A Li_2Br_2 Ring Trapped by *tert*-Butylaminotin(II) Bromide and *tert*-Butylamine as found by X-Ray Crystallography

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Reaction of the cyclic compound $[Bu^t(H)]\overline{N\text{–}Si(Me)_2\text{–}N(Bu^t)\text{–}Sn}Br$ with *tert*-butylamine intermediate yields the $[Bu^t(H)N\text{–}SnBr]_2$, which with excess *tert*-butylamine, ligates a four-membered Li_2Br_2 ring [2.61(2) and 2.69(2) Å] by multiple acid–base interactions between the metallic and the non-metallic centres giving a molecular product of the composition $\{Sn_2[N(H)Bu^t]_2Br_2\}_2 \cdot Li_2Br_2 \cdot 4Bu^tNH_2$ as shown by X-ray crystallography.

During the last decade special attention has been paid to the fact, that several donor molecules are able to coordinate alkali halides so efficiently that parts of their ionic crystal lattice break and are stabilized as molecular complexes.[1] Species such as $Li_4Cl_4 \cdot 4R$ [R = O=P(NMe$_2$)$_3$],[2] $Li_2Br_2 \cdot 2R$ (R = pentamethyldiethylenetriamine, PMDETA)[3] or LiX·3R (X = Cl, Br, I, R = 3,5-$Me_2C_5H_3N$)[4] have been isolated and structurally characterized. It has been pointed out, that coordination of the donor molecules to the lithium atom is highly facilitated if the lithium halide is synthesized as a transient species in an extremely dispersed manner instead of treating a block of the crystalline salt with the nucleophile.[5] Few attempts have been made to coordinate the lithium and halide centre at the same time by a complementary acid–base system, only recently LiCl has been 'trapped' by two molecular units of diisopropylaminolithium and PMDETA.[6] We have succeeded in complexing the anionic part of alkaline halides which partly leads to the dissolution of the salt in non-coordinating solvents such as benzene or toluene.[7]

We describe here the facile dissolution of crystalline blocks of lithium bromide by coordinating LiBr units to an acid–base system consisting of *tert*-butylaminotin(II) bromide.[8] This aminotinbromide is generated *in situ* as a highly dispersed phase (see above) by treating compound **1** with an excess of *tert*-butylamine in toluene [eqn. (1)].[8,9]

$$\underset{\mathbf{1}}{4\,Bu^t(H)\overline{N\text{–}Si(Me)_2\text{–}N(Bu^t)\text{–}Sn}Br} + 2\,LiBr + 8\,Bu^tNH_2$$
$$\rightarrow 4\,Me_2Si[N(H)Bu^t]_2 + \underset{\mathbf{2}}{\{[Bu^t(H)N\text{–}SnBr]\}_2 \cdot Li_2Br_2 \cdot 4\,Bu^tNH_2} \quad (1)$$

Compound **2** is an adduct of four aminotin(II)bromides, Li_2Br_2 and four *tert*-butylamines and is obtained in excellent yield by crystallization from the toluene solution.† The ^1H NMR spectrum shows only one broad signal for the two chemically different *tert*-butyl groups present in the molecule suggesting exchange equilibria of ligands in toluene. An X-ray structure determination for **2** gives more insight in the complex as well as in its structure (Fig. 1).‡ **2** consists of a central Li_2Br_2 four-membered ring, each lithium atom being coordinated by two *tert*-butylamines through N→Li donor bonds [mean Li–N 2.045(5) Å]. Almost in the plane of the Li_2Br_2-ring, which has a crystallographic inversion centre, two $Sn_2Br_2[NBu^t(H)]_2$ units are linked through bromine–tin bonds [3.174(2) Å] forming a layer of lithium, tin and bromine atoms. The overall C_{2h} ($2/m$) symmetry of **2** is only disturbed by the coordinating *tert*-butylamines. There is a marked resemblance in the $Sn_2Br_3[NBu^t(H)]_2$ part of **2** and the structure of $[SnCl_2 \cdot (SnNBu^t)_2]_x$[10] which displays a $Sn_3(NBu^t)_2$ trigonal bipyramid, the equatorial Sn···Sn edges being bridged by chlorine. The corresponding structural unit in **2** differs from this chlorine compound by the substitution of Cl by Br and the replacement of one of the tin^{II} atoms by two hydrogen atoms bonded to the four-coordinate nitrogen centres. The hydrogen atoms also display short contacts to the bromine atoms Br(2) and Br(3) [2.85(3)–3.03(3) Å] resulting in the formation of N–H···Br bridges. The Sn–Br bonds are unequal with a succession of long and short distances in the order Br(3)–Sn(1)–Br(1)–Sn(2)–Br(2) (compare with Fig. 1). This may be a reflection of the formation of **2** by addition of an intermediate $[BrSnN(H)Bu^t]_2$, displaying a four-membered Sn_2N_2 ring with

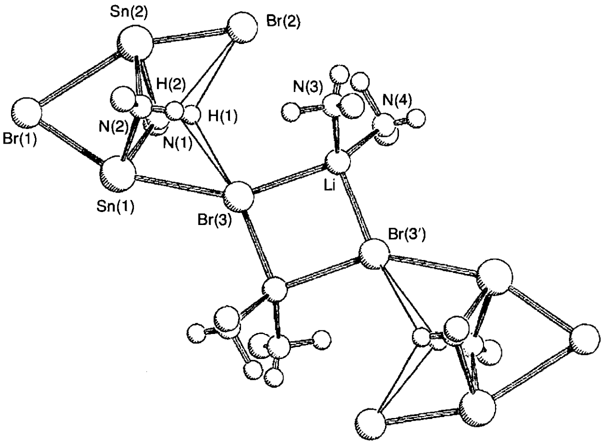

Fig. 1 The structure of **2** with atomic labelling (the dashed labels identify atoms which are related by inversion). The methyl substituents on the carbon atoms C(1), C(2), C(3) and C(4) (*tert*-butyl groups) have been omitted for clarity. Some important bond lengths (Å): Li–Br(3) 2.69(2), Li–Br(3′) 2.60(2), Sn(1)–Br(3) 3.174(2), Sn(1)–Br(1) 2.816(2), Sn(2)–Br(1) 3.241(2), Sn(2)–Br(2) 2.772(2), Sn(1)–N(1) 2.237(6), Sn(1)–N(2) 2.217(6), Sn(2)–N(1) 2.240(6), Sn(2)–N(2) 2.223(6), Li–N(3) 2.04(2), Li–N(4) 2.05(2), H(1)–Br(2) 2.97(3), H(1)–Br(3) 3.03(3), H(2)–Br(2) 2.97(3), H(2)–Br(3) 2.85(3).

Table 1 Li–Br bond distances in different compounds

Compound	Li–Br/Å	Coordination number at Li	Coordination number at Br
LiBr (crystal)	2.75	6	6
2[a]	2.61/2.69	4	5
$[Li_2Br_2 \cdot 2\ PMDETA]$[3]	2.57/2.87	5	2
$[Li_2Br_2 \cdot (2\text{-}MeC_5H_4N)]$[4]	2.56/2.57	4	2
$[Li_2Br_2 \cdot (3,5\text{-}Me_2C_5H_3N)]$[4]	2.51	4	1
$[Li_2Br_2 \cdot 3\ HMPA \cdot Toluene]$[5,b]	2.40	4	1

[a] This work. [b] HMPA = Hexamethylphosphoramide.

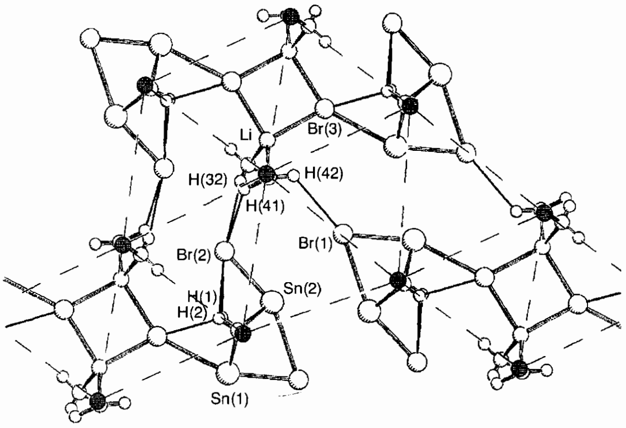

Fig. 2 A sheet segment of the crystal structure of **2** with intra- and intermolecular H···Br contacts. The tertiary carbon atoms of the *tert*-butyl groups are marked by hatching and are connected by broken lines showing the hexagonal packing. No methyl groups are drawn.

two terminal Br ligands on the tin atoms [compare with similar structure of $(Bu^tO)_2Sn_2Cl_2$].[9]

In Fig. 2 the interaction of the molecules in the crystal is shown with three remarkable features: (i) all molecules are coplanar with respect to each other forming a layer structure and the metal and halogen atoms are all assembled in one plane. The inorganic sheet is wrapped up above and under the plane by the *tert*-butyl-groups; (ii) the orientation of the molecules within the plane is governed by a nearly ideal hexagonal arrangement of the *tert*-butyl groups [C···C between tertiary carbon atoms of *tert*-butyl 5.92(1)–6.98(1) Å, C···C···C 58–69°]; (iii) there are short hydrogen bridges N–H···Br between the molecules [H(41)···Br(2) 2.77(3) Å, H(42)···Br(1) 3.03(3) Å] whereas the intermolecular Sn···Sn [3.959(2), 4.021(2)] and Br···Sn distances [smallest: Sn(2)···Br(1) 4.034(2) Å] are too long to be considered even as secondary bonds. Br(2) is coordinated to Sn(2) and two intra- [H(1), H(2)] and two inter-molecular [H(32), H(41)] hydrogen atoms (3.09, 2.77 Å) giving a distorted square pyramidal environment.

The rather long Li–Br distances in **2** (Fig. 1) can be correlated to a normal coordination number at lithium but a relatively high coordination number at Br(3) by comparison with other compounds (see Table 1). As expected the Li–Br distances in alkali halide acid–base complexes seem to be a function of the electron attracting and withdrawing power of the ligands present on both the lithium and the bromide atom. As a consequence, the data for **2** only fit in the experimental series, if the H–Br contacts are considered as part of the coordination figure around Br(3).

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Footnotes

† Reaction of **1**[8] with an excess (5 equiv.) of *tert*-butylamine in toluene and addition of crystalline LiBr yields, after stirring for 1 h at 40 °C 72% of **2** with mp 143 °C (decomp.) and δ ^{1}H 0.96.

‡ *Crystal data* for $C_{32}H_{84}Br_6Li_2N_8Sn_4$: M = 1549.17, triclinic, a = 11.144(9), b = 11.160(9), c = 12.663(9) Å, α = 89.11(3)°, β = 71.39(2)°, γ = 82.73(3)°, V = 1480(2) Å^3, space group $P\bar{1}$ (No. 2), Z = 1, D_c = 1.738 g cm^{-3}, $F(000)$ = 748, μ (Mo-Kα) = 5.74 cm^{-1}. 3817 data were recorded on a Siemens Stoe AED 2 diffractometer using a graphite monochromator, Mo radiation and ω-θ-scan. 2677 [$I > 2\sigma(I)$] reflections were classified as observed. The structure was solved by heavy-atom methods and refined by full-matrix least-squares analysis on all F_0^2 data (SHELX-93).[11] The final R, wR indices [$I > 2\sigma(I)$] were 0.0386 and 0.0923 for 296 parameters (non-hydrogen atoms anisotropic, hydrogen atoms on C in idealized positions, C–H = 0.96 Å with a common U_{iso} value). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallograpic Data Centre. See Information for Authors, Issue No. 1.

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