. H. *Aust. J. Chem.* **1988**, *41*, 413.

(17) Raston, C. L.; Skelton, B. W.; Whitaker, C. R.; White, A. H. *Aust. J. Chem.* **1988**, *41*, 1925.

(18) Raston, C. L.; Skelton, B. W.; Whitaker, C. R.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1988**, 987.

(19) Raston, C. L.; Whitaker, C. R.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1988**, 991.

(20) Raston, C. L.; Whitaker, C. R.; White, A. H. *Aust. J. Chem.* **1989**, *42*, 201.

(21) Raston, C. L.; Whitaker, C. R.; White, A. H. *Inorg. Chem.* **1989**, *28*, 163.

(22) Barr, D.; Doyle, M. J.; Mulvey, R. E.; Raithby, P. R.; Reed, D.; Snaith, R.; Wright, D. S. *J. Chem. Soc., Chem. Commun.* **1989**, 318.

(23) Patalinghug, W. C.; Whitaker, C. R.; White, A. H. *Aust. J. Chem.* **1990**, *43*, 635.

(24) Skelton, B. W.; Whitaker, C. R.; White, A. H. *Aust. J. Chem.* **1990**, *43*, 755.

(25) Raston, C. L.; Robinson, W. T.; Skelton, B. W.; Whitaker, C. R.; White, A. H. *Aust. J. Chem.* **1990**, *43*, 1163.

(26) Harvey, S.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1991**, *44*, 309.

(27) Hahn, F. E.; Rupprecht, S. *Z. Naturforsch.* **1991**, *46B*, 143.

(28) Gingl, F.; Hiller, W.; Strähle, J.; Borgholte, H.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1991**, *606*, 91.

(29) Edwards, A. J.; Paver, M. A.; Raithby, P. R.; Russel, C. A.; Wright, D. S. *J. Chem. Soc., Dalton Trans.* **1993**, 3265.

(30) Hoffmann, D.; Dorigo, A.; Schleyer, P. v. R.; Reif, H.; Stalke, D.; Sheldrick, G. M.; Weiss, E.; Geissler, M. *Inorg. Chem.* **1995**, *34*, 262.

(31) Smith, L. I. *Org. Syntheses*; Wiley: New York, 1943; Collect. Vol. II, p 95.

0020-1669/95/1334-6553$09.00/0

Table 1. Crystallographic Data for $[LiBr{\cdot}Et_2O]_4$

empirical formula	$C_{16}H_{40}Br_4Li_4O_4$
formula wt (g mol^{-1})	643.88
space group	*C*2/*c*
a (Å)^a	17.649(11)
b (Å)	11.684(8)
c (Å)	15.545(9)
β (deg)	111.60(5)
T (K)	173(2)
λ (Å) (Mo Kα)	0.710 73
D_{calc} (g cm^{-3})	1.435
$R1^b$	0.0652
$wR2$	0.1828^c
V (Å^3)	2980(3)
Z	4

[a] Standard deviations in the least significant figure are given in parentheses. [b] $(I > 4\sigma(I))$; $R1 = \sum|F_o - F_c|/\sum F_o$. [c] $wR2 = (\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2)^{0.5}$.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3)^a

	x	*y*	*z*	*U*(eq)
Li(1)	−832(12)	−3537(16)	7721(14)	66(6)
Br(1)	−1019(1)	−1340(1)	7778(1)	63(1)
Li(2)	−567(10)	−1464(17)	6409(11)	58(5)
Br(2)	−670(1)	−3663(1)	6166(1)	67(1)
O(1)	−1525(6)	−4484(8)	8072(6)	87(3)
C(1)	−2045(12)	−3993(20)	8587(13)	214(13)
C(2)	−1631(33)	−3793(40)	9484(16)	156(15)
C(2′)	−1679(70)	−3406(59)	9351(32)	156(15)
C(3)	−1554(30)	−5673(18)	8110(28)	156(12)
C(3′)	−1171(46)	−5570(35)	8304(27)	156(12)
C(4)	−1221(13)	−6228(12)	7553(14)	185(12)
O(2)	−1101(6)	−512(8)	5455(6)	99(3)
C(5)	−992(14)	643(13)	5311(12)	171(11)
C(6)	−338(25)	1056(45)	5981(30)	160(17)
C(6′)	−598(33)	1276(30)	6067(14)	160(17)
C(7)	−1907(10)	−903(18)	4824(10)	143(9)
C(8)	−1820(11)	−1416(13)	4129(11)	141(6)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

collected reflections, 3450 were unique and 750 with $I > 4\sigma(I)$ observed. The structure was solved by direct methods using SHELXTL Plus 4.11. A total of 139 parameters were refined with all data by full-matrix least-squares fitting on F^2 using SHELXL93.[32] All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were fixed in idealized positions using the riding model. The ether ligands exhibit disorder of the carbon atoms (C2, C2′, C3, C3′, C6, C6′) which was resolved using distance restraints. The largest peak and hole in the final difference map were 0.687 and −1.121 eÅ^{-3}.

Results and Discussion

The discrete tetramers of **1** exhibit a heterocubane structure. Li occupies four nonadjacent corners of a distorted cube, and Br the other four, as shown in Figure 1. The principal bond distances and angles are summarized in Table 3. Each Li is coordinated pseudotetrahedrally by three Br atoms (*r*(Li−Br) 2.54(2)−2.62(2) Å) and one oxygen of diethyl ether (*r*(Li−O) 1.82(2), 1.87(2) Å). The average Li−Br−Li and Br−Li−Br angles are 79.8° and 99.3°, respectively. Thus, the Li_4Br_4 cluster can be regarded as a small solvated fragment of the LiBr lattice. Similar tetrameric aggregates exist in solutions of LiBr in diethyl ether, as shown by EXAFS spectroscopy.[33,34] The Li−Br and Br−Br distances of 2.5 and 3.87 Å, found in solution, correspond very well to the respective separations in **1** (*r*(Br−Br) 3.90(2)−4.00(2) Å). In solid LiBr, *r*(Li−Br) is 2.748(4) Å;[35] in the gas phase, *r* is 2.1704(1) Å in the monomer[36] and 2.35 Å in the dimer.[37] The Li−Br distances found in **1** are between the values in the solid and in the dimer, as expected.

Table 3. Selected Bond Distances (Å) and Angles (deg)

Li(1)−Br(1)	2.59(2)	Li(2)−Br(2)	2.59(2)
Li(1)−Br(2)	2.54(2)	Li(2)−Br(1a)	2.62(2)
Li(1)−Br(2a)	2.58(2)	Li(1)−O(1)	1.87(2)
Li(2)−Br(1)	2.54(2)	Li(2)−O(2)	1.82(2)
Br(1)−Li(1)−Br(2)	98.6(6)	Li(2)−Br(1)−Li(2a)	78.0(5)
Br(1)−Li(2)−Br(2)	98.7(7)	Li(1)−Br(2)−Li(1a)	78.8(6)
Li(1)−Br(1)−Li(2)	80.3(6)	Li(2)−Br(2)−Li(1a)	81.1(5)
Li(1)−Br(2)−Li(2)	80.2(6)	O(1)−Li(1)−Br(1)	118.0(8)
Br(1)−Li(1)−Br(2a)	98.4(7)	O(1)−Li(1)−Br(2)	123.9(10)
Br(2)−Li(1)−Br(2a)	100.8(6)	O(1)−Li(1)−Br(2a)	113.0(9)
Br(1)−Li(2)−Br(1a)	101.7(5)	O(2)−Li(2)−Br(1)	114.9(9)
Br(2)−Li(2)−Br(1a)	97.5(6)	O(2)−Li(2)−Br(2)	120.0(8)
Li(1)−Br(1)−Li(2a)	80.5(6)	O(2)−Li(2)−Br(1a)	120.2(10)

The heterocubane tetramer type is well documented in a great variety of organolithium compounds.[1,38−42] Surprisingly, **1** is only the second pure lithium halide complex with this arrangement; the first such cluster was $[LiCl{\cdot}HMPTA]_4$.[10] Additionally, LiBr units have been found in a number of mixed-aggregate heterocubanes, e.g., one in $[(PhLi{\cdot}Et_2O)_3{\cdot}LiBr]$[43] (Ph = phenyl), two in $[(c\text{-}C_3H_5Li{\cdot}Et_2O)_2{\cdot}(LiBr{\cdot}Et_2O)_2]$,[44] ($c\text{-}C_3H_5$ = cyclopropyl) and three in $[(Me_3Si)_3CCd{\cdot}(LiBr{\cdot}THF)_3{\cdot}OSiMe_3]$.[45] A "double cubane with two corners missing" is realized in the cationic part of $[Li_6Br_4(Et_2O)_{10}][Ag_3Li_2Ph_6]_2$.[46]

It is of special interest to compare the structures of **1** and the polymeric complex $[LiBr{\cdot}THF]_\infty$,[29] reported recently. The structure of the latter, consisting of infinite folded ladder arrangements of cyclic $(LiBr)_2$ units, results from the polymerization of $(LiBr)_4$ heterocubanes by breaking the two opposite edges of one face.

Lithium compounds generally are more soluble in THF than in diethyl ether. Ab initio and semiempirical calculations of the thermodynamics of solvation of Li^+ and CH_3Li[47] have concluded that the solvating power of diethyl ether is slightly larger than that of THF for the first ligand to be attached. If more than one of these ligands per Li is present, THF is the superior solvent. Therefore, it is not obvious why solvation of LiBr by THF results in the formation of larger aggregates in the solid state than solvation by diethyl ether. The three structurally different complexes of the LiCl/TMEDA system[17,30] are instructive in this context. High-level ab initio and semiempirical calculations of several LiCl tetramer arrangements

---

(32) Sheldrick, G. M. *SHELXL93*; University of Göttingen: Göttingen, Germany, 1993.

(33) Chabanel, M. *J. Chim. Phys.* **1966**, *63*, 77.

(34) Goulon, J.; Goulon-Ginet, C.; Chabanel, M. *J. Solution Chem.* **1981**, *10*, 649.

(35) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1962; Vol. III, p 258.

(36) Honig, A.; Mandel, M.; Stitch, M. L.; Townes, C. H. *Phys. Rev.* **1954**, *96*, 629.

(37) Akischin, P. A.; Rambidi, N. G. *Z. Phys. Chem., Leipzig* **1960**, *213*, 111.

(38) Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353.

(39) Schade, C.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1987**, *27*, 159.

(40) Mulvey, R. E. *Chem. Soc. Rev.* **1991**, *20*, 167.

(41) Gregory, K.; Schleyer, P. v. R.; Snaith, R. *Adv. Organomet. Chem.* **1992**, *37*, 47.

(42) Weiss, E. *Angew. Chem.* **1993**, *105*, 1565; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1501.

(43) Hope, H.; Power, P. P. *J. Am. Chem. Soc.* **1983**, *105*, 5320.

(44) Schmidbaur, H.; Schier, A.; Schubert, U. *Chem. Ber.* **1983**, *116*, 1938.

(45) Buttrus, N. H.; Eaborn, C.; El-Kheli, M. N. A.; Hitchcock, P. B.; Smith, J. D.; Sullivan, A. C.; Tavakkoli, K. *J. Chem. Soc., Dalton Trans.* **1988**, 381.

(46) Chiang, M. Y.; Böhlen, E.; Bau, R. *J. Am. Chem. Soc.* **1985**, *107*, 1679.

(47) Kaufmann, E.; Gose, J.; Schleyer, P. v. R. *Organometallics* **1989**, *8*, 2577.

(including heterocubane and ladder structures) show that the potential energy surface is very flat.[30] Additionally, the oligomerization energies per LiCl monomer were found to be very similar for trimers and for tetramers. The same can be expected for LiBr clusters. Obviously, the formation of aggregates of different size depends on subtle steric and energetic differences. Ligands are necessarily more crowded in a ladder structure than in discrete tetramers. This is in accordance with the formation of the latter in the presence of diethyl ether, which is sterically more demanding than THF. However, a MNDO computational examination failed to reveal any clear-cut steric difference between Et_2O and THF with regard to the formation of the two different structures.

Another possible rationalization of the observed structural difference is based on entropy considerations. Tetramers with *one* ligand per LiBr unit are present in diethyl ether. Polymerization of these tetramers would lead to a decrease of entropy of the system, since the number of particles would decrease. However, in THF, smaller aggregates with *more than one* ligand per LiBr unit may be present, e.g., $[LiBr \cdot 2THF]_2$. Formation of a ladder structure from such complexes would increase the number of particles due to liberation of ligands. Therefore, the entropy of the system would increase upon polymerization.

Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates and isotropic displacement factors, bond lengths and angles, anisotropic displacement factors, and hydrogen coordinates for **1** (5 pages). Ordering information is given on any current masthead page. Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, GB-Cambridge CB2 1EW, by quoting the full journal citation.

IC950473K